

Long, Multicenter Bonding Present in Radical-Radical Interactions: A Computational Study

Marçal Capdevila i Cortada



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**Long, Multicenter Bonding Present in Radical···Radical
Interactions: A Computational Study**

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per a optar al grau de Doctor per la Universitat de Barcelona

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IN RADICAL...RADICAL INTERACTIONS:
A COMPUTATIONAL STUDY

Marçal Capdevila i Cortada

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A totes i cada una de les persones que m'han aportat una engruna de felicitat

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*"- You ready to be beaten, man? I see you rolled your way into the semis. Dios mio, man.
Seamus and me, we're gonna beat you up.
- Yeah, well, you know, that's just, like, your opinion, man.
- Let me tell you something, pendejo. You pull any of your crazy crap with us, you flash a piece
out on the lanes, I'll take it away from you, stick it up your ass and pull the damned trigger 'til it
goes 'click.'
- Jesus.
- You said it, man. Nobody plays with the Jesus.
- Eight-year-olds, Dude."*

Jesús Quintana, Walter Sobchak, and the Dude.
The Big Lebowski

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CHAPTER ONE

Introduction

1.1. Chemical Bonds: A Brief History

E. Frankland developed the concept of elements having a specific valence in 1852 to explain J. Dalton's claim that specific amounts of elements were present in a compound. This was an important advancement from the 18th century view that atoms interacted via electrostatic and magnetic forces. The term 'bond' originates from Frankland stating that "*Each unit of atom-fixing power will be named a bond, a term which involves no hypothesis as to the nature of the connexion*".¹ The valence of four was ascribed to carbon in benzene by F. A. Kekulé in 1856, and in 1874 to tetrahedral carbon by J. H. van't Hoff and J. A. LeBel.

The modern concept of a chemical bond evolved from G. N. Lewis' 1916 insight that a bond involves a shared pair of electrons.² Dots (:) representing valence electrons (octet of electrons) and 'Chemical Union' were also introduced by Lewis.² This is the basis of directional covalent bonding that today impact all aspects of chemistry, especially organic chemistry. Organic chemistry has been remarkably well served by this two-electron two-center ($2e^-/2c$) bonding description. Although other definitions exist, the most commonly used definition of a bond is attributed to L. Pauling, who stated: "... *there is a chemical bond between two atoms or groups of atoms in the case that the forces acting between them are such as to lead to an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species*".³

The subsequent discovery of electron deficient boranes (e.g. diborane, B_2H_6) led to the invocation of two-electron three-center ($2e^-/3c$) BHB bonds by W. N. Lipscomb in 1954 that explained the bonding and structures of now innumerable boranes and related compounds, but not carbon-based bonding.⁴ Three-center ($3c$) bonding, being a significant departure from the overwhelming number of two-center bonds, is a last resort when conventional $2c$ bonding descriptions fail, as occurs for boranes. In contrast, the structures and bonding for all organic compounds, even esoteric and exotic examples, are usually well described by $2e^-/2c$ bonding. However, some organic radical ions present a non-conventional bonding type that requires a more complex further description.

1.2. Long, Multicenter Bonding

The first organic radical ion ever isolated was the oxidized tetramethyl-substituted *p*-phenylenediamine (TMPD), synthesized by C. Wurster in 1879.⁵⁻⁸ Due to the color of the isolated solid ($[TMPD]^+$ is also known as Wurster's blue) he recognized the presence of an oxidized product, but he majorly failed in proposing its structure. Several subsequent attempts were also unable to elucidate $[TMPD]^+$ structure; for instance, J. Piccard suggested the formation of a molecular aggregate of neutral and dioxidized *p*-phenylenediamine derivatives with specific $N\cdots N$ bonds.⁹ The true nature of Wurster's blue was however not understood until 1928, when E. Weitz pointed out that it was monomolecular and contained an unpaired electron, by arising the term 'Kationradikale' to pure organic molecules.¹⁰ He stated that the positive charge was distributed between both halves of the cation and the anion should belong to both ammonium groups, albeit not bound to them. Seven years later, L. Michaelis assigned through

potentiometric methods its unusual stability to the resonance between the two ammonium-localized cations.¹¹

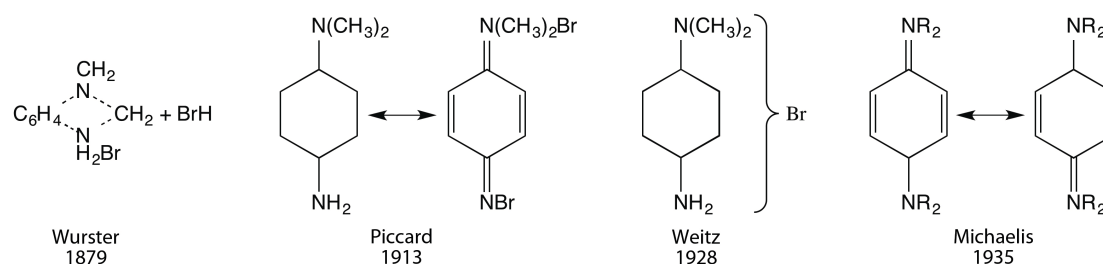


Figure 1.1. Evolution of the attempts in predicting the structure of the $[\text{TMPD}]^{\bullet+}$ radical cation.

The simultaneous radical and ionic nature of TMPD conducted it to become an early target for EPR and NMR investigations.^{12–14} Wurster's blue was one of the earliest organic radicals for which hyperfine splitting was observed, a fact that ultimately permitted H. M. McConnell to give rise to the McConnell equation.^{15,16} However, temperature-dependent magnetic measurements on $[\text{TMPD}]^{\bullet+}$ perchlorate salt evidenced an intriguing behavior: it exhibited large deviations from Curie's law at low temperatures (below 186 K).^{17,18} This behavior was already reported for organic neutral radicals and it was associated to the formation of a diamagnetic dimer. This is the case, for instance, of the first-ever reported organic radical, the triphenylmethyl radical, which has an unpaired electron localized on a carbon atom.^{19–21} It undergoes a dimerization process by the formation of a σ -bond, i.e., a $2e^-/2c$ CC bond.²² In contrast, the $[\text{TMPD}]^{\bullet+}$ radical cation is unlikely to form a σ -bonded dimer, due to the coulombic repulsion between both cations and the delocalization of its unpaired electron. The magnetic behavior was however attributed to the formation of a diamagnetic π -complex.¹⁸ Further X-ray studies evidenced that the diamagnetic salt $[\text{TMPD}][\text{ClO}_4]$ exhibits $[\text{TMPD}]_2^{2+}$ π -dimers, where only the lateral $\text{N}(\text{CH}_3)_2$ groups overlap (Figure 1.2).²³ 10 years later, the $[\text{TMPD}]_2[\text{Ni}(\text{mnt})_2]$ salt ($\text{nmt} = \text{S}_2\text{C}_2(\text{CN})_2$) was prepared, which presented almost fully eclipsed π - $[\text{TMPD}]_2^{2+}$ diamagnetic dimers (Figure 1.2).²⁴

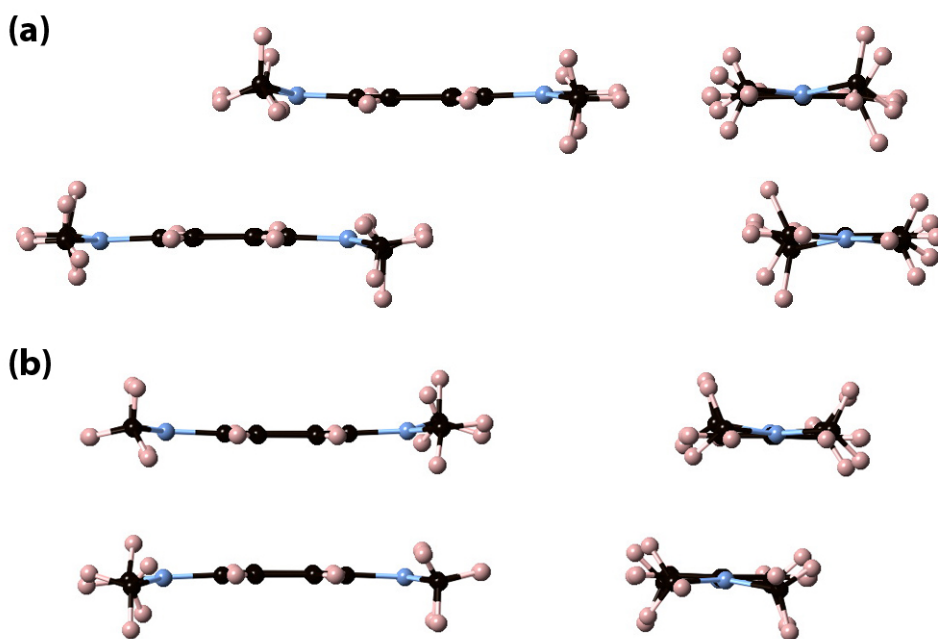


Figure 1.2. Crystal structure of the $[\text{TMPD}]_2^{2+}$ π -dimers extracted from the diamagnetic $[\text{TMPD}][\text{ClO}_4]$ and $[\text{TMPD}]_2[\text{Ni}(\text{mnt})_2]$ salts.

Simultaneously, the strong electron acceptor 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) was synthesized and found to yield a series of stable radical anion derivatives upon reduction.²⁵ Salts of reduced TCNQ early presented an exceptionally high electrical conductivity. These [TCNQ]^{•−} radical anions were also found to exhibit a temperature-dependent dimerization process in aqueous solution at very high concentrations ($6.47 \cdot 10^4$ M).²⁶ The authors suggested an attractive interaction between the radical anions in solvents where solvation effects are favorable, to the extent of even allowing dimerization. Likewise, next decade, the reduced tetracyanoethylene (TCNE) radical anion^{27,28} and the oxidized tetrathiafulvalene (TTF) radical cation²⁹ were also found to form diamagnetic π -dimers in crystals of their salts and in solution (in MTHF at $T < 77$ K for TCNE, and in ethanol at $T < 225$ K for TTF).

The structure of the four aforementioned radical ion π -dimers, extracted from their crystals, is shown in Figure 1.3. All four dimers present partial or fully eclipsed geometries, with intermonomer distances in the 2.8 – 3.5 Å range. No σ -bond is formed between the interacting radical ions of each diamagnetic dimer. Furthermore, at least two atoms present the shortest intermonomer distance in all four dimers, being even nine atoms exhibiting a 3.32 – 3.34 Å contact in the π -[TCNQ]₂^{2−} dimer. Therefore, the π -dimer entity led by the association process of two radical ions cannot be described via a 2e-/2c bond. Instead, it requires the invocation of a new bonding description: the two-electron multicenter bonds (2e[−]/mc).

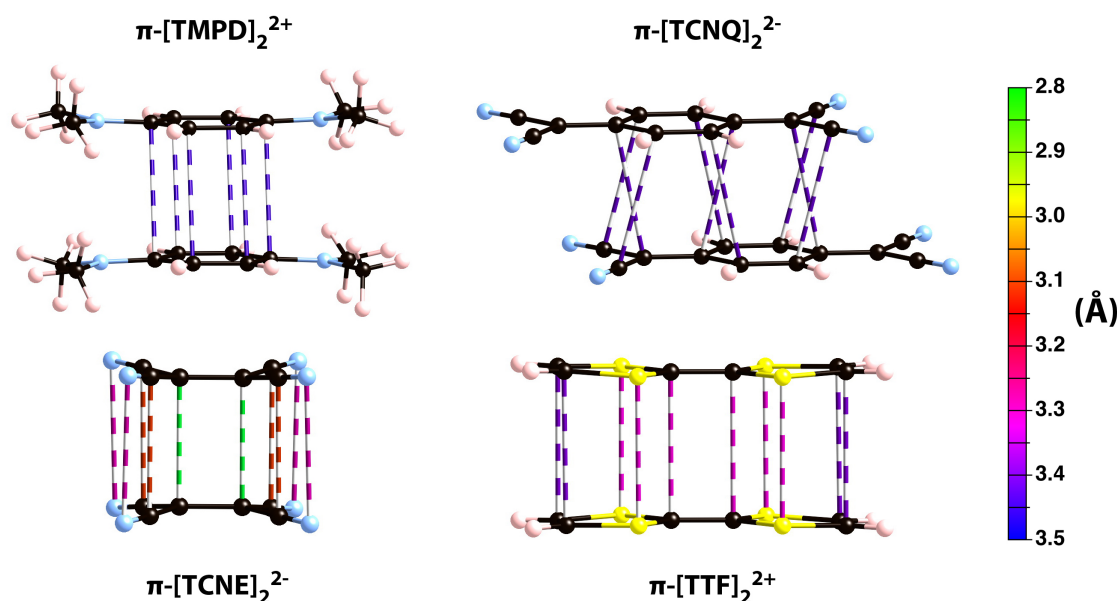


Figure 1.3. Crystal structure of the four aforementioned π -dimers. Intermonomer distances are shown in dashed lines, colored by length (see legend). Only the shortest contact involving each atom is depicted. Atom color legend: black (C), white (H), blue (N), yellow (S).

Two-electron multicenter bonds present an intermonomer distance substantially higher than conventional covalent bonds. π -[TCNE]₂^{2−} exhibits an intermonomer 2.89 Å distance between the central carbon atoms, while π -[TMPD]₂²⁺ has six intermonomer CC distances of 3.43 – 3.47 Å (Figure 1.3). A conventional CC covalent bond typically ranges 1.20 – 1.54 Å (r_{cov} , Table 1). On the other hand, all four dimers present intermonomer distances shorter than or about twice the van der Waals radii of C, S, or N (r_{vdW} , Table 1), indicative of bonding. Due to

the unusual bond length exhibited by these ($2e^-/mc$) bonds, they were ultimately defined as *long, multicenter bonds*. It is worth pointing out that electron pairing, manifested in the diamagnetic behavior of the π -dimer, makes them essentially differ from non-bonded van der Waals interactions.

Table 1.1. Non-bonded contact (van der Waals, r_{vdW}) and covalent radii (r_{cov}) of some selected atoms.

Atom	Pauling $r_{vdW},^3 \text{ \AA}$	Bondi $r_{vdW},^{30} \text{ \AA}$	Rowland & Taylor $r_{vdW},^{31} \text{ \AA}$	Cambridge Crystallographic Data Centre, $r_{vdW},^{32} \text{ \AA}$	$r_{cov},^{32}$ $\text{ \AA}$
H	1.2	1.20	1.10	1.09 ^c	0.23
C	-	1.70	1.77	1.70 ^b	0.68
N	1.5	1.55	1.64	1.55 ^b	0.68
O	1.40	1.52	1.58	1.52 ^b	0.68
F	1.35	1.47	1.46	1.47 ^b	0.64
S	1.85	1.80	1.81	1.80 ^b	1.02
Cl	1.80	1.75	1.76	1.75 ^b	0.99
Br	1.95	1.85	1.87	1.85 ^b	1.21
I	2.15	1.98	2.03	1.98 ^b	1.40

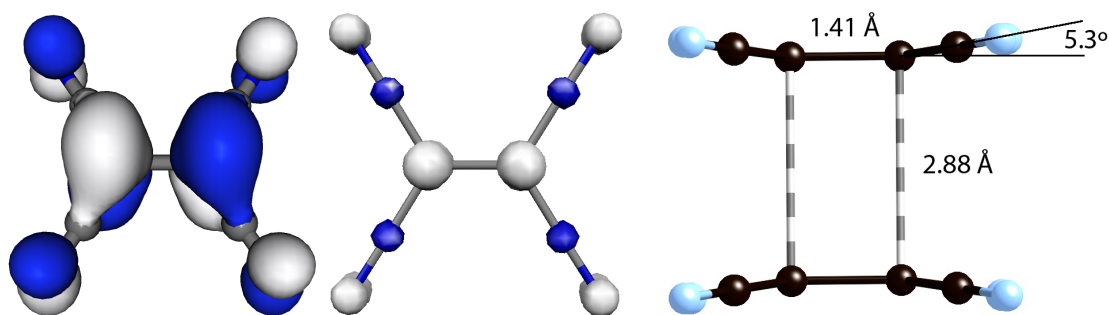


Figure 1.4. SOMO orbital, spin density, and geometry of the $[\text{TCNE}]^{\bullet-}$ radical anion.

1.3. π - $[\text{TCNE}]_2^{2-}$: A Complete Characterization

In the early 2000s, the π - $[\text{TCNE}]_2^{2-}$ dimer was chosen as a prototype example for an extensive characterization of long, multicenter bonding.^{33–35} Its small size and the exceptional stabilization given by the electron pairing make it an excellent target for thorough experimental and computational studies. The singly occupied molecular orbital (SOMO) and the spin density of the $[\text{TCNE}]^{\bullet-}$ radical anion are plotted in Figure 1.4. Although the unpaired electron is delocalized over the whole molecule, the two central carbon atoms host a larger amount of spin density. Additionally, the dimer presents a geometry where the nitrile groups are bended away the nominal plane of the central CC bonds by 5.3° . Both factors suggest that the dimer is bonded by its two central carbons. This fact is indeed manifested in the HOMO and LUMO orbitals of π - $[\text{TCNE}]_2^{2-}$ (Figure 1.5), which are the resulting bonding and antibonding combinations of the SOMOs of both $[\text{TCNE}]^{\bullet-}$. The region of the central C atoms present a significantly higher overlap. The orbital splitting between the HOMO and the LUMO, due to the high overlap between the SOMO orbitals, predicts an allowed $^1A_g \rightarrow ^1B_{3u}$ transition at lower energies than any of the parent $[\text{TCNE}]^{\bullet-}$ radical anion. The experimental UV-vis spectra of $[\text{TCNE}]^{\bullet-}$ and π - $[\text{TCNE}]_2^{2-}$ are shown in Figure 1.5. $[\text{TCNE}]^{\bullet-}$ has an absorption band at 23,400

cm^{-1} while the π -dimer exhibits an absorption at $17,150\text{ cm}^{-1}$, attributed to the transition predicted in the MO diagram. Furthermore, the IR spectrum also varies between the π -dimer and the parent radical anion. The three IR-allowed absorptions expected for the planar D_{2h} radical anion (that is, two ν_{CN} and one δ_{CCN} vibrations, since the ν_{CC} is symmetry-forbidden) turn into three ν_{CN} , three δ_{CCN} , and one ν_{CC} IR-allowed absorptions in the D_{2h} π -[TCNE] $_2^{2-}$ dimer. The experimental IR spectra of the π -dimer and the radical anion are given in Figure 1.5. Moreover, the 1A_g closed-shell singlet ground state described by the MO diagram is in good agreement with the temperature dependence magnetic susceptibility, which in addition to higher temperature EPR data, does not reveal signs for either doublet or triplet states. On the whole, the π -[TCNE] $_2^{2-}$ dimer is consistently well described by a $(2e^-/4c)$ long, multicenter bond.³⁶

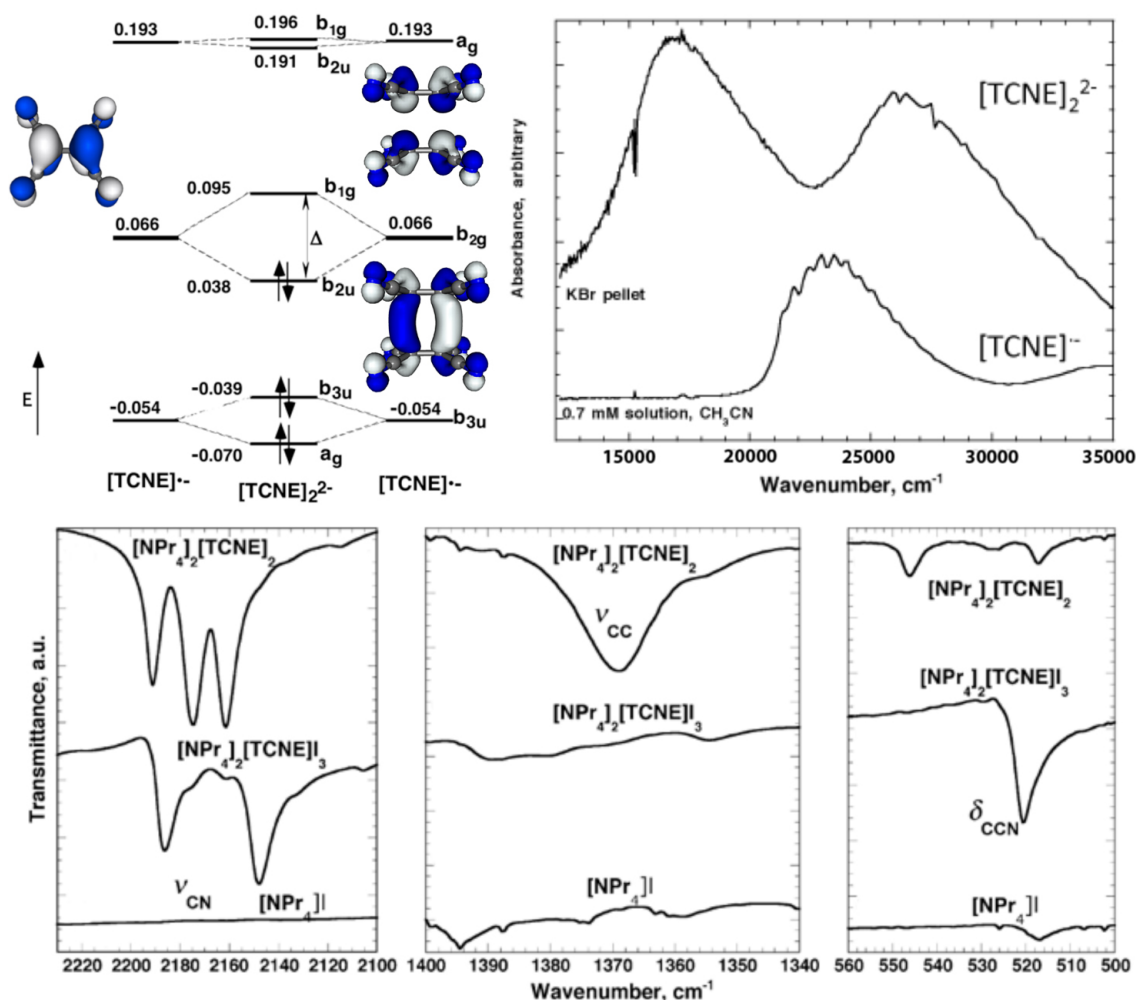


Figure 1.5. MO diagram of the π -[TCNE] $_2^{2-}$. Comparison of the UV-vis and IR spectra of the π -[TCNE] $_2^{2-}$ diamagnetic dimer and the $[\text{TCNE}]^{\bullet-}$ radical anion.

Given the anionic character of the moieties that form the π -[TCNE] $_2^{2-}$ dimer, the interaction energy the isolated π -dimer in the gas phase is repulsive. The coulombic repulsion cannot be overcome by the stabilization given by the electron pairing. It is evidenced in the interaction energy curve of the isolated π -dimer, depicted in Figure 1.6. However, a minimum is found at 2.9 Å with an interaction energy of $37\text{ kcal}\cdot\text{mol}^{-1}$, which exhibits an energetic barrier toward the dimer's dissociation of $6\text{ kcal}\cdot\text{mol}^{-1}$. Hence, the isolated π -[TCNE] $_2^{2-}$ is metastable in the gas phase. This fact arises the following question: how are long, multicenter bonded π -dimers

actually formed in salts and solution? Computational studies revealed strong interactions with the π -[TCNE] $_2^{2-}$ and its adjacent cations in the solid state.^{37,38} For instance, the K[TCNE] crystal can be rationalized as K₂[TCNE]₂ aggregates that replicate by symmetry operations. The total cohesive energy of the aggregate is stabilizing, since the sum of the cation⋯anion interactions overcome the anion⋯anion and cation⋯cation repulsions (Table 1.2). Similarly, [radical ion]⋯solvent interactions stabilize the π -dimer in solution, albeit they are much weaker than cation⋯anion interactions.^{39,40} The [TCNE] $_2^{2-}$ ⋯[TCNE] $_2^{2-}$ coulombic repulsions are overcome by [TCNE] $_2^{2-}$ ⋯CH₂Cl₂ interactions in a [TCNE] $_2^{2-}$ (CH₂Cl₂)_n aggregate, given a large enough *n* (Table 2). However, [TCNE] $_2^{2-}$ (CH₂Cl₂)_n aggregates are much weaker than (cation)₂[TCNE]₂ aggregates and thus π -[TCNE] $_2^{2-}$ dimers are only observed in solution at low temperature. Thus, long, multicenter bonded π -dimers are cation or solvent mediated in the solid state or in solution, respectively.

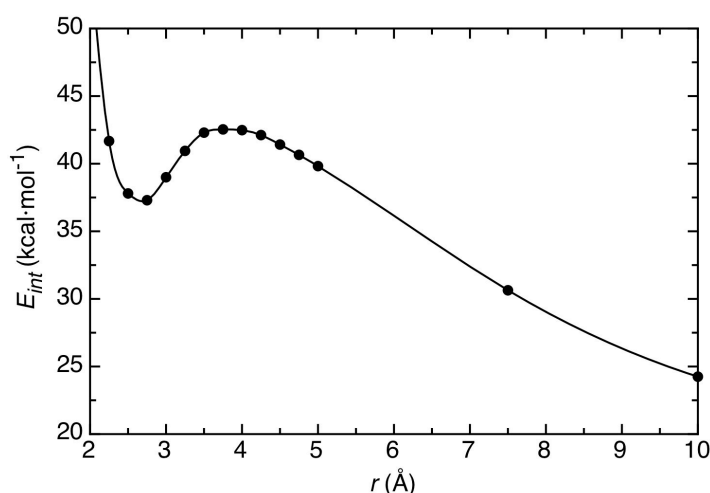


Figure 1.6. Interaction energy curve of the isolated π -[TCNE] $_2^{2-}$ in the gas phase.

Table 1.2. Interaction energy of K₂[TCNE]₂ and π -[TCNE] $_2^{2-}$ (CH₂Cl₂)₄ aggregates and the π -[TCNE] $_2^{2-}$ dimer in CH₂Cl₂ solution (modeled with the PCM continuous approach).

K ₂ [TCNE] ₂	<i>E</i> _{int}	[TCNE] $_2^{2-}$ (CH ₂ Cl ₂) ₄	<i>E</i> _{int}	[TCNE] $_2^{2-}$ PCM _{CH₂Cl₂}	<i>E</i> _{int}
[TCNE] $_2^{2-}$ ⋯[TCNE] $_2^{2-}$	53.8	[TCNE] $_2^{2-}$ ⋯[TCNE] $_2^{2-}$	50.1	[TCNE] $_2^{2-}$ ⋯[TCNE] $_2^{2-}$	-1.4
<K ⁺ ⋯[TCNE] $_2^{2-}$ >	-73.8	<CH ₂ Cl ₂ ⋯[TCNE] $_2^{2-}$ >	-6.2		
K ⁺ ⋯K ⁺	30.5	<CH ₂ Cl ₂ ⋯CH ₂ Cl ₂ >	-0.3		
<i>E</i> _{int}	-182.9	<i>E</i> _{int}	-1.3	<i>E</i> _{int}	-1.4

Temperature-dependent experimental studies analyzed the π -dimerization of [TCNE] $_2^{2-}$ in solution.⁴¹ Figure 1.7 shows the UV-vis spectral changes upon temperature variation for a dichloromethane solution of NBu₄[TCNE]. The π -[TCNE] $_2^{2-}$ characteristic band (530 nm, 18,800 cm⁻¹) is clearly observed at -98° C. However, it starts decreasing as the temperature increases, until it completely vanishes above -80° C. This study permitted to obtain the equilibrium constant (*K*_D = 7·10⁻⁴ M⁻¹), the enthalpy (Δ H_D = 8.8 kcal·mol⁻¹) and the entropy (Δ S_D = 41 eu) of dimerization in dichloromethane. It is worth mentioning that these thermodynamic parameters are still obtained regardless of the counterion used in the [TCNE] $_2^{2-}$ salt.

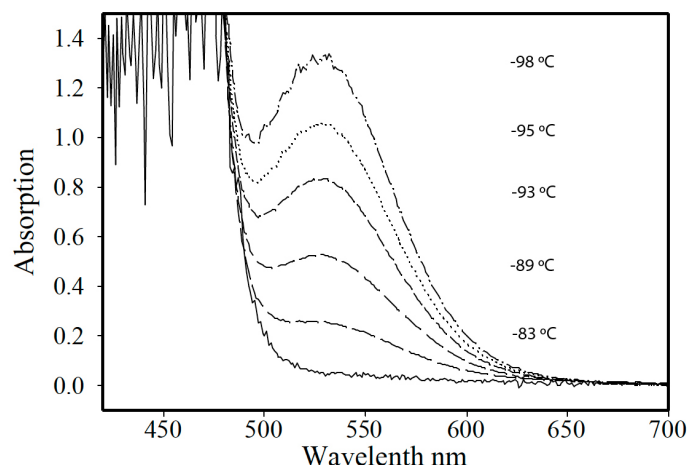


Figure 1.7. UV-vis spectrum of (NBu₄)[TCNE] in CH₂Cl₂ solution (6 mM) as a function of the temperature.

1.4. Long, Multicenter Bonding on a Greater Extent

In addition to the four aforementioned radical ions, a subsequent large amount of organic radicals have been found to present π -dimerization either in the solid state or in solution. All of them have their spin density highly delocalized and a geometry that allows an effective overlap of each radical's SOMO. Interestingly, some neutral radicals can also π -dimerize exhibiting long, multicenter bonding. In order to avoid σ -bond formation, their unpaired electron has to be delocalized either over a large planar conjugated system or over a heterocycle where the spin density is mainly hosted on non-C atoms (see below).

The main conclusions previously obtained on π -[TCNE]₂²⁻ dimers can be extended to the other radical ion π -dimers. Their interaction energy in the gas phase is repulsive, thus they are metastable (some examples are collected in Figure 1.8). On the other hand, π -dimers between neutral radicals have stable interaction energies; the 2,5,8-tri-*t*-butylphenalenyl has an interaction energy of -26.0 kcal·mol⁻¹.⁴² Various π -dimers have also been the focus of many theoretical studies, in order to disentangle their properties and stability in the solid state and in solution. Furthermore, temperature-dependent spectroscopic studies also obtained the thermodynamic details of the π -dimerization processes of several radical ions in solution.^{41,43}

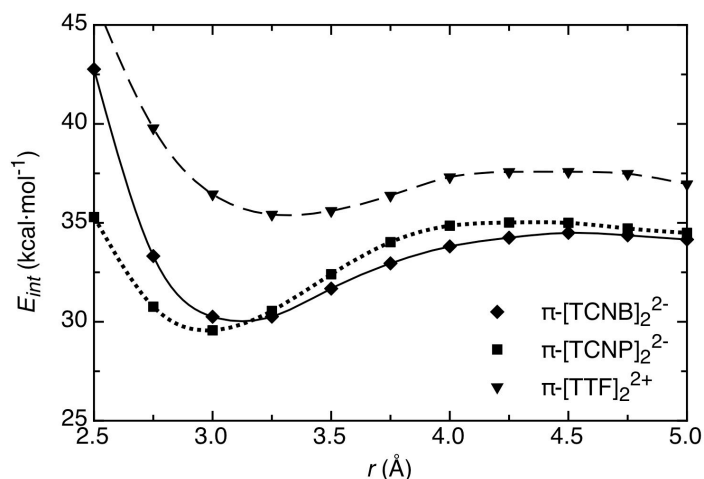
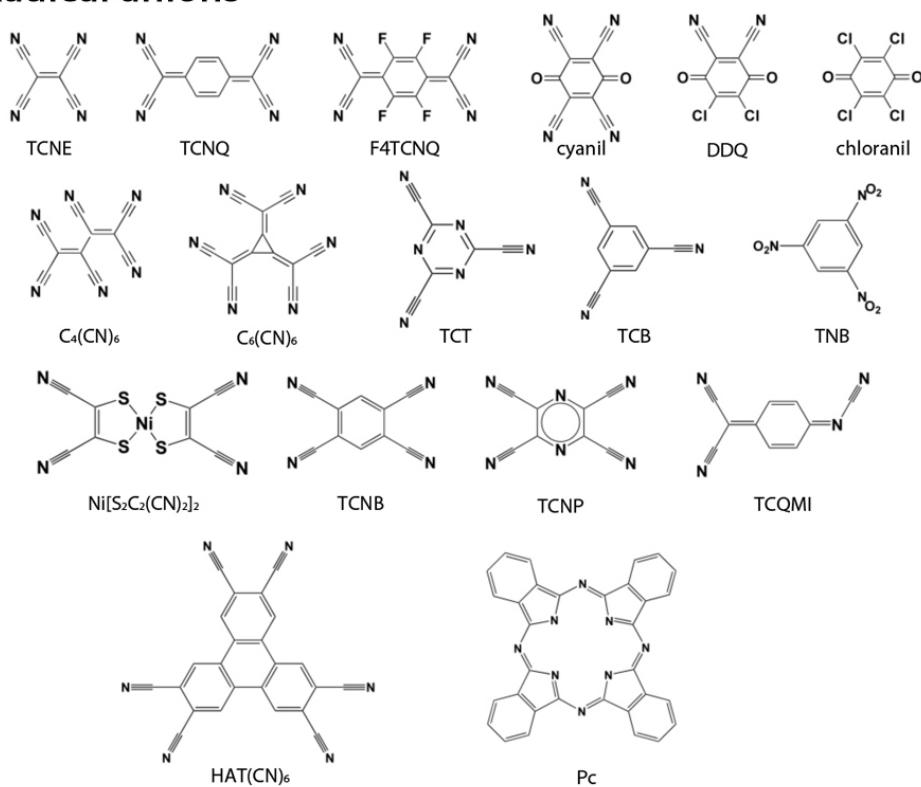
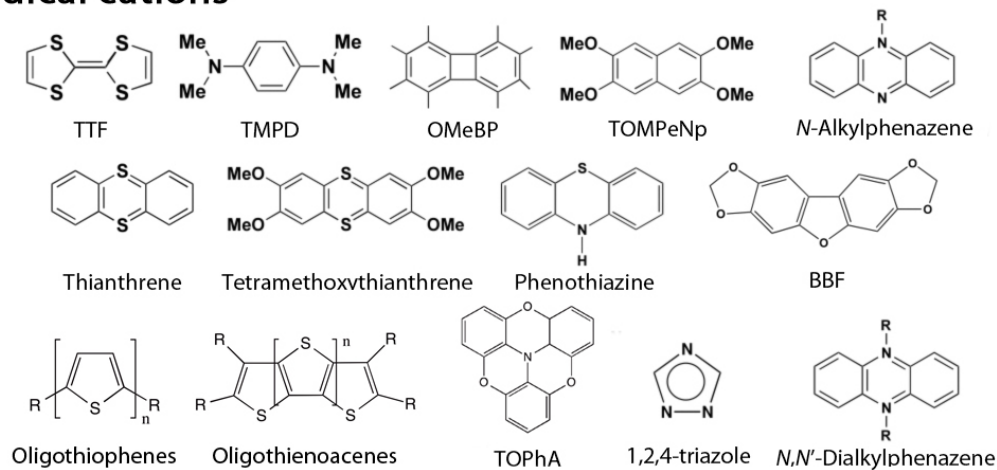


Figure 1.8. Interaction energy curve of the isolated π -[TCNB]₂²⁻, π -[TCNP]₂²⁻, and π -[TTF]₂²⁺ in the gas phase.

Radical anions



Radical cations



Neutral radicals

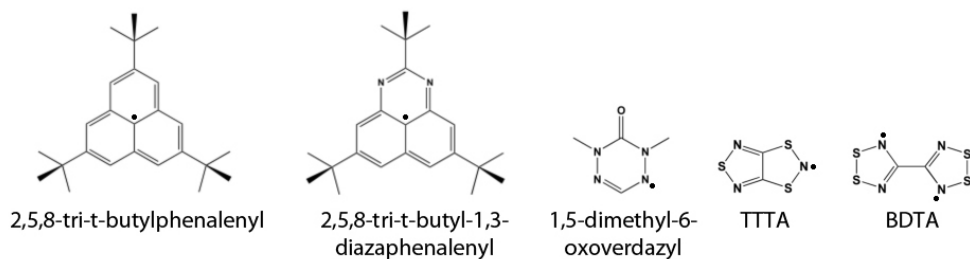


Figure 1.9. Organic radicals so far characterized to form long, multicenter bonded dimers.

1.5. Consequences of Long, Multicenter Bonding

Electron-transfer salts involving organic radical ions of Figure 1.8 are well characterized to exhibit technologically important properties. $[\text{FeCp}^*_2][\text{TCNE}]$ was synthesized and early characterized as a bulk ferromagnet with a T_c of 4.8 K.⁴⁴ Thereafter, $[\text{MnCp}^*_2][\text{TCNQ}]$ and $[\text{MnCp}^*_2][\text{TCNE}]$ were shown to present the same magnetic behavior with T_c of 6.2 and 8.8 K, respectively.^{45,46} TCNE, TCNQ, TCNB, and TCNP, upon reaction with $\text{V}(\text{CO})_6$, form molecule-based bulk ferromagnets having magnetic ordering temperatures above room temperature.⁴⁷ However, the electron pairing resulting from the formation of long, multicenter bonded π -dimers would form diamagnetic entities, thus preventing any magnetic ordering among them.⁴⁸

Thiophene polymers, polythiophene, were considered as suitable species for optoelectronic materials due to their electrical conducting properties when they are partially oxidized (p-doped).^{49–53} Their conducting mechanism was ascribed to the formation of polarons (a radical cation thiophene ring) and bipolarons (a dication localized on adjacent thiophene rings) along single conjugated chains.⁵⁴ However, the discovery of π -dimer formation between oxidized oligothiophenes in solution prompted the suggestion of an alternative mechanism, where the high electrical conductivity would result from the interaction among the polymer chains through π -dimerization (i.e., an *interchain* mechanism instead of an *intrachain* one).^{49,50} This issue is nowadays still in debate.

Furthermore, TCNQ salts early presented exceptionally high electrical conductivity. $[\text{TTF}][\text{TCNQ}]$ is the first example of an organic metal-like conductor.^{55–57} It is arranged in segregated stacks of $\cdots\text{D}\cdots\text{D}\cdots\text{D}\cdots$ and $\cdots\text{A}\cdots\text{A}\cdots\text{A}\cdots$ ($\text{D} = \text{TTF}$, $\text{A} = \text{TCNQ}$), and presents 1D conducting channels along the stacks. As long as the temperature is decreased, the stacks experiment a Peierls transition to a distorted phase and it becomes an insulator.⁵⁸ In this Peierls-distorted phase the TCNQ and the TTF π -dimerize, leading to stacks best described as $\cdots\text{D}-\text{D}\cdots\text{D}-\text{D}\cdots$ and $\cdots\text{A}-\text{A}\cdots\text{A}-\text{A}\cdots$. Similar charge-transfer salts experience the same behavior.⁵⁹

Therefore, a complete understanding of the dimerization process and its features is essential in order to control the formation of π -dimers and design materials with the desired physical properties.

1.6. Motivation and outline of the thesis

Although long, multicenter bonding was first perceived during the late 60s, it was not until 2001 where the first theoretical work emerged. The subsequent computational studies of π -dimerization were focused in small organic radicals, and no clues were given about which methodology was the appropriate to face their analysis. Moreover, organic compound exhibiting these interactions started to be synthesized as building blocks in supramolecular aggregates. The work presented in the present thesis is mainly devoted to: a) provide a deeper knowledge of long, multicenter bonding in the common environments (i.e., gas phase, solution, and solid state), and b) study the causes behind the room temperature stability of two families of long, multicenter dimers.

This thesis is structured as follows: **Chapter 2** describes the theoretical background behind the quantum chemistry methods used to conduct all the work provided in the present thesis. Chapters 3 and 4 comprise the results of the research performed all through the thesis.

Chapter 3 provides the description of fundamental aspects concerning long, multicenter bonding in several environments. The π -[TCNE] $_2^{2-}$, π -[TTF] $_2^{2+}$, π -[TCNB] $_2^{2-}$, and π -[TCNP] $_2^{2-}$ dimers are challenged in different manners in the gas phase. Moreover, a comprehensive description of the π -[TCNE] $_2^{2-}$ in solution is also given, as well as a solid state study of the π -[TCNB] $_2^{2-}$ and π -[TCNP] $_2^{2-}$ dimers and the [TTF][TCNE] charge-transfer crystal.

Chapter 4 describes the reasons of the extraordinary high stability of long, multicenter bonded dimers that are experimentally characterized at room temperature. In particular, the chapter focuses on π -dimers of oligothienoacenes and π -[TTF] $_2^{2+}$ dimers stabilized by supramolecular aggregates.

Finally, the conclusions of the thesis are given in **Chapter 5**.

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CHAPTER TWO

Quantum chemistry methods

The aim of the present chapter is to provide a general overview of the computational chemistry methods that lay out the groundwork for this thesis. It is important to begin by rationalizing each problem one encounters, in order to select the appropriate methods to solve them. As introduced in the previous chapter, the work described in this thesis centers on the analysis of the physical and chemical properties of long, multicenter bonded dimers in different environments. The methods described in this chapter will serve as the basis for any property obtained throughout this work.

2.1. Wavefunction-Based Methods

2.1.1. The Hartree-Fock Method

D. R. Hartree introduced in 1928 a methodology based on the independent particle model to obtain wavefunctions and energies of atoms and ions,¹ solving the Schrödinger equation through the variational principle.² This method was named the Hartree or Self-Consistent Field (SCF) method. As originally proposed, the obtained wavefunction failed to satisfy the antisymmetry principle. In 1930, V. A. Fock reformulated the theory by using Slater determinants, thus guaranteeing the fulfillment of the Pauli exclusion principle. This reformulation is known as the Hartree-Fock (HF) method. Slater determinants are antisymmetric products of monoelectronic space-spin coordinates functions (spinorbitals), i.e., a configuration.

$$\Psi_0 = (N!)^{-1/2} |\chi_1(1)\chi_2(2)\dots\chi_N(N)| \quad (2.1)$$

The HF method is set under the framework of the Born-Oppenheimer approximation,³ which allows the separation of the Hamiltonian into an electronic and a nuclear part, by assuming that the nuclei are much more massive than the electrons. This allows to solve the nuclear-electronic problem by considering two independent equations: the time-independent Schrödinger equation for the electronic Hamiltonian (2.3) and the nuclear motion.

$$\hat{H}_{el}\Psi_0 = E_{el}\Psi_0 \quad (2.2)$$

$$\hat{H}_{el} = \hat{T}_{el} + \hat{V}_{eN} + \hat{V}_{ee} = \sum_i \left(-\frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{R_{Ai}} \right) + \sum_i \sum_{j>i} \frac{1}{r_{ij}} = \sum_i \hat{h}_i + \sum_i \sum_{j>i} \frac{1}{r_{ij}} \quad (2.3)$$

The time-independent electronic part can be solved using the variational principle, thus obtaining the optimum spinorbitals that minimize the electronic energy for the selected configuration.

$$E_{el} = \min_{\Psi \rightarrow \Psi_0} \langle \Psi | \hat{H}_{el} | \Psi \rangle \quad (2.4)$$

In closed-shell systems (i.e., configurations where all orbitals are doubly occupied) the HF equations can be further simplified by considering that doubly occupied orbitals share the same spatial part. This fact allows integration over the spin part, thus leaving only the spatial part of each monoelectronic function. As a result, spinorbitals $((\chi_i | i = 1, 2 \dots N) \subset \{\mathbb{R}^3, \omega\})$ are

switched to orbitals $(\varphi_i | i = 1, 2 \dots N/2) \subset \mathbb{R}^3$, leading to the Restricted Hartree-Fock (RHF) method. The RHF energy can be now expressed as:

$$E_{el} = 2 \sum_i h_{ii} + \sum_i \sum_j (2J_{ij} - K_{ij}) \quad (2.5)$$

where

$$h_{ii} = \langle \varphi_i(1) | \hat{h} | \varphi_i(1) \rangle \quad (2.6)$$

$$J_{ij} = \langle \varphi_i(1) \varphi_j(2) | r_{ij}^{-1} | \varphi_i(1) \varphi_j(2) \rangle \quad (2.7)$$

$$K_{ij} = \langle \varphi_i(1) \varphi_j(2) | r_{ij}^{-1} | \varphi_j(1) \varphi_i(2) \rangle \quad (2.8)$$

The Coulomb integral (J_{ij}) represents the repulsion that the electron i causes to the electron j , while the exchange integral (K_{ij}) does not have a classical physical meaning, since its origin is set in the antisymmetry principle. Let $\hat{J}_j = \langle \varphi_j(2) | r_{ij}^{-1} | \varphi_j(2) \rangle$ and $\hat{K}_j = \langle \varphi_j(2) | r_{ij}^{-1} | \varphi_i(2) \rangle$ be the Coulomb and exchange operators, then the Fock operator is defined as:

$$\hat{F} = \hat{h} + \sum_j (2\hat{J}_j - \hat{K}_j) \quad (2.9)$$

which depends on the occupied orbitals φ_i , since J_{ij} and K_{ij} operators do. The diagonal terms of the Fock matrix, $F_{ij} = \langle \varphi_i | \hat{F} | \varphi_j \rangle$, are the orbital energies, or equivalently, $\varepsilon_i = \langle \varphi_i | \hat{F} | \varphi_i \rangle$.

Roothan reformulated the RHF equations by considering molecular orbitals φ_i as a linear combination of atomic orbitals (LCAO approximation) $\varphi_i = \sum_{\mu} c_{\mu i} \phi_{\mu}$.⁴ This arises the Roothan equation:

$$FC = SCE \quad (2.10)$$

where F is the Fock matrix, C the expansion coefficients matrix, S the overlap matrix $S_{ij} = \langle \phi_i | \phi_j \rangle$, and E the orbital energies diagonal matrix. This equation can be solved iteratively by means of the SCF approach starting from a given initial guess of atomic orbitals, until the desired convergence is reached. At this point, a set of canonical orbitals is obtained, together with their corresponding energies.

Open-shell systems can be solved with a similar procedure. Two implementations of the HF method for open-shell systems are usually found in the most common quantum chemistry software, the restricted open-shell Hartree-Fock (ROHF)⁵ and the unrestricted Hartree-Fock (UHF)⁶ methods. The former uses only one set of orbitals filling them up in order to satisfy the spin multiplicity requirement of the given configuration. On the contrary, the latter uses separated spatial orbitals for all α and β electrons. Although the UHF method is more often

employed than the ROHF, it has the drawback that its wavefunctions are not eigenfunction of the spin operator $\hat{S}^2$ (the spin contamination problem).

The HF method, although useful in many qualitative interpretations, does not usually provide an accurate description of the chemical phenomena since it does not account for the electron correlation. Several approaches were developed to describe the electron correlation in an accurate way, being the configuration interaction (CI), perturbation theory (PT), coupled cluster (CC), or multiconfigurational procedures (MCSCF, also combined with the previous approaches) the most relevant.

2.1.2. Rayleigh-Schrödinger Perturbation Theory

The time-independent perturbation theory applied to quantum mechanics for non-degenerate levels was developed in 1926 by E. Schrödinger,⁷ based on previous work of Lord Rayleigh.⁸ Its main idea is to split the Hamiltonian in two terms, a zeroth order unperturbed Hamiltonian, $\hat{H}^0$, whose eigenfunctions and eigenvalues are exactly known, and a perturbation term, $\hat{V}$, assumed to be remarkably small compared to $\hat{H}^0$.

In order to connect the eigenfunctions and eigenvalues of the perturbed and the unperturbed systems, a parameter $\lambda \in [0,1]$ is introduced to the Hamiltonian, so when $\lambda=0$ the Hamiltonian remains unperturbed while when $\lambda=1$ it becomes fully perturbed.

$$\hat{H} = \hat{H}^0 + \lambda \hat{V} \quad (2.11)$$

Therefore, the wavefunction and the energy get the following expressions:

$$\phi_n = \phi_n^{(0)} + \lambda \phi_n^{(1)} + \lambda^2 \phi_n^{(2)} + \dots + \lambda^k \phi_n^{(k)} + \dots \quad (2.12)$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots + \lambda^k E_n^{(k)} + \dots \quad (2.13)$$

Assuming $\phi_n^{(0)}$ normalized, let us consider the intermediate normalization for ϕ_n , i.e., $\langle \phi_n^{(0)} | \phi_n \rangle = 1$. Therefore, all i th order corrections to the wavefunction are orthogonal to $\phi_n^{(0)}$, i.e., $\langle \phi_n^{(0)} | \phi_n^{(i)} \rangle = 0 \quad \forall i$.

Substituting equations (2.11), (2.12), and (2.13) into the Schrödinger equation and equating coefficients of λ^n , then:

$$\hat{H}^0 \phi_n^{(0)} = E_n^{(0)} \phi_n^{(0)} \quad (2.14)$$

$$\hat{H}^0 \phi_n^{(1)} + \hat{V} \phi_n^{(0)} = E_n^{(0)} \phi_n^{(1)} + E_n^{(1)} \phi_n^{(0)} \quad (2.15)$$

$$\hat{H}^0 \phi_n^{(2)} + \hat{V} \phi_n^{(1)} = E_n^{(0)} \phi_n^{(2)} + E_n^{(1)} \phi_n^{(1)} + E_n^{(2)} \phi_n^{(0)} \quad (2.16)$$

...

Multiplying by $\phi_n^{(0)}$ and integrating applying the intermediate orthogonality condition, it is found:

$$E_n^{(0)} = \langle \phi_n^{(0)} | \hat{H}^0 | \phi_n^{(0)} \rangle \quad (2.17)$$

$$E_n^{(1)} = \langle \phi_n^{(0)} | \hat{V} | \phi_n^{(0)} \rangle \quad (2.18)$$

$$E_n^{(2)} = \langle \phi_n^{(0)} | \hat{V} | \phi_n^{(1)} \rangle \quad (2.19)$$

...

Since $\hat{H}^0$ is hermitian and thus has a set of non-degenerate eigenfunctions that are orthogonal and form a complete space, each $\phi_n^{(i)}$ correction can be expressed as a linear combination of $\hat{H}^0$ eigenfunctions:

$$\phi_n^{(i)} = \sum_m a_m^{(i)} \phi_m^{(0)} \quad \text{where} \quad a_m^{(i)} = \langle \phi_m^{(0)} | \phi_n^{(i)} \rangle \quad (2.20)$$

From equation (2.15) it can be obtained, in the case of the first order correction, the following relation:

$$(E_m^{(0)} - E_n^{(0)})a_m = -\langle \phi_m^{(0)} | \hat{V} | \phi_n^{(0)} \rangle \quad (2.21)$$

which can be substituted in equation (2.20) to express the first order correction to the wavefunction in terms of zeroth order energies and eigenfunctions.

$$\phi_n^{(1)} = \sum_{m \neq n} \frac{\langle \phi_m^{(0)} | \hat{V} | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \phi_m^{(0)} \quad (2.22)$$

Likewise, the second order correction to the energy can also be expressed in terms of zeroth order energies and eigenfunctions substituting equation (2.22) in equation (2.19).

$$E_n^{(2)} = \sum_{m \neq n} \frac{\langle \phi_m^{(0)} | \hat{V} | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \langle \phi_n^{(0)} | \hat{V} | \phi_m^{(0)} \rangle = \sum_{m \neq n} \frac{|\langle \phi_n^{(0)} | \hat{V} | \phi_m^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \quad (2.23)$$

Similar expansions can be done for higher order corrections, on both energies and wavefunctions.

2.1.3. Møller-Plesset Partitioning

In 1934 C. Møller and M. S. Plesset published an approach to introduce electron correlation in atomic and molecular systems,⁹ based on the Rayleigh-Schrödinger perturbation theory starting from the HF wavefunction as its zeroth order wavefunction. The sum of fock operators are taken as the zeroth order Hamiltonian (2.24), while the perturbed Hamiltonian is defined as follows (2.25):

$$\hat{H}^0 = \sum_i \hat{f}(i) = \sum_i \left(\hat{h}(i) + \sum_j \left(\hat{J}_j(i) - \hat{K}_j(i) \right) \right) \quad (2.24)$$

$$\hat{V} = \sum_i \sum_{j>i} \frac{1}{r_{ij}} - \sum_i \sum_j \left(\hat{J}_j(i) - \hat{K}_j(i) \right) \quad (2.25)$$

It is straightforward to realize that the first order correction leads to the closed-shell HF energy.

$$E_0^{(0)} + E_0^{(1)} = \langle \Psi_0 | \hat{H}^0 | \Psi_0 \rangle + \langle \Psi_0 | \hat{V} | \Psi_0 \rangle = 2 \sum_i \varepsilon_i + \sum_i \sum_j (2J_{ij} - K_{ij}) = E_{HF} \quad (2.26)$$

Equation (2.23) provides second order correction to the energy. Due to Condon-Slater rules and Brillouin's theorem for canonical orbitals, only double excitations will have non-zero contributions to the energy. Therefore, the second order correction to the energy gets the following expression:

$$E_0^{(2)} = \sum_{a<b} \sum_{r<s} \frac{\left| \langle \Psi_0 | \hat{V} | \Psi_{ab}^{rs} \rangle \right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \quad (2.27)$$

The sum of first and second order corrections to the energy give rise to the MP2 total energy.

$$E_{MP2} = E_{HF} + \sum_{a<b} \sum_{r<s} \frac{\left| \langle \Psi_0 | \hat{V} | \Psi_{ab}^{rs} \rangle \right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \quad (2.28)$$

Higher energy terms can be thereafter obtained, leading to MP3, MP4, etc energies. Terms up to fifth order are sometimes used in quantum chemistry, although they are increasingly expensive. Furthermore, since MP n are not variational methods, moving to a higher order correction does not guarantee a better solution.

2.1.4. Multi-Configurational Methodologies

As outlined in section 2.1.1, the determinant associated to the ground state configuration is, in general, a single Slater determinant. There are many chemical systems that cannot be sufficiently described by one single determinant, since they require of more than one electronic configuration to be properly described. This is the case for ground states nearly degenerate with low-lying excited states or bond-breaking reactions, for instance.

An elegant way of dealing with these systems is to express the wavefunction as a linear combination of Configuration State Functions (CSF) (i.e., a Slater determinant or a symmetry-

adapted linear combination of Slater determinants), giving rise to the Multi-Configurational Self-Consistent Field (MCSCF) method.

$$\Psi_{MCSCF} = \sum_I C_I \phi_I \quad (2.29)$$

In this method, both the coefficients on the CSF (C_I) and the coefficients on the orbitals (c_i) are variationally optimized simultaneously.

Equation (2.29) must be restricted to a finite subset of CSF. In order to do so, the most common MCSCF approach is the Complete Active Space Self-Consistent Field (CASSCF),¹⁰ where the initial set of orbitals is divided into three subsets: inactive, active, and external orbital spaces. The first consists of a set of orbitals that remain doubly occupied in all CSF. The active orbital space allows all possible CSF combination among the number of electrons chosen and the orbitals of this subset. Finally, all external orbitals remain unoccupied in all CSF.

When the size of a CASSCF active space becomes prohibitively large, it can be reduced while still keeping the most relevant properties of the CASSCF method, by using the RASSCF method.^{11,12} In this method, the active space is subdivided into three subsets, namely RAS1, RAS2, and RAS3 (Figure 2.1). Restrictions are introduced into the RAS1 and RAS3 subspaces such that in RAS1 a maximum number of holes are allowed, while in RAS3 a maximum number of electrons are. The RAS2 subspace is equivalent to the CASSCF's active space. This procedure is called Restricted Active Space Self-Consistent Field (RASSCF) and permits a description of bigger active spaces at lower computational cost.

...	(0)	Virtual
—		
—		
...	(0-2)	RAS3: orbitals containing a max. number of electrons
—		
...	(0-2)	RAS2: orbitals of arbitrary occupation
↑↓		
↑↓	(0-2)	RAS1: orbitals containing a max. number of holes
...		
↑↓	(2)	Inactive
...		
↑↓		

Figure 2.1. Scheme of the orbitals' subset division within the RASSCF framework.

Both CASSCF and RASSCF methods usually succeed in accounting for the whole static correlation. However, they cannot properly reproduce the dynamic correlation. The most widely

used approach to introduce dynamic correlation is a perturbative treatment of the CASSCF (or RASSCF) wavefunction. Among them, the most common one is the CASPT2 (or RASPT2) method,^{13,14} which is analogous to MP2 for HF wavefunctions. Another common methodology is the MR-MP2,¹⁵ which mainly differs from the CASPT2 method in the reference wavefunction, for which a diagonal zeroth-order Hamiltonian is used. Both the CASPT2 and the MR-MP2 methods are based on the *diagonalize-then-perturb* approach. Whenever near-degeneracy systems are treated, multistate approaches have to be introduced, giving rise to the MS-CASPT2 and the MCQDPT methods.^{16,17} These methods are based on the *diagonalize-then-perturb-then-diagonalize* approach.

2.2. Density-Based Methods

2.2.1. Density Functional Theory

An alternative approach to study the electronic structure of many-body systems is the density functional theory (DFT). The core spirit of DFT is to substitute the complicated and thus hard-to-compute many-electron wavefunction, which contains $3N$ variables, for a functional of one-electron density, which contains only 3 variables. In this scope, P. Hohenberg and W. Kohn (HK) formulated two theorems in 1964 that eventually became the basis of the DFT.¹⁸ Based on the Thomas-Fermi model,^{19,20} the authors stated in the first theorem that the one-electron density determines the total energy, whenever this electron density is N -representable (i.e., $\rho(r) \geq 0$ and $\int \rho(r) dr = N$) and v -representable (i.e., $\rho(r)$ can be derived from an external potential $\hat{V}_{ext}$). Defining the Hamiltonian as:

$$\hat{H} = \hat{F}_{HK} + \hat{V}_{ext} \quad (2.30)$$

then the energy is thus described as a functional of the electron density as follows:

$$E_v[\rho] = F_{HK}[\rho] + \int \rho(r) V_{ext}(r) dr \quad (2.31)$$

The second HK theorem brings the variational principle up, since it states that the electron density that minimizes the total energy is the ground state electron density.

$$E_v[\rho] \geq E_0 \quad (2.32)$$

equation that can be rewritten as:

$$\frac{\partial E_v[\rho]}{\partial \rho} = 0 \quad (2.33)$$

Substituting equation (2.31) onto equation (2.33) and introducing the N -representable restriction by means of the Lagrange multipliers method it is obtained the Fundamental equation of DFT.

$$\mu = \frac{\partial E_v[\rho]}{\partial \rho(r)} = v_n(r) + \frac{\partial F_{HK}[\rho]}{\partial \rho(r)} \quad (2.34)$$

The HK theorems served as the foundation of modern DFT, but since they do not provide an explicit expression for $F_{HK}[\rho]$, extra steps needed to be taken. W. Kohn and L. J. Sham (KS) proposed in 1965 a methodology almost analogous to the HF method, based on a system of non-interacting electrons.²¹ In it, the wavefunction associated to the ground state electron density can be expressed as a Slater determinant. Also within the framework of the Born-Oppenheimer approximation, it assumes that the external potential is the electron-nuclei potential V_{Ne} , so the Hamiltonian has the following expression:

$$\hat{h}_{KS}(r) = -\frac{1}{2}\nabla^2 + v_{KS}(r) \quad (2.35)$$

and the energy can be expressed as a functional of the density as follows:

$$E[\rho] = F_{HK}[\rho] + V_{Ne}[\rho] \quad (2.36)$$

where

$$F_{HK}[\rho] = T_g[\rho] + J[\rho] + E_{XC}[\rho] \quad (2.37)$$

$T_g[\rho]$ is the kinetic energy of a non-interacting gas of density $\rho(r)$, $J[\rho]$ the classical coulombic energy, and $E_{XC}[\rho]$ the exchange-correlation energy, which expression is:

$$E_{XC}[\rho] = (T[\rho] - T_g[\rho]) + (V_{ee}[\rho] - J[\rho]) \quad (2.38)$$

The first term in (2.38) is the difference between the kinetic energies of the interacting and non-interacting systems, while the second term is the correction on the total electron interaction energy and the coulombic electron-electron repulsion. In the end, the KS method consists in solving self-consistently the one-electron Schrödinger equations.

$$\left[-\frac{1}{2}\nabla^2 + v_{KS}(r) \right] \varphi_i(r) = \varepsilon_i \varphi_i(r) \quad (2.39)$$

$$\text{where} \quad v_{KS}(r) = v_n(r) + \int \frac{\rho(r_2)}{|r_1 - r_2|} dr_2 + v_{XC}(r) \quad (2.40)$$

and the density is given by $\rho(r) = \sum_i |\varphi_i(r)|^2$

The electron density will approach the exact density whenever $v_{XC}(r)$ approaches the exact exchange-correlation potential. Consequently, the whole correlation energy would be included and all properties of the given system could be calculated exactly. The main problem in KS-DFT is that there is not an analytical expression for the exact $E_{XC}[\rho]$ exchange-correlation

energy, since $v_{XC}(r)$ is unknown and it thus must be approximated. There are several ways to approximate $E_{XC}[\rho]$; among them, LDA, GGA, mGGA, and hybrids functionals are the most common approximations. The local density approximation (LDA) was first introduced by P. Dirac²² within the Thomas-Fermi model^{19,20} and it is based on the homogeneous electron gas density. LDA functionals depend locally on the density.

$$E_{XC}^{LDA}[\rho] = \int \varepsilon_{LDA}(\rho) dr \quad (2.41)$$

The LDA approximation can be improved by considering separately alpha and beta densities, arising the local spin density approximation (LSDA).²³ In the generalized gradient approximation (GGA) the exchange-correlation energy not only depends on the density, but also on its gradient.

$$E_{XC}^{GGA}[\rho] = \int \varepsilon_{GGA}(\rho, \nabla \rho) dr \quad (2.42)$$

Another level of improvement was achieved by adding also a dependence on the second derivative of the density. This approximation is called meta-GGA (mGGA). It is the approximation that the M06L functional,²⁴ the most extensively used throughout this thesis, is based on.

$$E_{XC}^{mGGA}[\rho] = \int \varepsilon_{mGGA}(\rho, \nabla \rho, \tau, \nabla^2 \rho) dr \quad (2.43)$$

Although not mentioned before, the $E_{XC}[\rho]$ is usually split into an exchange ($E_X[\rho]$) and a correlation ($E_C[\rho]$) terms. Within this assumption, hybrid functionals include a portion of HF exchange (the K_{ij} term of equation (2.8)) in $E_X[\rho]$. For instance, the widely used B3LYP hybrid functional^{25,26} includes a 20% of HF exchange.

An alternative and perhaps more sophisticated approach to the exact functional are the range-separated hybrid (RSH) functionals,²⁷ where the two-electron operator is separated into the short-range and long-range parts by means of the standard error function $erf(x)$ such that:

$$\frac{1}{r_{12}} = \frac{1 - erf(\omega r_{12})}{r_{12}} + \frac{erf(\omega r_{12})}{r_{12}} \quad (2.44)$$

where ω is a parameter that determines the ratio of these parts. The short-range is treated as any of the schemes shown before, while the long-range is the full HF exchange.

2.2.2. Time-Dependent Density Functional Theory

Whenever one wants to move beyond static ground state properties (for instance, when the optical properties are evaluated) within the DFT framework, the description of the molecular response to time-dependent fields has to be somehow introduced. E. Runge and E. K. U. Gross published a theorem in 1984 that permitted a generalization of the first HK theorem to the time-

dependent density framework.²⁸ In it, the non-relativistic time-dependent Schrödinger equation has to be solved for a given time-dependent external potential.

$$i \frac{\partial}{\partial t} \varphi_i(r, t) = \left[-\frac{1}{2} \nabla^2 + v_{KS}(r, t) \right] \varphi_i(r, t) \quad (2.45)$$

$$v_{KS}(r, t) = v_n(r, t) + \int \frac{\rho(r_2, t)}{|r_1 - r_2|} dr_2 + v_{XC}(r, t) \quad (2.46)$$

The external potential is now described as a dynamical electron-nuclei potential plus an interaction potential with an external field. It can be treated as a perturbation, which is turned on at $t = 0$ for some time, thus obtaining the dipole of interest as a function of time.

$$v_{ext}(r, t) = v_{ext,0}(r) + \delta v_{ext}(r, t) \quad (2.47)$$

The density can thus be expressed as a Taylor series with respect to $\delta v_{ext}(r, t)$, usually truncated at the first order. Hence, the density depends linearly on the external potential perturbation, which gives rise to the linear response TD-DFT. Within this assumption, the first order correction to the electron density can be expressed by means of the density response function χ .

$$\delta \rho(r, t) = \int_0^\infty dt' \int \chi(rt, r't') \delta v_{ext}(r', t') dr' \quad (2.48)$$

This equation can also be expressed in terms of a KS non-interacting system, switching $\chi(rt, r't')$ and $\delta v_{ext}(r', t')$ for $\chi_{KS}(rt, r't')$ and $\delta v_{KS}(r', t')$. Let $\varphi_i^{(0)}(r)$ be the KS orbitals, then the KS density response function can be expressed, after being Fourier-transformed, as the following Lehman representation:

$$\chi_{KS}(r, r', \omega) = \lim_{\eta \rightarrow 0^+} \sum_{k,j} (f_k - f_j) \delta_{\sigma_k \sigma_j} \frac{\varphi_k^{(0)*}(r) \varphi_j^{(0)}(r) \varphi_j^{(0)*}(r') \varphi_k^{(0)}(r')}{\omega - (\varepsilon_j - \varepsilon_k) + i\eta} \quad (2.49)$$

where f_i are the usual Fermi occupation factors and σ_i the spin orientation of the i th orbital. χ_{KS} has poles at KS single-particle orbital energy differences ($\omega = \varepsilon_j - \varepsilon_k$) and their oscillator strengths are related to the numerator. For a true interacting system, the expression of the density response function is given as follows:

$$\begin{aligned} \chi(rt, r't') &= \chi_{KS}(rt, r't') + \int dt_1 \int dr_1 \int dt_2 \int dr_2 \chi_{KS}(rt, r_1 t_1) \\ &\quad \left[\frac{\delta(t_1 - t_2)}{|r_1 - r_2|} + f_{xc}(r_1 t_1, r_2 t_2) \right] \chi(r_2 t_2, r't') \end{aligned} \quad (2.50)$$

This equation turns to be the fundamental linear response equation of TD-DFT. From this equation a matrix formulation can be derived, whose eigenvalues and eigenvectors yield the true excitation energies and oscillator strengths. If the couplings with all other transitions are

neglected, the poles of an interacting system are defined as the non-interacting KS poles plus the diagonal elements of the matrix M .

$$\Omega = (\varepsilon_j - \varepsilon_k) + M_{qq} \quad (2.51)$$

$$M_{qq} = \iint \varphi_k^{(0)*}(r) \varphi_j^{(0)}(r) \left[\frac{1}{|r-r'|} + f_{xc}(r, r', \omega) \right] \varphi_j^{(0)*}(r') \varphi_k^{(0)}(r') dr dr' \quad (2.52)$$

This approach is the single-pole approximation (SPA). It is worth mentioning that the exchange-correlation potential is usually described through the adiabatic approximation, which plugs the density at time t into a ground state functional.

$$v_{xc}^{adiab}(r, t) = v[\rho(r)_{\rho=\rho(t)}] \quad (2.53)$$

2.3. Basis Sets

In quantum chemistry the wavefunction is represented as a set of functions that spans the spatial part where the Schrödinger equation is applied. The most common approach is to define the spinorbitals that compose the Slater determinant (equation (2.1)) as a linear combination of atomic orbitals (LCAO). Ideally, the complete basis set would involve an infinite number of functions, but in practice a finite set has to be chosen. Hence, the election of such finite set is crucial for the proper description of the given system of interest. The atomic orbitals are represented by two types of functions: the Slater-type orbitals (STO) and the Gaussian-type orbitals (GTO).

$$\text{STO} \quad \phi_{\zeta, n, l, m}(r, \theta, \varphi) = N r^{n-1} e^{-\zeta r} Y_{l, m}(\theta, \varphi) \quad (2.54)$$

$$\text{GTO} \quad \phi_{\zeta, n, l, m}(r, \theta, \varphi) = N r^{(2n-2-l)} e^{-\zeta r^2} Y_{l, m}(\theta, \varphi) \quad (2.55)$$

The former preserves the same exponential dependence on the electron-nucleus distance as hydrogen-like orbitals, while the latter does not have the right behavior near the nucleus. On the other hand, GTO can be integrated analytically, while STO cannot. This is a vast drawback for STO, which in practice are almost limited to the description of small systems. A common procedure is to use a combination of n GTO to mimic the STO behavior. Valence electrons are usually described with several GTO combinations. Further improvement of basis sets can be achieved by the addition of extra functions (polarization and/or diffuse functions).

2.4. Quantum Mechanical Solvation Models

An important part of day-to-day chemistry is solution chemistry. There are two main approaches to model solution environments within quantum chemistry: the discrete and the implicit (or continuum) models. The former consists in adding n solvent molecules around the solute trying to emulate the first solvation shell. Given the obvious fact that computational resources are limited, usually not even half of the true first solvation shell can be taken into

account. Moreover, the bigger the solute is, the larger the number of solvent molecules needed to properly describe it. Therefore, oftentimes only a small number of solvent molecules can be included in the calculation, even for the cases where these solvent molecules are described at a lower computational level.

On the other hand, the continuum model provides a simplified but extended description of a diluted solution environment. In this model the solvent is described as a homogeneous dielectric around the solute, which is placed in a cavity dug out in the solvent. The main idea is that the charge distribution of the solute polarizes the dielectric continuum, which in return polarizes the solute charge distribution. This procedure is evaluated self-consistently. The solute-solvent interactions are described in terms of a solvent reaction field, which is introduced as a reaction potential into the Hamiltonian as a perturbation. Among the reaction field methods, the polarizable continuum method (PCM) is the most common one.²⁹ In this method, the reaction potential is described in terms of a set of induced point charges placed at the center of small surface elements (tesserae), covering the cavity in the dielectric medium.

Discrete and implicit models can also be combined, providing an accurate description of (part of) the first solvation shell, using the discrete model, surrounded by a long-range dielectric continuum. This approach is called the mixed discrete-continuum solvation model.

2.5. Quantum Chemistry Methods for the Description of Non-Covalent Interactions

Non-covalent interactions are quantitatively characterized by the interaction energy that arises between two or more interacting fragments. This interaction energy is usually obtained by means of the supermolecule approach

$$E_{\text{int}} = E - \sum_i E_i \quad (2.56)$$

where the energy of the fragment E_i is obtained at the geometry of the complex, using the computational methods described above. This approach includes an implicit overestimation of the E_{int} due to the usage of finite sets of spinorbitals, the so-called basis set superposition error. The most common method to correct this error is given hereafter in this section. It is worth mentioning that instead of E_{int} , the formation energy can be used

$$E_{\text{for}} = E - \sum_i E_i^{\text{opt}} \quad (2.57)$$

where the energy of the fragments is given at their optimum geometry, E_i^{opt} . This description is required for instance in bond formation/breaking processes.

This section now describes two methodologies that provide insight into the nature of non-covalent interactions, where their interaction energy is decomposed into its main contributions. Moreover, an approach to correct the aforementioned basis set superposition error and a

methodology to assess the topology of the electron density around the intermolecular contacts are also described.

2.5.1. Symmetry-Adapted Perturbation Theory for Closed-Shell Fragments

Since non-covalent interactions will always be weaker than regular covalent bonds they can be treated by means of perturbation formalisms. In this sense, several methodologies have been proposed, such as intermolecular perturbation theory (IMPT)³⁰ or symmetry-adapted perturbation theory (SAPT).³¹ Both methods permit an accurate decomposition of the interaction energy in terms of several components. In the SAPT, the total Hamiltonian for the supermolecule is partitioned as $H = F + V + W$, where $F = F_A + F_B$ is the sum of the Fock operators of fragments A and B, V is the intermolecular interaction operator, and $W = W_A + W_B$ is the sum of the Møller-Plesset fluctuation operators. Then, the interaction energy is expanded as a perturbative series

$$E_{\text{int}} = \sum_{n=1} \sum_{j=0} (E_{\text{pol}}^{(nj)} + E_{\text{exch}}^{(nj)}) \quad (2.58)$$

where n and j denote the orders of the operators V and W , respectively. $E_{\text{pol}}^{(nj)}$ are identical to the corrections obtained by regular Rayleigh-Schrödinger perturbation theory, while $E_{\text{exch}}^{(nj)}$ arise from the use of a global antisymmetrizer to force the correct permutational symmetry of the dimer wavefunction in each order. First-order corrections on the V operator provide the electrostatic and exchange contributions, whereas its second-order corrections give rise to the induction and dispersion terms. When second-order corrections are given on the V operator and no expansion is set on the W operator, the interaction energy obtained is equivalent to the HF interaction energy. If second-order corrections on the W operator are included, then the expression obtained is roughly equivalent to second-order MBPT calculation. The terms obtained on the given V and W expansions are ultimately grouped on four major components:

$$E_{\text{int}} = E_{\text{exch}} + E_{\text{el}} + E_{\text{ind}} + E_{\text{disp}} \quad (2.59)$$

These components of the interaction energy have the following physical meaning: (a) the exchange component (E_{exch}) is caused by to the repulsion that electrons feel when they occupy the same region of the space, in accord with the Pauli exclusion principle; (b) the electrostatic term (E_{el}) is associated to the electrostatic interaction of both non-polarized monomers; (c) the induction component (E_{ind}) is attributed to the interaction of the permanent multipole moments of one monomer and the induced multipole moments on the other; and (d) the dispersion term (E_{disp}) comes from the correlation of electron motions on one monomer with those on the other monomer.

2.5.2. Interaction Energy Decomposition for Open-Shell Fragments

Whenever the interacting fragments are open-shell systems, an additional term may arise if their SOMO orbitals present an efficient overlap. This term is the bonding component of the

interaction energy (E_{bond}), and it cannot be evaluated by the SAPT or the IMPT methods. Instead, our group developed an alternative approach that provides a rough but meaningful estimation of the interaction energy components of such interactions.³² Within this approach, the interaction energy is decomposed as follows:

$$E_{int} = E_{exch} + E_{el} + E_{disp} + E_{bond} \quad (2.60)$$

where each term has the same physical meaning as above. The electrostatic term is evaluated using the coulombic expressions from a multipole expansion, commonly truncated at first (charge) or second order (dipole).

$$\begin{aligned} E_{el} = & E(q, q) + E(q, \mu) + E(\mu, \mu) + \dots = \\ & \frac{1}{4\pi\epsilon_0} \left(\frac{q_A q_B}{r} - \frac{q_A \mu_B}{r^2} \cos \theta_1 - \frac{\mu_A q_B}{r^2} \cos \theta_2 \right. \\ & \left. - \frac{\mu_A \mu_B}{r^3} [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi] \right) - \dots \end{aligned} \quad (2.61)$$

where r is the distance between the two centers of mass, θ_i the angle between the dipole of the fragment i and the axis that connects it with the center of mass (c.m.), ϕ the dihedral angle of the dipoles through the c.m.-c.m. axis, and q_i and μ_i the charge and dipole of the fragment i .

The dispersion term is evaluated as the difference between the MRPT2 and MCSCF interaction energies, assuming that the MRPT2 method accounts for the whole dynamic correlation. The bonding term is approximated as the difference between the total energies of the closed-shell and high-spin electronic states.

$$E_{disp} = E_{int}^{MRPT2} - E_{int}^{MCSCF} \quad (2.62)$$

$$E_{bond} = E^{CS} - E^{HS} \quad (2.63)$$

2.5.3. Quantum Theory of Atoms-in-Molecules

The topology of the electron density can be analyzed by means of the quantum theory of atoms-in-molecules (QTAIM or, simply, AIM), developed by R. W. F. Bader.³³ The AIM methodology provides an evaluation of the electron density characterizing its critical points (i.e., each point where its gradient value is zero, $\nabla \rho(\vec{r}) = 0$), which in turn permit to identify the nature of intra and intermolecular bonds. The signature of the Hessian provides a straightforward classification of the aforementioned critical points.

- (3,-3) All three eigenvalues are negative; therefore it is a maximum of the electron density. They are usually placed on atomic nuclei.
- (3,-1) Two negative and one positive eigenvalues. It is a maximum on two directions and a minimum on one direction. These are the bond critical points (BCP).
- (3,+1) One negative and two positive eigenvalues. Thus, it is a minimum on two directions

and a maximum on one direction. These critical points are known as ring critical points.

- (3,+3) All three eigenvalues are positive, it is a local minimum of the electron density. Commonly called cage critical points.

The line of maximum electron density linking two (3,-3) nuclei is called bond path, and the (3,-1) point on the bond path is the BCP. The ring and cage critical points arise as a consequence of particular geometry arrangements of the bond paths. The Poincaré-Hopf relationship provides the number and the type of critical points that can coexist for a given system

$$n - b + r - c = 1 \quad (2.64)$$

where n is the number of nuclei, b the number of BCP, r the number of ring critical points, and c the number of cage critical points. BCP can be identified into intra and intermoleculars in terms of their density and Laplacian ($\nabla^2 \rho(\vec{r})$, the trace of the Hessian). Intermolecular BCP present low electron density values and positive Laplacian, whereas intramolecular BCP have higher density and negative Laplacian.

2.5.4. Basis Set Superposition Error

As mentioned in section 2.1.1, the wavefunction is defined by a complete set of spinorbitals through a single Slater determinant or a linear combination of the two. However, in practice these spinorbitals are expressed as a linear combination of a finite set of atomic orbitals, which is commonly called basis set. Whenever the supermolecule approach is used to obtain the interaction energy, the use of nucleus-centered atomic orbitals causes the basis set superposition error (BSSE). This error is due to the different description of the fragments within the supermolecule and isolated, since in the former the basis set is spread over both fragments while when they are isolated it is defined only over each fragment. The most common approach to estimate the BSSE is the Counterpoise (CP) method, suggested by S. F. Boys and F. Bernardi.³⁴ In this method, instead of obtaining the energy of each isolated fragment with its own basis functions, it is obtained with the basis functions of the whole supermolecule, thus having the same set of orbitals describing both the supermolecule and each fragment. Then the BSSE can be estimated as the difference between the energies of each fragment obtained with its own basis functions and the energies of each fragment with the basis functions of the supermolecule.

$$\delta_{BSSE} = E_A^A + E_B^B - (E_A^{AB} + E_B^{AB}) \quad (2.65)$$

$$E_{\text{int},AB}^{(CP)} = E_{\text{int},AB} + \delta_{BSSE} = E_{AB}^{AB} - (E_A^{AB} + E_B^{AB}) \quad (2.66)$$

2.6. Time-Dependent Simulation Methods: Molecular Dynamics

Up to this point, only static quantum chemistry methods have been discussed. However, dynamic effects are sometimes crucial when describing chemical or physical processes, such

as reactivity or vibrational motions in solid state. Such dynamic effects can be obtained by integrating Hamilton's equations of motion on a given system with a certain initial conditions (coordinates, q_i , and linear momenta, p_i , of each atom i).

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} \quad (2.67)$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad (2.68)$$

The choice of the Hamiltonian is critical, since the evaluation of the energy and its gradient will be the most computationally expensive part of the simulation (*vide infra*). Given the fact that any Hamiltonian can be decomposed into its kinetic and potential terms, $H(p, q) = T(p) + U(q)$, then the equation of motion can be expressed as follows:

$$m_i \ddot{q}_i = f_i = -\nabla_{q_i} U \quad (2.69)$$

which is numerically integrated usually through the Verlet, leap-frog, or Beeman algorithms. Once equation (2.69) is integrated, the position of the atoms can be updated, and this process is repeated until some user-defined criterion is fulfilled.

The thermodynamic variables to be controlled (i.e., the statistical ensemble) need to be specified. The most widely used ensembles are the canonical (where N , V , and T variables are controlled), the microcanonical (where N , V and the energy are controlled), and the isothermal-isobaric ensemble (N , T , and P are controlled).

2.6.1. Force-Field Molecular Dynamics

A common procedure to perform molecular dynamics (MD) runs is by using a classical force-field to describe the energy and, hence, the Hamiltonian. It might have several definitions, such as the expression of equation (2.70), which is the one used in chapter 3 of this thesis.

$$U = \sum_{bonds} K_r (r - r_{eq})^2 + \sum_{angles} K_\theta (\theta - \theta_{eq})^2 + \sum_{dihedrals} \sum_n V_n (1 + \cos n\phi) + \sum_{i < j} \left(\frac{q_i q_j}{R_{ij}} - 2\varepsilon_{ij} \left(\frac{R_{ij}^*}{R_{ij}} \right)^6 + \varepsilon_{ij} \left(\frac{R_{ij}^*}{R_{ij}} \right)^{12} \right) \quad (2.70)$$

The potential energy is accounted by a sum of bonds, angles, and dihedral angles deformation energies and a pairwise additive 1-6-12 term including coulombic and van der Waals interactions. This procedure does not take into account the electronic structure of the system (only by the 6-12 Lennard-Jones van der Waals correction), a fact that might be crucial when dealing with some processes.

2.6.2. *Ab Initio* Molecular Dynamics

An alternative approach is the *ab initio* molecular dynamics (AIMD), which combines atomistic MD with internuclear forces obtained from *ab initio* electronic structure, usually DFT, calculations. Under the Born-Oppenheimer approximation, nuclear and electron motions are completely decoupled, a fact that allows a separation of the Hamiltonian into its nuclear and electronic parts, as previously explained in section 2.1.1. This fact also permits considering only the nuclei into the left part of the equation of motion (2.69), while the Hamiltonian includes the DFT electronic energy and the nuclear-nuclear terms. Thus, the electrons respond instantaneously to the nuclear motion and then the ground state electronic eigenvalue $\varepsilon_0(R)$ (obtained from equation (2.35)) gives rise to an electronic surface on which the nuclear dynamics is described by the time-dependent Schrödinger equation on the time-dependent nuclear wavefunction $X(R,t)$.

$$[T_N + V_{NN}(R) + \varepsilon_0(R)]X(R,t) = i\hbar \frac{\partial}{\partial t} X(R,t) \quad (2.71)$$

By this means, the Schrödinger equation of the electronic Hamiltonian has to be evaluated at each nuclear configuration, which might be computationally expensive. In order to solve this issue, R. Car and M. Parrinello developed in 1985 an efficient approach, introducing a fictitious electronic kinetic energy that allows the electrons to follow the nuclear motion adiabatically.³⁵ This approach is called Car-Parrinello MD (CPMD).

$$K_{fict} = \mu \sum_i \langle \dot{\phi}_i | \dot{\phi}_i \rangle \quad (2.72)$$

Introducing a Lagrangian that includes the orbitals as fictitious dynamical degrees of freedom, then the Euler-Lagrange equations give rise to the following coupled equations of motion:

$$M_I \ddot{R}_I = -\nabla_I E[\{\phi\}, R] \quad (2.73)$$

$$\mu \ddot{\phi}_i(r) = -\frac{\partial}{\partial \phi_i^*(r)} E[\{\phi\}, R] + \sum_j \Lambda_j \phi_j(r) \quad (2.74)$$

where Λ_j is a set of Lagrange multipliers introduced in order to preserve orthonormality. Therefore, starting from an initial set of minimized orbitals at an initial nuclear configuration, the position of the nuclei and “the orbitals” evolve according to equations (2.73) and (2.74), respectively.

2.7. Quantum Chemistry Software

The methods that have been described in this chapter provide the right tools to compute all properties in the systems challenged throughout the following chapters. The calculations concerning these methods were carried out using the packages collected in Table 2.1.

Table 2.1. Summary of the packages used throughout this thesis.

Method	Software	Chapter
DFT	Gaussian ³⁶	3, 4
TD-DFT	Gaussian ³⁶	4
CASSCF/CASPT2	Molcas ³⁷	3
RASSCF/RASPT2	Molcas ³⁷	3
CASSCF/MCQDPT	Gamess ³⁸	3
FFMD	Amber ³⁹	3
AIMD	CPMD ⁴⁰	3
AIM	ProAIMs ⁴¹	3, 4

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CHAPTER THREE

Fundamental description of long, multicenter bonding

3.1. Introduction

Long, multicenter bonding has been the focus of attention of many theoretical investigations since its first characterization in the π -[TCNE]₂²⁻ dimers.^{1,2} This early work on π -[TCNE]₂²⁻ undoubtedly set a milestone in the long, multicenter bonding field. The exceptionally long intermonomer distance and the metastable character of these interactions subsequently prompted several authors the study of their nature.

As aforementioned in Chapter 1, (cation)₂(anion)₂ aggregates (where either the anion or the cation is a radical ion forming a long, multicenter bonded dimer) are widely used to model the solid state properties of these dimers.³⁻¹⁰ The K₂[TCNE]₂ aggregate has been used in various studies to assess the nature of the π -[TCNE]₂²⁻ dimer in different manners.³⁻⁵ All studies conclude that although the long, multicenter bond in the K₂[TCNE]₂ aggregate is driven by the K⁺ cations, its nature is described by the SOMO-SOMO overlap (the bonding term) and the dispersion component. Additionally, the properties of long, multicenter dimers in solution are commonly studied using [radical ion]₂(solvent)_n aggregates.^{8,9,11} Continuum models were also employed to model π -dimers in solution by some authors.¹² However, no computational studies have ever been made on the solvation of long, multicenter bonded dimers in the condensed phase with an explicit consideration of the solvent molecules and finite temperature effects, which would provide a consistent and most realistic description of the whole environment. All these studies in the solid state and in solution agree that the properties and nature of long, multicenter bonding are unaffected by the environment. It is worth mentioning that such results are in good agreement with previous experimental findings.^{13,14}

Many computational methods have been used to model long, multicenter bonding. Clearly, DFT and MR-MP2 (analogously, CASPT2 and MCQDPT) are the most common approaches. Although B3LYP was commonly used on the early stages, it has been shown that it is unable to describe their properties.^{3,8,9} In contrast, the highly parameterized Minnesota set of functionals has lately been revealed as reliable DFT methods to describe long bonded π -dimers.¹⁵ Long, multicenter bonds have been shown to possess a non-negligible multiconfigurational character, where the bonding and antibonding combinations of the SOMOs should form the active space. However, density functionals still provide good qualitative results.¹⁵ MR-MP2 calculations are usually based on this (2,2) active space.^{3-5,8,9,15} Other perturbational approaches are analogously used on CASSCF wavefunctions, such as MCQDPT or NEVPT2.^{3,8,9,16} Not so common is the use of other methodologies, although some authors also modeled π -dimers through MP2/MP3,¹² PP (Perfect Pairing),⁴ MR-CISD,⁵ MR-AQCC (Multireference Averaged Quadratic Coupled Cluster),⁵ or CCSD(T)⁶ approaches.

Moreover, a study of the π -[TCNE]₂²⁻ based on the Valence Bond (VB) description suggested the need of expanding the (2,2) active space to a (6,4) (see Figure 3.1), and they defined its bonding as a resonating combination of classical 3-e⁻ bonds.⁶ VB calculations also revealed significant contributions from charge-shift effects on π -[TCNE]₂²⁻ long, multicenter bonding.¹⁷ Charge-shift bonding is a bonding type recently suggested by S. Shaik and P. C. Hiberty based on electron-pair fluctuation due to covalent-ionic mixing.¹⁸

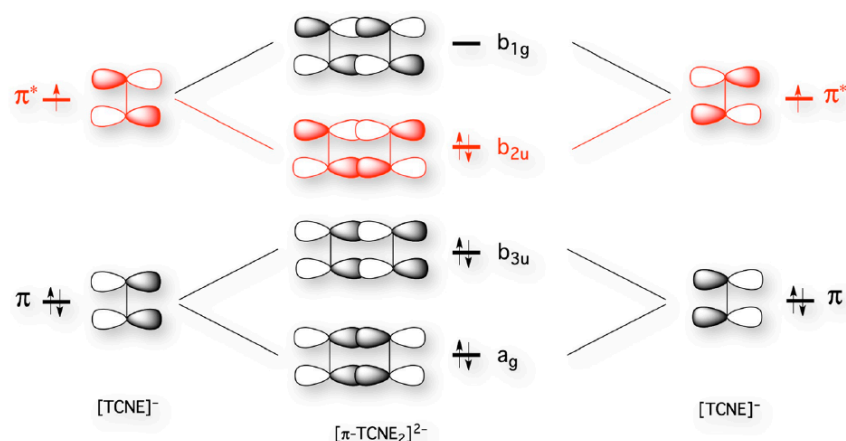


Figure 3.1. Molecular Orbital diagram of the π -[TCNE] $_2^{2-}$ dimer for the description of its minimum (6,4) active space, according to ref. 6.

The present chapter focuses in the fundamental description of long, multicenter bonding in several environments. An extensive characterization with a wide variety of density functionals and active spaces is performed in the gas phase, for the π -[TCNE] $_2^{2-}$, π -[TTF] $_2^{2+}$, π -[TCNB] $_2^{2-}$, and π -[TCNP] $_2^{2-}$ dimers. Moreover, a comprehensive study of the π -[TCNE] $_2^{2-}$ dimer in explicit dichloromethane solution is performed by means of molecular dynamics. Finally, the last two articles focus in solid state long, multicenter bonded dimers. The relative orientation of the π -[TCNB] $_2^{2-}$ and π -[TCNP] $_2^{2-}$ dimers is challenged in the former, while a thorough characterization of the four polymorphs of the [TTF][TCNE] charge-transfer crystal is done in the latter. In the latter, the two established kinds of π -[TCNE] $_2^{2-}$ dimers (Figure 3.2), actually only found in the α - and β -polymorphs of [TTF][TCNE], are revised.

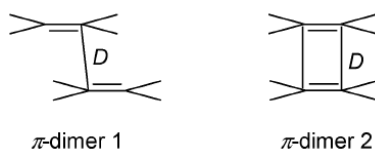


Figure 3.2. Schematic representation of lateral displaced (1) and D_{2h} (2) π -[TCNE] $_2^{2-}$ dimers.

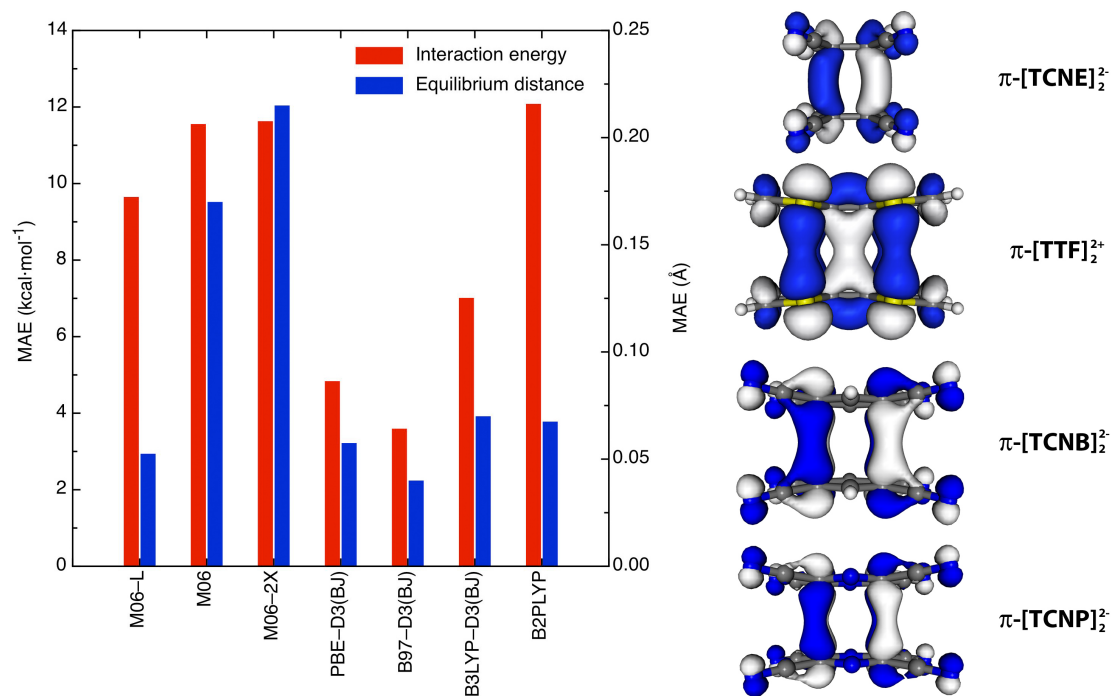
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3.2. Publication 1

Assessing the Performance of CASPT2 and DFT Methods for the Description of Long, Multicenter Bonding in Dimers between Radical Ions



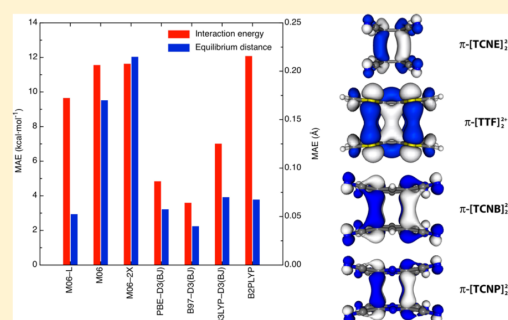
Assessing the Performance of CASPT2 and DFT Methods for the Description of Long, Multicenter Bonding in Dimers between Radical Ions

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Supporting Information

ABSTRACT: The performance of a wide variety of density functionals for the description of long, multicenter bonding in dimers between radical ions has been addressed in this work. Results on interaction energies and equilibrium distances have been evaluated through pure GGA and meta-GGA, hybrid, RSH, and double hybrid functionals. Grimme's dispersion corrections have also been assessed. All results are systematically analyzed and compared for the π -[TCNE] $_2^{2-}$, π -[TTF] $_2^{2+}$, π -[TCNB] $_2^{2-}$, and π -[TCNP] $_2^{2-}$ dimers. The DFT results are benchmarked against RASPT2 calculations based on large active spaces. It is shown that small active spaces do not quantitatively describe the interaction energy curves of these dimers. B97-D3(BJ) turns to be the functional that best reproduces the finest RASPT2 results, while PBE-D3(BJ), B3LYP-D3(BJ), and M06-L also provide satisfactory results.



INTRODUCTION

Organic compounds with a large electron donor (acceptor) capability have been the subject of great interest over the last decades.¹ These compounds are commonly used in solids presenting conducting,² superconducting,³ magnetic,⁴ or other physical properties.⁵ However, their mono-oxidized (reduced) form can dimerize resulting in a diamagnetic long, multicenter bonded entity, where the SOMOs of the radical ions overlap leading to doubly occupied bonding and an empty antibonding combination. Such long, multicenter bonds present spectroscopic similarities to covalent bonds but differ in their nature, strength, and equilibrium distance.⁶ Isolated long bonded dimers of radical ions are metastable, with a small barrier toward dissociation, because the stabilization obtained by the bonding term (as a result of the double occupation of the SOMOs bonding combination) plus the dispersion term results in the presence of a minimum, although it is not large enough to defeat the Coulombic repulsion between the radical ions. However, they do form in the solid state and in low temperature solutions due to the interactions between the long bonded dimer and the adjacent counterions or solvent molecules, respectively, which overcome the repulsion between the radical ions that form the dimer.⁷ Because their first characterization in salts of reduced tetracyanoethylene⁸ (TCNE, whose π -[TCNE] $_2^{2-}$ diamagnetic dimers present an intermonomer distance of ~ 2.9 Å), several other radical ions have been shown to exhibit long, multicenter bonding, such as tetracyanobenzene (TCNB),⁹ tetracyanopyrazine (TCNP),¹⁰

and tetrathiafulvalene (TTF).¹¹ They have also been observed in zwitterionic π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] charge-transfer dyads.¹²

Because of the multireference character of these long bonded dimers at the equilibrium distance range, second-order perturbation theory calculations on multireference wave functions are considered to be the best affordable method to accurately evaluate these interactions. Although their nature can be qualitatively described by a minimum (2,2) active space,^{7b,c} a recent study based on a VB description¹³ suggests that π -[TCNE] $_2^{2-}$ requires a (6,4) active space, where the full π -space of the central C–C of both [TCNE] $^{\cdot-}$, parallel to the bonding axis, should be included to reach quantitative accuracy.¹⁴ VB calculations also revealed significant contributions from charge-shift effects on π -[TCNE] $_2^{2-}$ long, multicenter bonding.¹⁵ DFT methods are also frequently used on the modeling of such interactions, mainly the Minnesota set of functionals (more precisely, M05-2X,¹⁶ M06-L,¹⁷ M06,¹⁸ and M06-2X)^{17c,19} and previously B3LYP.^{7c,d,8,10a,11,20} Yet, the correct description of di-ionic π -dimers presenting long, multicenter bonds by DFT methods is not straightforward due to their multireference character at the equilibrium range, even if density functionals tend to avoid symmetry breaking at equilibrium distances.²¹

Despite the common use of DFT to model such interactions, a systematic assessment of the performance of density functionals in this context is still missing. A first step toward this aim was done by Kertesz and co-workers, who recently

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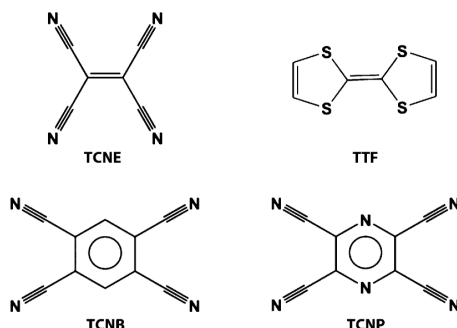
Published: January 6, 2014

studied the performance of several density functionals compared to MRPT2(2,2) results on a neutral dithiadiazolyl long bonded π -dimer and its diselenadiazolyl analogue.²² This study concludes that M06 is the best functional, among the ones used in the work, to properly describe this system. A similar study has been recently reported in a large group of neutral and monoionic charged π -dimers, although they excluded di-ionic long bonded π -dimers.²³

The methodical DFT benchmark is not only missing but also a pressing issue in view of the fact that long, multicenter bonding has been observed in several supramolecular and large complex molecules with potential applications as room temperature molecular switches.^{17c,24} It is clear that correlated wave function methods are unaffordable in these cases. Hence, the use of a proven reliable functional becomes essential on such large systems instead of dealing with resource-demanding CASPT2 calculations based on large active spaces.

In this work, we provide a systematic study on the description of long, multicenter bonds between charged radicals by means of CASPT2 (RASPT2) calculations based on various CASSCF (RASSCF) active spaces. Furthermore, we benchmark a wide class of density functionals, considering GGA and meta-GGA pure and hybrid functionals, long-range corrected hybrid functionals, double hybrid functionals, and empirical dispersion corrections. The results are systematically carried out and compared for the π -[TCNE]₂²⁻, π -[TCNB]₂²⁻, and π -[TCNP]₂²⁻ dianion dimers and the π -[TTF]₂²⁺ dication dimer (Scheme 1). On the whole, it will be proven that density functional methods can successfully reproduce CASPT2 results.

Scheme 1. Chemical Structures of TCNE, TTF, TCNB, and TCNP Molecules



METHODOLOGY

First, the commonly used (2,2) active space has been tested against larger active spaces in the π -[TCNE]₂²⁻ and π -[TCNP]₂²⁻ dianion dimers. This active space results from the bonding and antibonding combination of the SOMO of both monomers. Then, according to the literature, the first larger active space that has been assessed comprises the direct π -space parallel to the bonding axis, that is, (6,4) and (14,12) for the π -[TCNE]₂²⁻ and π -[TCNP]₂²⁻ dimers, respectively. The second larger active space considered is (22,20) for the π -[TCNE]₂²⁻ dimer and (30,28) for the π -[TCNP]₂²⁻ dimer. This results from also considering the π -space of the cyano groups, and it is treated at the RASSCF/RASPT2 level. All multireference

calculations are performed on B3LYP/6-31+G(d) optimum geometries.

This work analyzes 23 density functionals, including a standard generalized gradient approximation (GGA), meta-GGA, hybrid GGA, hybrid meta-GGA, range-separated hybrid (RSH), and double hybrid functionals, which are systematically compared to the RASPT2 results. Grimme's empirical dispersion corrections D2, D3, and D3(BJ) are also considered. PBE²⁵ and BP86²⁶ are the only pure GGA functional among the list of functionals considered herein. The hybrid GGA functionals B3LYP²⁷ and BH&HLYP²⁸ (as implemented in Gaussian09) and the hybrid meta-GGA functional BMK²⁹ are also included in the benchmark. The RSH functionals CAM-B3LYP,³⁰ HSE06,³¹ and ω B97X³² are considered. The D2, D3, and D3(BJ) Grimme's empirical dispersion are added to the pure GGA PBE and the hybrid B3LYP functionals, whereas D2 is also added to the RSH ω B97X. In addition, B97-D2,³³ B97-D3,³⁴ and B97-D3(BJ)³⁵ are also considered. Finally, four Minnesota functionals are included in this work, the pure meta-GGA M06-L,³⁶ hybrid meta-GGA functionals M06³⁷ and M06-2X,³⁶ and RSH M11.³⁸ The double hybrid functional B2PLYP³⁹ has also been considered for the π -[TCNE]₂²⁻ and π -[TTF]₂²⁺ dimers. Table 1 summarizes the information

Table 1. Density Functionals Used in This Work

density functional	type	% HF exch.	ref.
PBE	GGA	—	25
PBE-D2	GGA	—	33
PBE-D3	GGA	—	34
PBE-D3(BJ)	GGA	—	35
BP86	GGA	—	26
M06-L	meta-GGA	—	36
B97-D2	GGA	—	33
B97-D3	GGA	—	34
B97-D3(BJ)	GGA	—	35
B3LYP	hybrid GGA	20	27
B3LYP-D2	hybrid GGA	20	33
B3LYP-D3	hybrid GGA	20	34
B3LYP-D3(BJ)	hybrid GGA	20	35
BH&HLYP	hybrid GGA	50	28
BMK	hybrid meta-GGA	42	29
M06	hybrid meta-GGA	27	37
M06-2X	hybrid meta-GGA	54	37
CAM-B3LYP	range-separated hybrid	19/65 ^a	30
HSE06	range-separated hybrid	25/0 ^a	31
ω B97X	range-separated hybrid	15.8/100 ^a	32
ω B97X-D2	range-separated hybrid	22.2/100 ^a	41
M11	range-separated hybrid	42.8/100 ^a	38
B2PLYP	double hybrid	53 (27) ^b	39

^aHF exchange percentage at short-range/long-range. ^bPT2 correlation percentage given within parentheses.

about the density functionals used in this work. A (75,305) Lebedev⁴⁰ grid is used in all functionals besides M06-L, M06, M06-2X, and M11, for which more precise (99,590) and (150,974) grids are also considered.

Interaction energies are obtained from ground-state relaxed potential energy surfaces, as a function of the intermonomer distance (r : in π -[TCNE]₂²⁻ and π -[TTF]₂²⁺, this distance is defined as the distance between both centers of mass of the central C—C carbons, while in π -[TCNB]₂²⁻ and π -[TCNP]₂²⁻ dimers, it is set between the centers of mass of each aromatic

ring). All geometries are constrained to D_{2h} point group symmetry. The broken-symmetry approach is used within the unrestricted Kohn–Sham formalism (UDFT) in order to converge to open-shell singlet ground states (further details are given in the Supporting Information). The RASPT2 reference values are based on active spaces formed from the full π -space parallel to the bonding axis of each dimer, keeping a (2,2) in each RAS2 (i.e., (22,2,2;10,2,8)⁴² for π -[TCNE]₂²⁻, (26,2,2;12,2,6) for π -[TTF]₂²⁺, and (30,2,2;14,2,12) for both π -[TCNB]₂²⁻ and π -[TCNP]₂²⁻). Previous calculations on [TCNE]⁻ and [TTF]⁺ monomers are also based on such active spaces.⁴³

The standard 6-31+G(d) Pople basis set is used in all calculations, besides in the Basis Set Analysis section, where the 6-31G(d), 6-311G(d,p), 6-311+G(d,p), and 6-311+G(2d,p) basis sets are also used.⁴⁴ All interaction energy values are BSSE corrected by means of the Counterpoise method.⁴⁵ The standard IPEA Hamiltonian and the Cholesky decomposition of two-electron integrals were used on all multireference calculations.⁴⁶ DFT calculations were done using the Gaussian09 package,⁴⁷ while multireference calculations were carried out with the Molcas7.6 package.⁴⁸

RESULTS AND DISCUSSION

1. Reference CASPT2/RASPT2 Interaction Energy Curves

Interaction energy curves are performed with several active spaces for the π -[TCNE]₂²⁻ and π -[TCNP]₂²⁻ dianion dimers (Figure 1) not only to assess the validity of the minimum (2,2) active space but also to analyze the achievement of an active space convergence. Three more active spaces are considered for the π -[TCNE]₂²⁻ dimer, (6,4), and (22,20) (see Methodology section), for which two variations of the

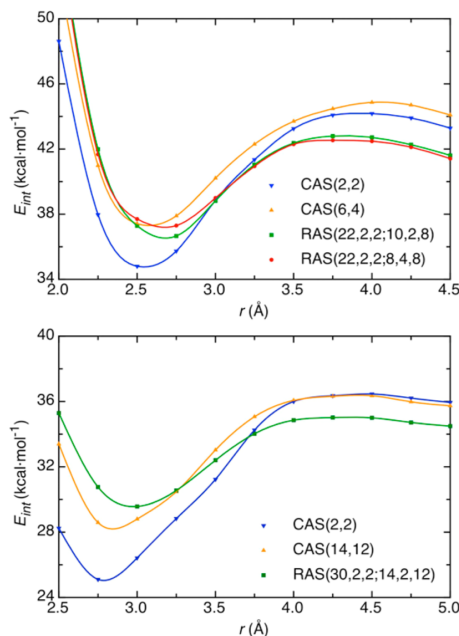


Figure 1. Interaction energy curves for the π -[TCNE]₂²⁻ (top) and π -[TCNP]₂²⁻ (bottom) dimers, computed at the CASPT2(RASPT2)/6-31+G(d) level with various active spaces. All values are BSSE corrected.

RAS active space have been chosen, (22,2,2;10,2,8) and (22,2,2;8,4,8). The former results are from considering a (2,2) active space as the RAS2, while the latter are from considering a (6,4) active space as the RAS2. The CASPT2-(2,2) curve exhibits a minimum at ~ 2.5 Å, slightly overestimating the interaction energy by about 2.5 kcal mol⁻¹ compared to the RASPT2(22,2,2;8,4,8). The largest active space shows a minimum at around 2.7 Å with an interaction energy value of ~ 37 kcal mol⁻¹.⁴⁹ The minimum region is accurately described with the CASPT2(6,4) curve, which is only slightly shifted from the optimum distance (<0.1 Å). The RASPT2(22,2,2;10,2,8) curve almost overlaps the RASPT2-(22,2,2;8,4,8), although it slightly overbinds the minimum region. On the other hand, the dissociation region perfectly matches with both (22,20) RASPT2 active spaces, while the smaller active spaces underestimate the interaction energy by about 2 kcal mol⁻¹. It thus means that the π -space of the cyano groups increases significantly in the dissociation region, in agreement with the geometry evolution, which gradually becomes planar as long as the intermolecular distance increases (note that the four curves finally converge at larger distances; Figure S1, Supporting Information). Moreover, each CASSCF/RASSCF wave function has been analyzed in terms of its natural orbitals occupation (Table S1, Supporting Information). The bonding and antibonding combinations of the SOMOs have an occupation of 1.76 and 0.24 at the equilibrium distance, respectively, on the (2,2) active space, while they reach a value of 1.81 and 0.23 on the largest RAS active space. The (6,4) active space almost shows the same occupation (1.82 and 0.21) as the largest RAS, providing a similar result to the smaller RAS active space. The other orbitals have an occupation number greater than 1.96 for the occupied orbitals and around 0.03–0.04 for the virtual orbitals. On the whole, we can state that the wave function is accurately described at the equilibrium range with a (6,4) active space, although (2,2) already provides a good enough qualitative description.

The close similarity of the interaction curves obtained with both (22,20) RASPT2 spaces, together with the small deviation observed in the CASPT2(6,4) curve, constitutes a strong piece of evidence that the (22,20) multireference calculations carried out on the π -[TCNE]₂²⁻ dimer are converged with respect to the size of the active space. The same argument applies when considering the natural orbitals occupation collected in Table S1 of the Supporting Information. In addition, it should be mentioned that, to the best of our knowledge, the (22,20) active space is the largest active space ever used for the π -[TCNE]₂²⁻ dimer. Hence, the green and red curves of Figure 1 (top) should be viewed as the best benchmark interaction curves thus far reported for this long, multicenter bonded dimer.⁵⁰

The (2,2) active space is compared to the (14,12) and (30,28) active spaces for the π -[TCNP]₂²⁻ dimer. The (30,28) active space corresponds to a RASPT2(30,2,2;14,2,12) calculation, which considers a (2,2) active space as the RAS2. Because only one restricted active space is now considered, the (30,28) notation will be used to refer to the (30,2,2;14,2,12) RAS. Figure 1 (bottom) shows for the π -[TCNP]₂²⁻ dimer the same trends exhibited by the π -[TCNE]₂²⁻ dimer. The CASPT2(2,2) curve overbinds the minimum region by about 5 kcal mol⁻¹, and it is shifted to a shorter equilibrium distance. The CASPT2(14,12) is in better agreement compared to the RASPT2(30,28) curve, reaching a close result in energy and distance terms, although the dissociation region is under-

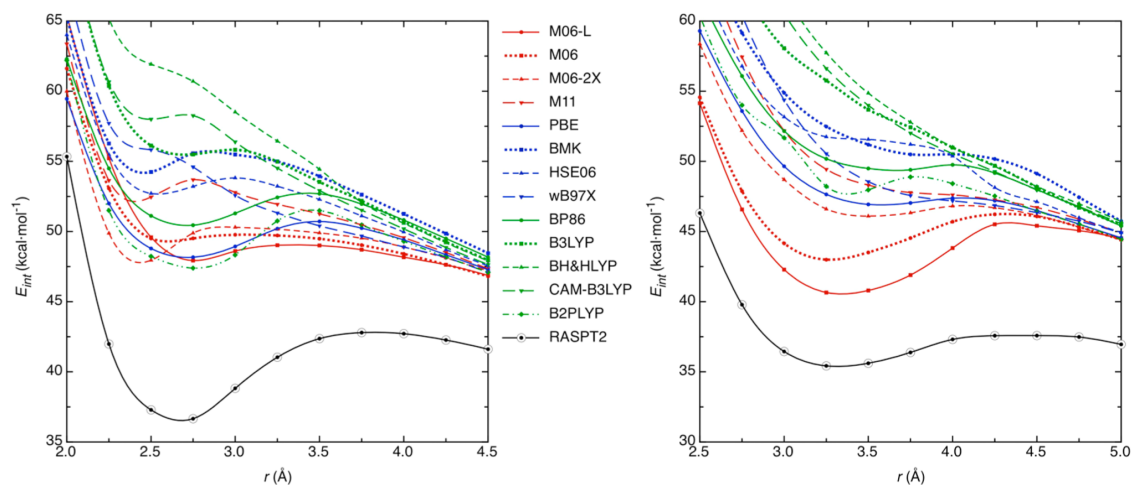


Figure 2. Interaction energy curves for the π -[TCNE] $_2^{2-}$ (left) and π -[TTF] $_2^{2+}$ (right) dimers computed with several density functionals. RASPT2 serves as the reference value. All values are BSSE corrected, and the 6-31+G(d) basis set was used. An enlarged view of the density functionals region for the π -[TCNE] $_2^{2-}$ dimer is found in Figure S2 of the Supporting Information.

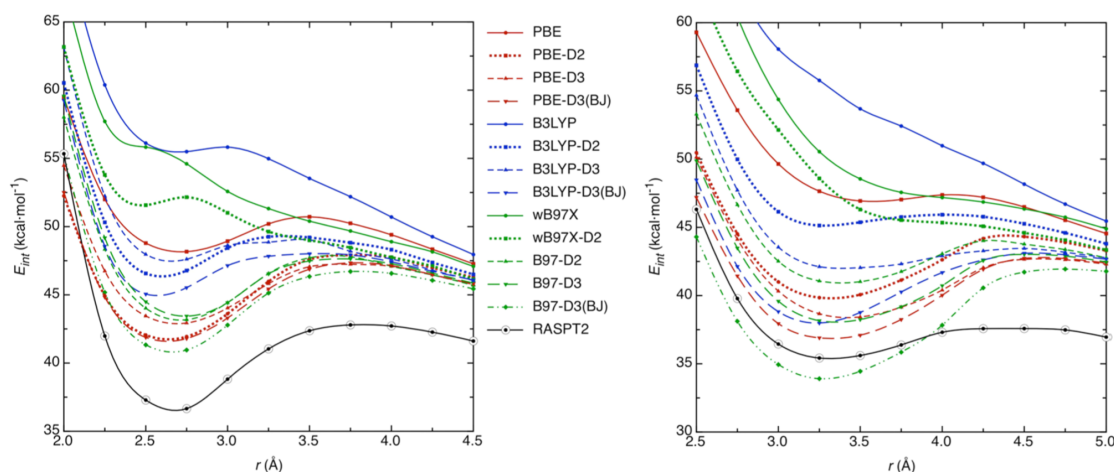


Figure 3. Interaction energy curves for the π -[TCNE] $_2^{2-}$ (left) and π -[TTF] $_2^{2+}$ (right) dimers computed with PBE, B3LYP, ω B97X, and B97 density functionals with D2, D3, and D3(BJ) Grimme's dispersion corrections. RASPT2 serves as the reference value. All values are BSSE corrected, and the 6-31+G(d) basis set was used.

estimated by about 2 kcal mol $^{-1}$. Similarly, the (30,28) active space here performed is, to the best of our knowledge, the best benchmark interaction curve reported so far for the description of the π -[TCNP] $_2^{2-}$ dimer.⁵¹

Therefore, it can be concluded that to accurately describe the long bond metastable minimum the direct π -space parallel to the bonding axis should be added to the (2,2) active space. However, because the geometry of each monomer gradually becomes planar when the intermonomer distance is increased, the π -space of the cyano groups (parallel to the bonding axis) should be also included along the dissociation regime.

2. Density Functionals Assessment. A total of 23 density functionals are evaluated in the present section in terms of interaction energies compared to the RASPT2 reference values (see Methodology section for the active spaces description). Interaction energy curves of a first subset of density functionals for the π -[TCNE] $_2^{2-}$ and π -[TTF] $_2^{2+}$ dimers are plotted in

Figure 2. As shown in the previous section, the RASPT2 curve for the π -[TCNE] $_2^{2-}$ dimer exhibits a minimum at ~ 2.7 Å of about 37 kcal mol $^{-1}$, around 11 kcal mol $^{-1}$ more stable than the most stable DFT curves. Among them, the B2PLYP, M06-L, and PBE functionals show the best performance, providing a minimum at about the same intermonomer distance. M06 and M06-2X exhibit a minimum at similar energies, although they underestimate the equilibrium distance by 0.1–0.3 Å. On the other hand, BP86 provides a minimum at the same intermonomer distance but is 3 kcal mol $^{-1}$ less stable than the B2PLYP, M06-L, and PBE functionals. M11, HSE06, BMK, B3LYP, and CAM-B3LYP predict a minimum at slightly lower equilibrium distances about 5–10 kcal mol $^{-1}$ less stable than the M06-L and PBE functionals. BH&HLYP and ω B97X fail in reproducing any bound minimum. Note also that the barrier toward dissociation is underestimated by all functionals, with B2PLYP, PBE, and BP86 providing the higher barrier.

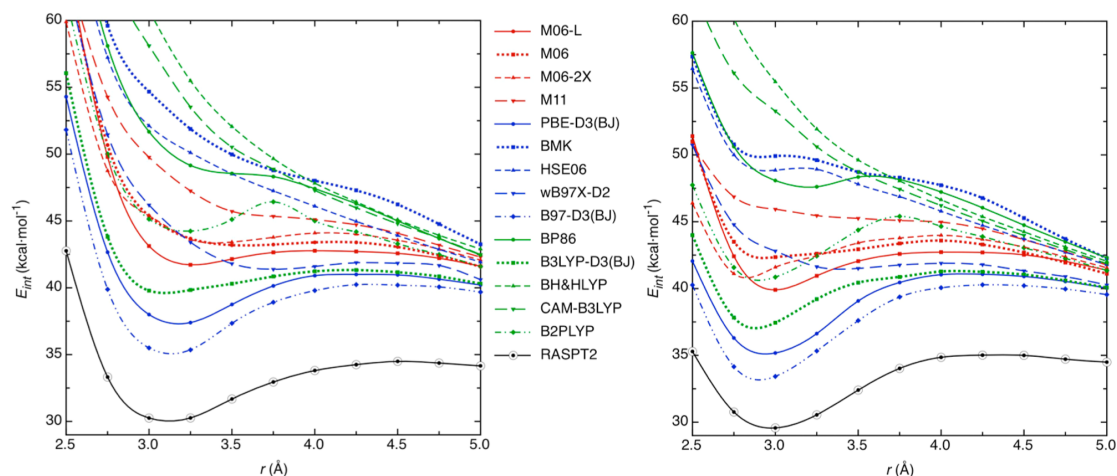


Figure 4. Interaction energy curves for the π -[TCNB] $_2^{2-}$ (left) and π -[TCNP] $_2^{2-}$ (right) dimers computed with several density functionals. RASPT2 serves as the reference value. All values are BSSE corrected, and the 6-31+G(d) basis set was used.

For the π -[TTF] $_2^{2+}$ dimer, the RASPT2 curve exhibits a minimum of 35 kcal mol $^{-1}$ at about 3.3 Å. The M06-L functional provides a minimum at the same equilibrium distance only 5 kcal mol $^{-1}$ less stable than the RASPT2 minimum. M06 also performs reasonably well and shows a minimum at $\sim$ 3.2 Å of about 43 kcal mol $^{-1}$. B2PLYP provides a bound dimer at $\sim$ 3.3 Å of around 48 kcal mol $^{-1}$. M06-2X, PBE, BP86, and BMK functionals exhibit a shallow minimum at slightly higher equilibrium distances of 6–10 kcal mol $^{-1}$ less stable than the M06-L minimum. The other functionals are not able to reproduce a bound minimum for the π -[TTF] $_2^{2+}$ dimer. It is worth mentioning that the larger (150,974) grid must be used in conjunction with the Minnesota functionals (M06-L, M06, M06-2X, and M11) for both dimers in order to describe their dissociation regime (a comparative study between (75,305), (99,590), and (150,974) grids is given in Figures S3–S4 of the Supporting Information).

Grimme's empirical dispersion corrections D2, D3, and D3(BJ) are evaluated in Figure 3 on both π -[TCNE] $_2^{2-}$ and π -[TTF] $_2^{2+}$ dimers. D2, D3, and D3(BJ) corrections are added to PBE and B3LYP functionals, while D2 is added to ω B97X. Additionally, the B97-D2, B97-D3, and B97-D3(BJ) functionals are also included in Figure 3. The inclusion of dispersion corrections improves the results in all the cases studied here, always providing a minimum except for the ω B97X-D2 functional on the π -[TTF] $_2^{2+}$ dimer. D3(BJ) correction provides the best results compared to the RASPT2 curves, while D2 and D3 corrections perform similarly on PBE and B3LYP functionals. D2 reaches better results on the π -[TCNE] $_2^{2-}$ dimer and D3 on the π -[TTF] $_2^{2+}$ dimer, providing bound minima about 5–12 kcal mol $^{-1}$ more stable than their parent curves. Among the 23 functionals considered, the functional that shows the best performance is B97-D3(BJ). It provides the most stable curve in both cases, being about 5 kcal mol $^{-1}$ less stable than the RASPT2 curve for the π -[TCNE] $_2^{2-}$ dimer and overbinding the RASPT2 curve by about 1.5 kcal mol $^{-1}$ for the π -[TTF] $_2^{2+}$ dimer. Also the equilibrium distance perfectly matches the RASPT2 one. Although PBE and B97 dispersion corrected curves reproduce well the barrier toward dissociation for the π -[TCNE] $_2^{2-}$ dimer, it is overestimated for the π -[TTF] $_2^{2+}$ one.

Figure 2's functionals are now assessed on π -[TCNB] $_2^{2-}$ and π -[TCNP] $_2^{2-}$ dimers. PBE-D3(BJ), B3LYP-D3(BJ), and ω B97X-D2 have been considered instead of their uncorrected parent functionals, and B97-D3(BJ) has also been added. Their interaction energy curves are plotted in Figure 4. The RASPT2 curve exhibits the metastable minimum at 3.1 Å of $\sim$ 30 kcal mol $^{-1}$ for the π -[TCNB] $_2^{2-}$ dimer. B97-D3(BJ) is the density functional that better reproduces the RASPT2 results, providing a minimum at the same intermonomer distance and about 5 kcal mol $^{-1}$ less stable. PBE-D3(BJ), B3LYP-D3(BJ), M06-L, and B2PLYP show a minimum at 3.1–3.2 Å of about 37, 40, 42, and 44 kcal mol $^{-1}$, respectively. The ω B97X-D2 functional also provides a minimum at around 42 kcal mol $^{-1}$, although it overestimates the equilibrium distance by 0.7 Å and its barrier toward dissociation is very small. The M06-2X and M06 curves exhibit very close results to ω B97X-D2, although 2 kcal mol $^{-1}$ less stable. M11, BMK, HSE06, BP86, BH&HLYP, and CAM-B3LYP functionals are not able to provide a bound dimer. Note that, as expected, all functionals finally converge at large distances (Figure S5, Supporting Information).

A similar landscape is obtained for the π -[TCNP] $_2^{2-}$ dimer. B97-D3(BJ) is again the density functional that yields results in closer agreement with the RASPT2 curve, which provides a minimum at about 3.0 Å of 29.6 kcal mol $^{-1}$. The B97-D3(BJ) functional shows a minimum of 33.2 kcal mol $^{-1}$ at 2.9 Å, 3 kcal mol $^{-1}$ more stable than the minimum provided by the PBE-D3(BJ) functional, although the latter matches the 3.0 Å equilibrium distance of the RASPT2 curve. B3LYP-D3(BJ), M06-L, and B2PLYP show a minimum within the 2.9–3.0 Å range, 5–7 kcal mol $^{-1}$ less stable than the B97-D3(BJ) functional. The M06-2X and M06 curves also present a minimum within a similar energy range, although at a slightly shorter equilibrium distance. The minimum observed in the ω B97X-D2 curve is within the same energy range than the previous functionals. However, its equilibrium distance is much higher (around 3.4 Å), and its barrier toward dissociation is lower than 0.5 kcal mol $^{-1}$. Also the HSE06 functional exhibits a minimum with a very low barrier toward dissociation, 20 kcal mol $^{-1}$ less stable than the B97-D3(BJ) curve. The BP86 functional shows a minimum 0.2 Å higher than the RASPT2

minimum, with a similar energy to that shown by the HSE06 curve. M11, BMK, BH&HLYP, and CAM-B3LYP curves do not present any minima at the studied distance range.

Figure 5 outlines the key concepts of the results obtained in this section. Among the density functionals employed on all

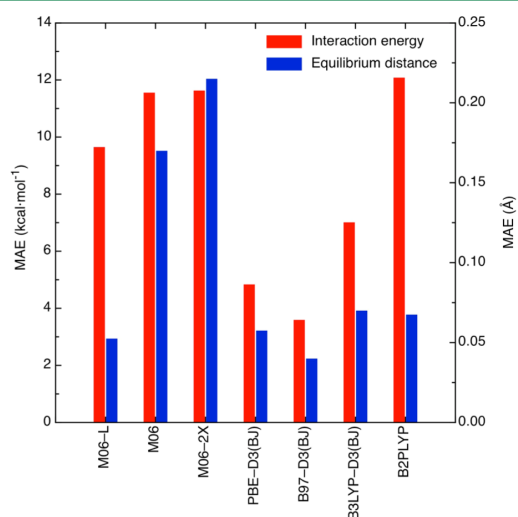


Figure 5. Interaction energy (red, left y-axis) and equilibrium distance (blue, right y-axis) MAEs of the seven functionals that provided a bound minimum on each four dimers compared to their RASPT2 reference curves. The 6-31+G(d) basis set was used.

four dimers, only seven provided a bound minimum in each system: M06-L, M06, M06-2X, PBE-D3(BJ), B97-D3(BJ), B3LYP-D3(BJ), and B2PLYP. Their mean absolute errors (MAE) against the minimum of each RASPT2 curve are shown in Figure 5 concerning their interaction energy and equilibrium distance. B97-D3(BJ) is the functional that best reproduces the RASPT2 results, both in energy and geometry terms, followed by the PBE-D3(BJ) density functional. M06-L provides slightly better equilibrium distances than PBE-D3(BJ), although its MAE in interaction energies almost reaches a value of 10 kcal mol⁻¹ (twice the value of PBE-D3(BJ)). Dispersion corrections seem thus essential to successfully describe these interactions, either by means of empirical dispersion addition or using highly parametrized functionals. It is noteworthy that empirical dispersion corrections provide satisfactory results despite the fact that they were parametrized with ordinary van der Waals aggregates, whose equilibrium distance is longer than that of the systems herein studied. In this sense, it is not surprising that D3(BJ) performs better than D3/D2 because the use of the BJ-damping function avoids repulsive interatomic forces at short distances.³⁵ On the other hand, all RSH functionals here considered failed to reproduce the long bonded dimers interactions, even when empirical dispersion corrections are added.

3. Basis Set Effects. In this section, we evaluate the impact of the basis set on the interaction energy curves done so far for the π -[TCNE]₂²⁻ dimer. CASPT2 curves based on CASSCF(6,4) wave functions are shown in Figure 6, obtained with the 6-31G(d), 6-31+G(d), 6-311G(d), 6-311+G(d), and 6-311+G(2d) basis sets. The largest basis set, the 6-311+G(2d), provides the most stable curve, which is about 2.5 kcal mol⁻¹

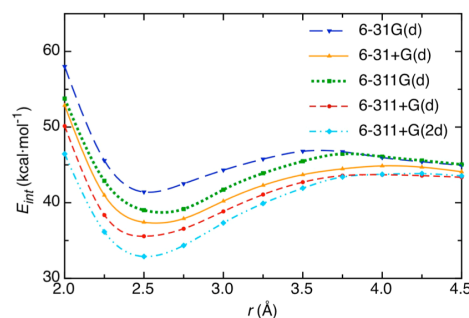


Figure 6. Interaction energy curves for the π -[TCNE]₂²⁻ dimer obtained at CASPT2/CASSCF(6,4) level with several basis sets. All values are BSSE corrected.

more stable than the 6-311+G(d) basis set around the equilibrium distance. An interesting result is that diffuse functions become more important than increasing from double- ζ to triple- ζ basis sets. As a matter of fact, 6-311+G(2d), 6-311+G(d), and 6-31+G(d) provide very similar curves when the BSSE is not corrected (Figure S6, Supporting Information), but the larger the basis set is the more reduced is the BSSE (Figure S7, Supporting Information).

The 6-31+G(d) and the 6-311+G(d) basis sets are compared for the π -[TCNE]₂²⁻ dimer with the seven best functionals outlined in the previous section (Figure 7). DFT curves are not

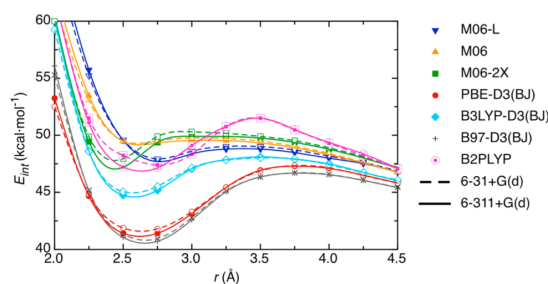


Figure 7. Interaction energy curves for the π -[TCNE]₂²⁻ dimer obtained with several density functionals along with the 6-31+G(d) (dashed lines) and 6-311+G(d) (solid lines) basis sets. All values are BSSE corrected.

very basis set dependent when increasing from double- ζ to triple- ζ . In all cases, the energy difference between both curves is <1.0 kcal mol⁻¹, and they provide the same equilibrium distance, besides the B2PLYP double hybrid functional, on which the minimum is shifted ~0.2 Å. It thus follows that 6-31+G(d) is of sufficient quality for practical purposes (especially for large molecules or supramolecular aggregates).

4. Symmetry Breaking as a Tool To Reproduce Multireference Character in DFT. A discussion on how well DFT approaches the multireference character of the wave function is now presented. In the Introduction section, we pointed out the general trend of density functionals to avoid symmetry breaking at the equilibrium range. This issue is evaluated in Figure 8, where the occupation number of the HOMO of π -[TCNE]₂²⁻ and π -[TTF]₂²⁺ dimers is plotted as a function of the intermonomer distance. Figure 2's functionals are included in this analysis. A clear general trend is observed from Figure 8, where the higher percentage of HF exchange

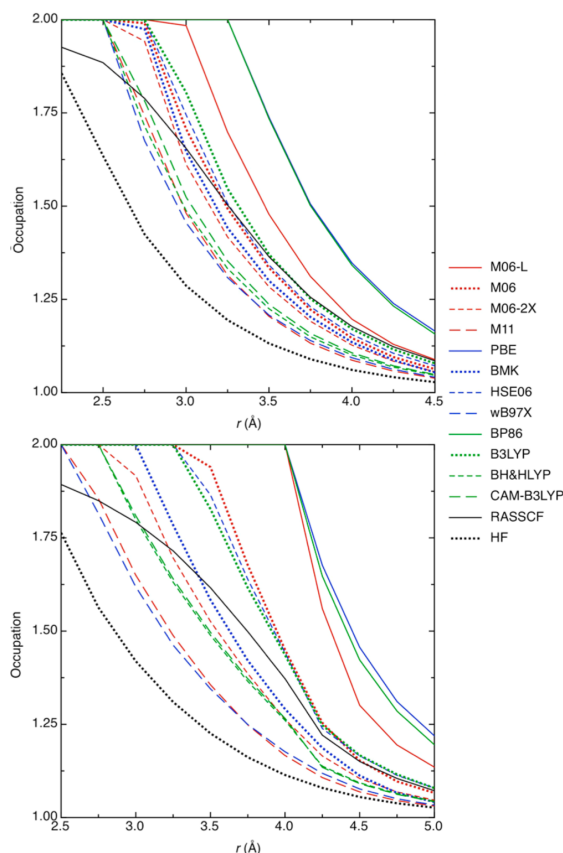


Figure 8. Occupation number of the HOMO of the π -[TCNE] $_2^{2-}$ (top) and π -[TTF] $_2^{2+}$ (bottom) dimers as a function of the intermonomer distance, obtained from the diagonalization of the first-order reduced density matrix from the UDFT calculations.

leads to a greater symmetry breaking. Hence, pure density functionals avoid symmetry breaking at the equilibrium range, while RSH functionals and hybrid functionals with high percentage of HF exchange, such as BH&HLYP or M06-2X, do not. On the other hand, B3LYP and M06 functionals, which contain a small amount of HF exchange, exhibit an average behavior. The behavior among RSH functionals strongly depends on the range parameter. The higher this value is the more long-range corrections the functional considers, and thus, a higher amount of HF exchange is included. Therefore, M11 and ω B97X ($\omega = 0.25$ and 0.30 bohr $^{-1}$, respectively) exhibit symmetry breaking at remarkably short distances, while HSE06 ($\omega = 0.11$ bohr $^{-1}$) and CAM-B3LYP ($\omega = 0.33$ bohr $^{-1}$, with only 65% HF at long-range) present a similar behavior as hybrid functionals containing 30–50% of HF exchange. The same analysis can be carried out taking into account the LUMOs instead of the HOMOs (Figure S8, Supporting Information). Besides the closed-shell ground state at short distances, the smooth variation of the HOMO//LUMO occupation to the eventual 1.0//1.0 fully dissociated state is well reproduced by all density functionals, although hybrid functionals provide a closer match to the RASSCF occupations.

CONCLUSIONS

On the basis of a thorough computational study on four different model systems, we have gauged the performance of a wide variety of state-of-the-art density functionals when it comes to modeling the intriguing chemistry of long, multicenter bonding in dimers between radical ions. The DFT results have been benchmarked against CASPT2/RASPT2 calculations, which have been carried out based on different active spaces.

With reference to the wave function-correlated ab initio calculations, our investigation has revealed that the minimal (2,2) active space in CASPT2 calculations does not suffice to obtain quantitatively correct results. Indeed, the use of larger active spaces including the direct π -space parallel to the bonding axis is mandatory to accurately evaluate the interaction energy of the minima of the long, multicenter bonded dimers. The correct description of the energy barrier for dissociation of these dimers in turn requires even larger spaces that are tractable by means of RASSCF/RASPT2 calculations. In the case of a π -[TCNE] $_2^{2-}$ dimer, for instance, CASPT2(6,4) properly describes the interaction energy at the metastable minimum, while one has to resort to RASPT2(22,2,2;8,4,8) calculations to accurately deal with the dissociation energy barrier.

Concerning the performance of DFT, our benchmark study has demonstrated that the currently available density functionals tend to underestimate the interaction energy of long, multicenter-bonded dimers between charged radicals. In fact, some of the assessed functionals are not even able to predict the existence of the minima associated with the metastable dimers. The functional that best reproduces the CASPT2/RASPT2 interaction energy curves is the B97-D3(BJ) functional. For this particular functional, both the interaction energy of the dimers and their equilibrium distance are in reasonable agreement with CASPT2/RASPT2. Following the B97-D3(BJ) functional, PBE-D3(BJ), B3LYP-D3(BJ), and M06-L also provide notable results. The latter provides slightly better equilibrium distances albeit significantly worse interaction energies than the former two. Furthermore, our analysis has shown that going beyond a 6-31+G(d) basis set does not result in appreciably improved results when using the best functionals. It is thus concluded that this particular cost-efficient basis set offers enough quality for practical purposes. This is important in view of the fact that long, multicenter bonding has been recently observed in large complex molecules and supramolecular aggregates.

ASSOCIATED CONTENT

Supporting Information

Methodological details. Figure 1a extended at larger distances. Enlarged view of Figure 2a. π -[TCNE] $_2^{2-}$ and π -[TTF] $_2^{2+}$ dimers interaction energy curves obtained with several integration grids with the Minnesota functionals. Figure 4a extended at larger distances. BSSE-uncorrected interaction energy curves for the π -[TCNE] $_2^{2-}$ dimer obtained at CASPT2 level with several basis sets. BSSE curves for the π -[TCNE] $_2^{2-}$ dimer obtained at CASPT2 level with several basis sets. Figure 8 analogue with LUMO orbitals instead. Natural orbitals occupation of the π -[TCNE] $_2^{2-}$ dimer obtained with several active spaces. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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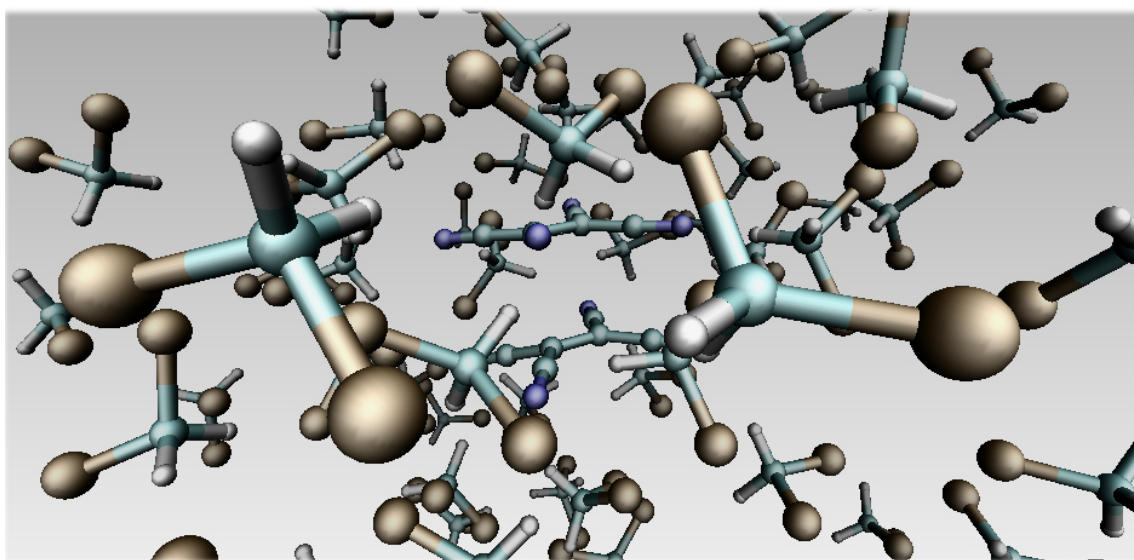
(49) Note that the positive sign of this interaction means that the dimer is less stable than the dissociated monomers.

(50) The (6,4) complete active space involves 10 determinants, while the (22,2,2;10,2,8) and the (22,2,2;8,4,8) restricted active spaces involve 28,290 and 91,750 determinants, respectively.

(51) The (14,12) complete active space involves 314,028 determinants, while the (30,2,2;14,2,12) restricted active space involves 120,526 determinants.

3.3. Publication 2

Study on the Solvation and Stability of $[\text{TCNE}]_2^{2-}$ Dimers in Dichloromethane through Molecular Dynamics Simulations



Study on the Solvation and Stability of $[\text{TCNE}]_2^{2-}$ Dimers in Dichloromethane through Molecular Dynamics Simulations

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ABSTRACT: A molecular dynamics (MD) study has been conducted in the present work aiming to untangle the complexities with regard to the description of long, multicenter bonded radicals in solution. The $\pi\text{-}[\text{TCNE}]_2^{2-}$ dimer is the cornerstone of this study, on which Force-Field and *ab initio* MD simulations have been performed in an explicit CH_2Cl_2 simulation box. FFMD simulations of $(\text{NBu}_4^+)_2[\text{TCNE}]_2^{2-}$ at 175 and 300 K evidenced a non crucial role of the cations in the dimer's stabilization. More accurate AIMD simulations revealed the characteristics of the first solvation shell around the $\pi\text{-}[\text{TCNE}]_2^{2-}$ dimer, which is formed by 20 CH_2Cl_2 molecules. Among them, the 8 solvent molecules located in the surrounding region equidistant from both monomers provide a greater stabilization. Both FFMD and AIMD successfully reproduce the experimental behavior at 175 and 300 K. The free energy profile at 175 K obtained by means of AIMD simulations predicts a stable dimer with a ΔA of around $-5.5 \text{ kcal}\cdot\text{mol}^{-1}$, an equilibrium distance of 3.0 Å, and a barrier toward dissociation of $9.6 \text{ kcal}\cdot\text{mol}^{-1}$. This is the first time that long, multicenter bonded organic radicals are reported in the condensed phase with an explicit consideration of the solvent molecules and finite temperature effects.

INTRODUCTION

It is well established that organic radical-anions, such as reduced tetracyanoethylene (i.e., $[\text{TCNE}]^\cdot$), may form dianionic dimers exhibiting long, multicenter bonding.¹ This bond arises from the overlap of the b_{2g} SOMOs of $[\text{TCNE}]^\cdot$ to form a doubly-occupied bonding and an empty antibonding combination of orbitals of b_{2u} and b_{1g} symmetry, respectively, leading to a diamagnetic $\pi\text{-}[\text{TCNE}]_2^{2-}$ dimer.¹ Long, multicenter bonds were first experimentally and theoretically characterized in crystals of $[\text{TCNE}]^\cdot$ salts, whose dimers exhibit an intermonomer distance of ~ 2.9 Å, and they were found to present the same electronic properties as conventional covalent bonds.^{2–4} Further studies in dichloromethane solution at low temperature determined its equilibrium constant K_D and enthalpy and entropy of dimerization (ΔH_D and ΔS_D) by UV-vis and EPR measurements.⁵ Since their first characterization several other organic radicals have been shown to exhibit long, multicenter bonding; among them, other radical-anions such as tetracyanobenzene (TCNB)⁶ or 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ),^{7–9} radical-cations such as tetrathiafulvalene (TTF),^{10,11} or neutral radicals such as phenalenyl derivatives.^{12,13} They have also been observed in zwitterionic $\pi\text{-}[\text{TTF}^{\delta+}\cdots\text{TCNE}^{\delta-}]$ charge-transfer dyads.¹⁴

Salts of the aforementioned organic radical-ions are well known to exhibit technologically important properties such as magnetic ordering,¹⁵ metal-like electrical conductivity,¹⁶ and even superconductivity.¹⁷ TCNE ,¹⁸ TCNQ ,¹⁹ and TCNP ,²⁰ to list a few examples, are building blocks in molecule-based bulk ferromagnets having magnetic ordering temperatures above room temperature. However, the electron pairing resulting from the formation of long, multicenter dimers would impede these physical properties. Moreover, recent experimental and theoretical work showed the presence of long, multicenter bonded $\pi\text{-}[\text{TTF}]_2^{2+}$ dimers in supramolecular aggregates at room temperature.^{21–25} These supramolecular aggregates were recently proposed as an emerging class of materials with potential ability on molecular switching applications.²⁶ It is thus of high importance to achieve a complete understanding on the formation and nature of such interactions.

Theoretical studies showed that long, multicenter bonds between isolated radical-ions are metastable, since the dispersion and bonding stabilizing terms cannot overcome the coulombic repulsive term.^{27,28} However, they do form in the solid state and in solution at low temperature due to the interactions with counterions and solvent molecules, respectively. Such formation in the solid state can be rationalized by means of cation₂anion₂ aggregates, whose cation $\cdots$ anion interactions are larger than the sum of cation $\cdots$ cation and anion $\cdots$ anion repulsions.²⁹ These

aggregates keep the structure of the radical-ion...radical-ion interaction, thus preserving the long, multicenter bonding properties.⁵ On the other hand, their formation in solution is rationalized in terms of (radical-ion)₂(solvent)_n aggregates, given a large enough number of solvent molecules whose radical-ion...solvent interactions overcome the radical-ion...radical-ion repulsion.³⁰ However, since radical-ion...solvent interactions are much weaker than cation...anion interactions, the solvation shell can only hold the dimer at low enough temperatures (typically, lower than -83°C for the π -[TCNE]₂²⁻ dimer in CH₂Cl₂ solutions).⁵ The long, multicenter bonding properties are also preserved in the (radical-ion)₂(solvent)_n aggregates.^{5,31} Moreover, experimental studies showed that the thermodynamic magnitudes of the dimerization remain unaffected by the size or nature of the counterion.⁵

Many efforts have been made from a computational chemistry perspective to describe these aggregates. Static quantum mechanics (QM) calculations revealed the preferred orientation of K⁺ cations in a K₂[TCNE]₂ aggregate^{29,32} and CH₂Cl₂ solvent molecules in a [TCNE]₂²⁻(CH₂Cl₂)₄ aggregate.³⁰ Similar analyses were also made on [TCNQ]₂²⁻(CH₂Cl₂)₄ and [TTF]₂²⁺(CH₂Cl₂)₈ aggregates.^{33,34} Furthermore, continuum models are also used as a common approach to describe such dimers in solution.^{35,36} However, no computational studies have ever been made on the solvation of long, multicenter bonded dimers in the condensed phase with an explicit consideration of the solvent molecules and finite temperature effects, which would provide a consistent and most realistic description of the whole environment. The present work makes use of molecular dynamics (MD) simulations in the condensed phase to disentangle the precise role of the entire solvation shell and the effects of the counterions present in a dichloromethane solution of the (NBu₄)₂[TCNE]₂ salt. These conditions (salt and solvent) were chosen because they have previously been the object of an exhaustive experimental study.⁵ Classical force-field and *ab initio* MD simulations serve as the tool to accurately analyze most aspects of the π -[TCNE]₂²⁻ long, multicenter bonded dimer and its dissociation profile in a CH₂Cl₂ solution environment. On the whole, the computational study carried out herein will provide an in depth knowledge on the stability and thermodynamics of the dimerization process and the solvation pattern around the π -[TCNE]₂²⁻ dimer in dichloromethane solution and this will not only be interesting by itself, but also will serve as a first

milestone towards the rationalization of organic radical-ions pairing in solution.

METHODOLOGY

Classical Force-Field MD (FFMD) simulations were performed using the AMBER 10 software,³⁷ where the potential energy U is described by a sum of bond, angle, and dihedral deformation energies and pairwise additive 1-6-12 interactions between non-bonded atoms (electrostatic and van der Waals terms).

$$U = \sum_{\text{bonds}} K_r (r - r_{eq})^2 + \sum_{\text{angles}} K_\theta (\theta - \theta_{eq})^2 + \sum_{\text{dihedrals}} \sum_n V_n (1 + \cos(n\phi)) + \sum_{i < j} \left(\frac{q_i q_j}{R_{ij}} - 2\epsilon_{ij} \left(\frac{R_{ij}^*}{R_{ij}} \right)^6 + \epsilon_{ij} \left(\frac{R_{ij}^*}{R_{ij}} \right)^{12} \right)$$

Cross terms in van der Waals interactions were constructed using the Lorentz-Berthelot rules. TCNE⁻ and NBu₄⁺ charges were obtained from electrostatic potential (ESP) analyses based on M06-L/6-31+G(d) calculations. The OPLS model³⁸ was used for the CH₂Cl₂ solvent description. The 1-4 van der Waals and the 1-4 coulombic interactions were scaled down by a factor of 2.0. An atom based cutoff of 12 Å for non-bonded interactions was used and the long-range electrostatics were calculated using the PME (particle-particle mesh Ewald) summation method.³⁹

Table 1 collects the characteristics of the simulations performed herein. The MD simulations were carried out at 175 and 300 K starting with random velocities. The former temperature reproduces the dynamics of the bound dimer, while the latter simulates the dissociated monomers. Stability of the dimer is mainly due to quantum-phenomena which are not included in the force field, hence in order to the study the solvation of the dimer we used harmonic restraints to keep the dimer bound. We used a first restraint between the centers of mass of the central C=C bond of each TCNE of 2.732 Å with a harmonic potential of 50.0 kcal·mol⁻¹ in ± 1.0 Å to keep both TCNE together. The near-*D*_{2h} symmetry was preserved through a restraint in the dihedral angle of the central carbon atoms of both TCNE, also using a harmonic potential of 50.0 kcal·mol⁻¹ in $\pm 20.0^\circ$. Such restraints were only set on the 175 K runs. The temperature was tracked by

Table 1. Characteristics of the simulations carried out in the present work.

Solute	Solvent	Box Size (Å x Å x Å)	Time (ns)	T (K)
FFMD				
TCNE ⁻ , NBu ₄ ⁺	464 CH ₂ Cl ₂	35.1 x 35.1 x 35.1	9.0	175
TCNE ⁻ , NBu ₄ ⁺	464 CH ₂ Cl ₂	36.9 x 36.9 x 36.9	9.0	300
2 TCNE ⁻ , 2 NBu ₄ ⁺	459 CH ₂ Cl ₂	35.2 x 35.2 x 35.2	5.0	175
2 TCNE ⁻ , 2 NBu ₄ ⁺	459 CH ₂ Cl ₂	36.9 x 36.9 x 36.9	6.0	300
2 TCNE ⁻ , 2 NBu ₄ ⁺ ^b	464 CH ₂ Cl ₂	35.3 x 35.3 x 35.3	5.0	175
2 TCNE ⁻ , 2 NBu ₄ ⁺ ^b	464 CH ₂ Cl ₂	37.1 x 37.1 x 37.1	3.0	300
AIMD			(ps)	
2 TCNE ⁻	64 CH ₂ Cl ₂	18.3 x 18.3 x 18.3	46.3	175
2 TCNE ⁻	64 CH ₂ Cl ₂	19.2 x 19.2 x 19.2	52.3	300 ^a

^a The temperature was increased to 350 K during 18 ps in order to accelerate the dissociation process.

^b In its initial configuration both NBu₄⁺ cations start ca. 16 Å away from the [TCNE]₂²⁻ dimer.

coupling the system to a thermal bath using the Berendsen algorithm⁴⁰ with a relaxation time of 1.0 ps. In the (NPT) simulations, the pressure was similarly coupled to a barostat⁴⁰ with a relaxation time of 1.0 ps. A time step of 2 fs was used to integrate the equations of motion via the Verlet leapfrog algorithm.

The solutes were initially immersed in solution. After 20000 steps of energy minimization, 250 ps of dynamics were performed with fixed solutes (BELL option of AMBER) in order to allow solvent relaxation around the solute. This was followed by 250 ps of dynamics at constant volume and 500 ps of dynamics at constant temperature and at a constant pressure of 1 atm. Finally a production run at constant volume and temperature (NVT) was performed. The coordinates were saved every 1 ps.

The change in the (Helmholtz) free energy profile for the dimerization process as a function of the $[\text{TCNE}]^+ \cdots [\text{TCNE}]^-$ distance d was linearly decreased from 15.0 Å ($\lambda = 1$) to 3.0 Å ($\lambda = 0$). This d parameter was set as the distance between the two midpoints of the C=C bond of each TCNE. The inverse association process was also performed to get information on the reliability of the obtained values. The computed free energies are Helmholtz free energies as simulations were performed in the NPT ensemble.

$$\Delta A = \int_0^1 \left\langle \frac{\partial H}{\partial \lambda} \right\rangle_\lambda d\lambda$$

Such change in ΔA at each step λ was calculated by the thermodynamic integration method based on the equation above.⁴¹ The potential of mean force is obtained through the blue moon ensemble method.^{42,43} The transformation from the initial to the final state was achieved in 120 steps, i.e., with increments $\Delta\lambda$ corresponding to $\Delta d = 0.1$ Å. 1260 + 2560 ps equilibration + data collection times at 175 K and 160 + 320 ps at 300 K, at each step λ . The higher equilibration and data collection times results from the slower diffusion at 175K compared to 300K.

Ab initio MD (AIMD) simulations were performed using the Car–Parrinello (CP) scheme for propagating the wavefunctions and the ionic configurations as implemented in the CPMD package.⁴⁴ The PBE density functional⁴⁵ was used for the electronic structure calculations, together with Vanderbilt pseudopotentials,⁴⁶ and a wavefunction cutoff of 25 Ry. Empirical corrections introduced by Grimme to account for the van der Waals intermolecular interactions were used.⁴⁷ The PBE-D2 density functional is proven to accurately reproduce the long, multicenter bonding properties of π - $[\text{TCNE}]_2^{2-}$ and π - $[\text{TTF}]_2^{2+}$ dimers compared to high-level RASPT2 calculations.⁴⁸ The time step was set to 4 a.u. and the fictitious mass for the orbitals was chosen to be 400 a.m.u. A cubic simulation box (of 18.331 Å side at 175 K and 19.165 Å side at 300 K) containing 64 CH_2Cl_2 molecules and one $[\text{TCNE}]_2^{2-}$ dimer was used. Periodic boundary conditions were applied. The initial configurations were taken from equilibrated FFMD simulations. This was followed by a further equilibration of 2 ps in the canonical ensemble, in order to let the systems relax in the new (*ab initio*) interaction potential. The Nosé–Hoover thermostat^{49–}

⁵¹ was used to get an average temperature of 175 or 300 K.

The free energy profile of the dissociation process at 175 K has been obtained as well by means of the thermodynamic integration method described above using the “dynamic distance” reaction coordinate (a mass-weighted mean of selected distances).⁵² This approach has been proven to be a versatile reaction coordinate for the study of processes involving the rupture and formation of a series of chemical bonds or contacts. The dynamic distance was defined as the mean distance of the two intermonomer C $\cdots$ C distances defined as r_1 and r_2 in Figure 1.

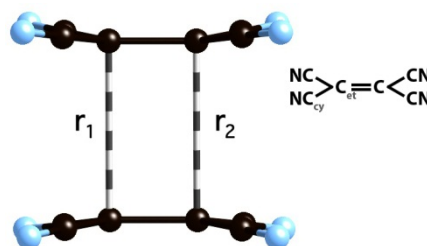


Figure 1. $[\text{TCNE}]_2^{2-}$ dimer structure extracted from the $[\text{NBu}_4][\text{TCNE}]$ crystal. The intermonomer distances considered for the “dynamic distance” reaction coordinate are indicated as r_1 and r_2 . Inset: labeling used along this work.

Static calculations were also carried out to support some of the AIMD results. These static calculations were performed with Gaussian 09,⁵³ using the PBE-D2 density functional⁴⁷ with the 6-31+G(d) basis set.⁵⁴ The PCM continuous model was used to model solution environment.^{55,56}

RESULTS AND DISCUSSION

FFMD Simulations on $(\text{NBu}_4)^+(\text{TCNE})^-$ Single Ion Pairs and $(\text{NBu}_4)_2(\text{TCNE})_2$ Aggregates in CH_2Cl_2 Solution. In order to understand the behavior of NBu_4^+ and TCNE^- solutions, we first performed FFMD runs of $(\text{NBu}_4)^+(\text{TCNE})^-$ single ion pairs (run details are collected in Table 1). The initial configuration was that of an ion pair (Figure S1). The single ion pair dissociates at both 175 and 300 K (Figure 2), showing a high diffusion of both ions along the simulation box. Therefore, both ions are well solvated enough to overcome the coulombic attraction that would keep the ion pair together.

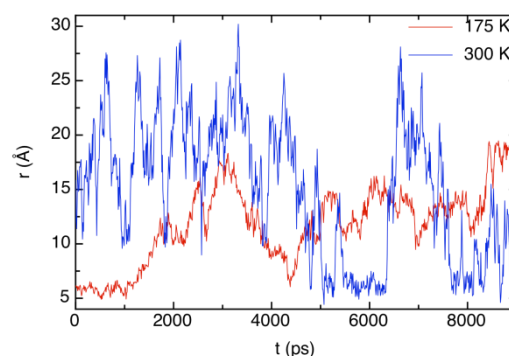


Figure 2. Distance (Å) as a function of time (ps) on $(\text{TCNE})^-(\text{NBu}_4)^+$ ion pair in CH_2Cl_2 , at 175 and 300 K. r is defined as the distance between the center of mass of the TCNE^- and N atom of the NBu_4^+ .

Classical FFMD runs are carried out on $(\text{NBu}_4^+)_2(\text{TCNE}^-)_2$ aggregates, at 175 and 300 K (details in Table 1). According to the experimental reported data, in CH_2Cl_2 the $[\text{TCNE}]_2^{2-}$ dimer would be preserved at the lower temperature, while it would dissociate at room temperature. In order to simulate so, restraints are added at 175 K, while no restraints are introduced at 300 K (see the Methodology section). Due to the quantum mechanics nature of the electron pairing in long, multicenter bonding interactions, they cannot be described with classical tools and thus constraints/restraints are needed to simulate the $[\text{TCNE}]_2^{2-}$ dimer. Time evolution of the distances between solute molecules are shown in Figure 3. At the initial configuration the solutes were taken as a $(\text{NBu}_4^+)_2(\text{TCNE}^-)_2$ aggregate (Figure S2). At 175 K the solutes stay aggregated for around 1.5 ns; one cation dissociates afterwards, and remains dissociated during the rest of the simulation. On the other hand, at 300 K no pattern is found and the solutes diffuse quite randomly along the whole simulation box.

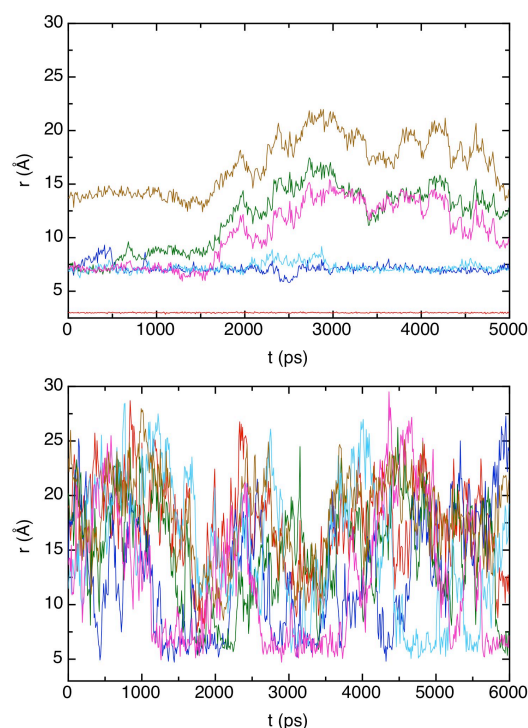


Figure 3. Distances (Å) as a function of time (ps) on the $(\text{TCNE}^-)_2(\text{NBu}_4^+)_2$ aggregate in CH_2Cl_2 at 175 K (top) and 300 K (bottom). $\text{TCNE}^- \cdots \text{TCNE}^-$ distance is depicted in red, $\text{NBu}_4^+ \cdots \text{NBu}_4^+$ in brown, and the four different $\text{TCNE}^- \cdots \text{NBu}_4^+$ distances in pink, dark blue, sky blue, and green.

The influence of the NBu_4^+ cations is now analyzed by running simulations at 175 and 300 K with an initial configuration where both cations are ca. 16 Å away from the dimer (Figure S3). Time evolution of the distances between solutes are shown in Figure 4. At 175 K, after 5 ns simulation the $[\text{TCNE}]_2^{2-}$ dimer remains fully solvated and no interaction with NBu_4^+ cations is observed. It is worth mentioning that in a less polar solution such as CHCl_3 , 3 ns is enough to obtain the $(\text{NBu}_4^+)_2(\text{TCNE}^-)_2$ aggregate formation (Figure S4) at such temperature. Therefore, NBu_4^+ cations do not play a crucial role in the stabilization

of $[\text{TCNE}]_2^{2-}$ dimers in CH_2Cl_2 , in good agreement with the experimental results.⁵ At 300 K the pattern is similar to that found in the previous section, where $(\text{NBu}_4^+)(\text{TCNE}^-)$ ion pairs keep forming and dissociating, although here, since the concentration is twice the previous value, at least one ion pair is more likely to be formed.

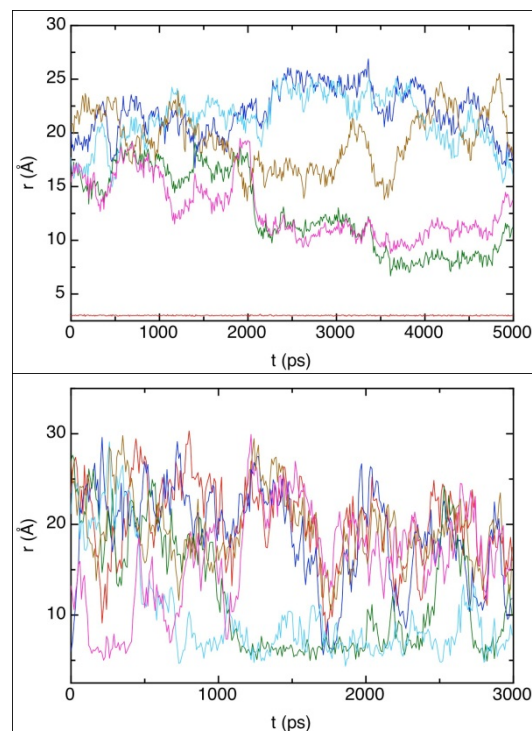


Figure 4. Distances (Å) as a function of time (ps) on the $(\text{TCNE}^-)_2(\text{NBu}_4^+)_2$ aggregate in CH_2Cl_2 at 175 K (top) and 300 K (bottom), starting from remote initial geometry. $\text{TCNE}^- \cdots \text{TCNE}^-$ distance is depicted in red, $\text{NBu}_4^+ \cdots \text{NBu}_4^+$ in brown, and the four different $\text{TCNE}^- \cdots \text{NBu}_4^+$ distances in pink, dark blue, sky blue, and green.

The free energy profiles of the dissociation process at 175 and 300 K are plotted in Figure 5 (several snapshots of the process at 175 K are shown in Figure S5). These energy profiles are obtained through PMF simulations (see Methodological details for further information). A metastable minimum is found for both processes at 175 K, with a barrier toward dissociation of 0.5–0.8 $\text{kcal}\cdot\text{mol}^{-1}$. On the contrary, no minimum is found for the bound dimer at the higher temperature. This result is fully consistent with the experimental reported data. However, since the stabilization given by the bonding component due to the SOMOs overlap is by no means included in these FFMD simulations, the dimer stability is certainly underestimated. It however shows that TCNE^- anions can approach each other with bonding distance without an enormous energy penalty.

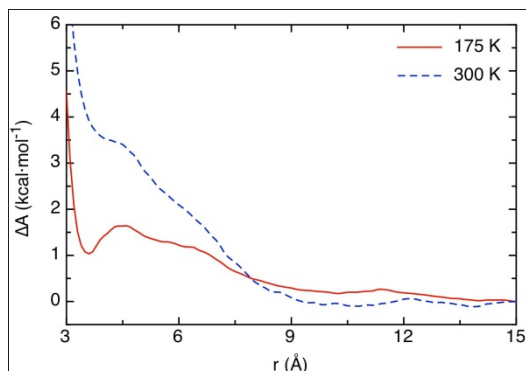


Figure 5. Free energy profiles of the $(\text{TCNE})_2(\text{NBu}_4^+)_2$ aggregate's association and dissociation processes in CH_2Cl_2 at 175 and 300 K. r is defined as the intermonomer $\text{TCNE}\cdots\text{TCNE}$ distance (between the two midpoints of the $\text{C}=\text{C}$ bonds of each TCNE).

AIMD Simulations on $[\text{TCNE}]_2^{2-}$ Dimers in CH_2Cl_2 Solution. FFMD simulations provide a rough estimation of the behavior of the solutes in the media. The solute $\cdots$ solvent interactions lack of enough precision to get a reliable description of the solvation shell, even more given the use of the OPLS solvent description with implicit hydrogens. Furthermore, the use of restraints results in a fictitious stabilization of a quantum-mechanics phenomenon that cannot be modeled by means of classical FFMD approaches. AIMD simulations based on PBE-D2 density functional can, on the other hand, provide a more accurate description of the system without the use of any constraint/restraint. Thus, AIMD simulations at 175 and 300 K of a $[\text{TCNE}]_2^{2-}$ dimer in CH_2Cl_2 have been performed (see Table 2 for further details). No cations have been introduced in the simulations because we demonstrated in the previous section that they are not crucial in the dimer's stabilization. The probability distribution functions (PDFs) associated with the distance between both TCNE (defined as the distance between the centers of mass of the $\text{C}=\text{C}$ central carbons of each TCNE), the mean value of both $\text{C}=\text{C}\cdots\text{C}$ and $\text{C}\cdots\text{C}=\text{C}$ angles between both TCNE and the $\text{C}=\text{C}\cdots\text{C}=\text{C}$ dihedral angle are given in Figure 6. The three PDFs present a Gaussian-shaped distribution, centered at 2.9 Å, 90°, and 0°, respectively. Hence, the π - $[\text{TCNE}]_2^{2-}$ dimer preserves its geometry (i.e., a D_{2h} -like orientation) during the whole simulation at 175 K. The $\text{TCNE}\cdots\text{TCNE}$ distance is also tracked at 300 K during its 52.3 ps of simulation (Figure 7). The temperature was increased to 350 K during 18 ps (shown between dashed lines in Figure 7) to accelerate the dissociation process. After 6 ps at 350 K, the dimer starts dissociating. Once this process is completed, the temperature is decreased again to 300 K and the dimer remains dissociated. The experimental observation that the dimers are mostly dissociated at room temperature is therefore reproduced by the AIMD simulations.

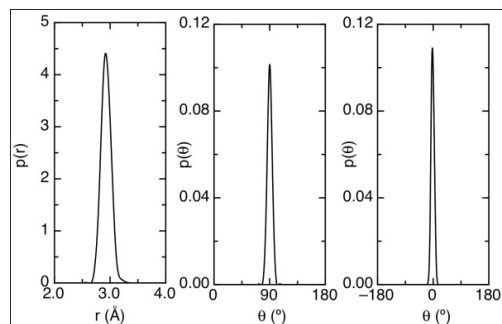


Figure 6. Probability distribution functions associated with the distance between the centers of mass of each TCNE (right), the $\text{C}=\text{C}\cdots\text{C}$ angle between both TCNE (center), and the $\text{C}=\text{C}\cdots\text{C}=\text{C}$ dihedral angle between both TCNE (left) along the whole 175 K simulation.

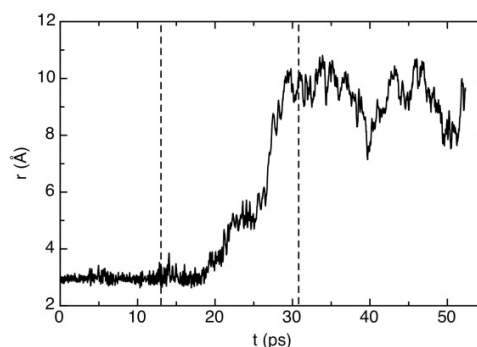


Figure 7. Time evolution of the $\text{TCNE}\cdots\text{TCNE}$ distance, at 300 K. The temperature was raised to 350 K during the 18 ps comprised between the two dashed lines in order to accelerate such dissociation process.

Once it is demonstrated that the dimer structure is preserved during the whole simulation at 175 K, its solvation by the dichloromethane molecules is now analyzed. Radial distribution functions (RDFs) of dichloromethane's H atoms (from now on, H_{DCM}) around the three atoms types of a TCNE (that is, N, C_{cy} , and C_{et} ; see Figure 1 inset) are shown in Figure 8. The eight N atoms exhibit a RDF maximum at 2.4–2.6 Å, while the eight C_{cy} and the four C_{et} show a maximum at 3.2–3.4 Å and 4.25–4.75 Å, respectively. Given the nature of the $\text{C}-\text{H}\cdots\text{A}$ hydrogen bonds, which typically have a length around 2.4 Å,⁵⁷ we can conclude that the $\text{C}-\text{H}\cdots\text{N}$ interactions play the main role in the stabilization of the TCNE dimer in solution. The integration of the $\text{H}_{\text{DCM}}\cdots\text{N}$ RDF (up to the first peak) provides a coordination number of 4 hydrogens around each nitrogen.

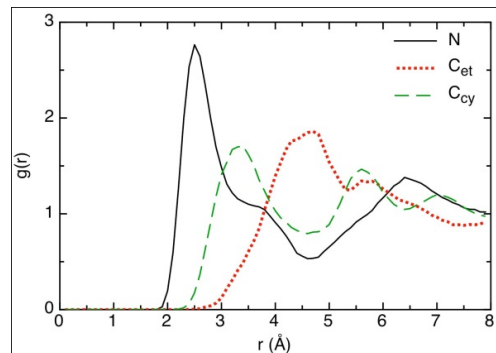


Figure 8. RDF of H_{DCM} atoms around each TCNE atom type at 175 K.

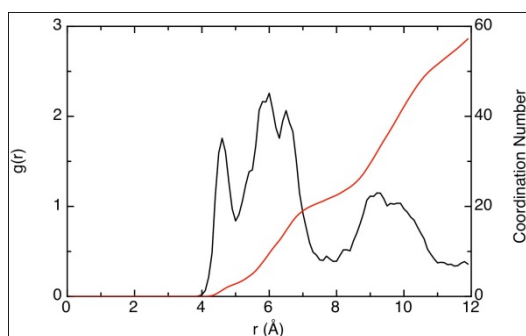


Figure 9. RDF of C_{DCM} atoms around the center of mass of the $[\text{TCNE}]_2^{2-}$ dimer at 175 K.

In order to explore the entire solvation shell, the RDF between the C_{DCM} and the center of mass of the four C_{et} is plotted in Figure 9. The integration at 7.3 Å provides a coordination number of 20 CH_2Cl_2 molecules (Figure 10). However, a first peak is observed, with a coordination number of three CH_2Cl_2 molecules (from now on, the closest solvation shell). These three molecules are highlighted in Figure 10 linked to the center of mass with dashed blue lines. They are preserved within the closest solvation shell during the whole simulation, where the two hydrogens of each CH_2Cl_2 exhibit a short contact simultaneously with two nitrogen atoms (Figure S7). Static calculations at PBE-D2/6-31+G(d) level revealed that CH_2Cl_2 molecules are slightly more stabilized in position **1** or **2** rather than in position **3** (Figure 11), by around 1.5 kcal·mol⁻¹ (position **1** is only 0.14 kcal·mol⁻¹ more stable than position **2**). This result is consistent with our simulations, given the fact that two CH_2Cl_2 molecules are placed in position **1**, whereas only one dichloromethane is located in position **3**. The static calculations also confirmed that while positions **1** and **3** can fit into the closest solvation shell, CH_2Cl_2 molecules located at position **2** are more distant to the center of mass and thus do not contribute to the first peak of Figure 9. Such position **2** molecules are actually found, although they are not as static as the three CH_2Cl_2 within the closest solvation shell. They thus contribute to the main peak of the first solvation shell. The remaining position **3** dichloromethane can also be assigned, but its distance with the center of mass is always about 0.5-1.5 Å larger than the other position **3** CH_2Cl_2 molecules. Overall, the AIMD simulations reveal that each position denoted in Figure 11 is occupied with a CH_2Cl_2 molecule (Figure 10). This set of eight solvent molecules can be divided into two subsets: the first subset comprises the three closest solvent molecules (highlighted and linked with dashed blue lines in Figure 10), while the second subset includes the molecules located at positions **2** and one of the molecules located at position **3** (depicted in four parts and linked with red dashed lines). Although the eight molecules stay within the first solvation shell during the whole simulation, the molecules belonging to the latter subset undergo larger thermal fluctuations than those belonging to the former subset. Figure 12 (top) tracks the distance of both H atoms of one CH_2Cl_2 of the closest solvation shell with their closest nitrogen, showing that almost during the whole simulation each hydrogen makes a short contact (< 3.5 Å) with any of the TCNE nitrogens. On the other hand, the

solvent molecules within the 6 Å peak only have one of their H atoms presenting a short contact with any of the nitrogens, even switching the interacting hydrogen, as seen in Figure 12 (the rest of the molecules of both groups exhibit the same behavior, see Figure S8). Molecules in positions **1**, **2**, and **3** are located in the red region of the scheme of Figure 10 (i.e., the volume around the plane perpendicular to the bonding axis that contains the center of mass). The other twelve CH_2Cl_2 molecules fill the remaining sphere of 7.3 Å radius leaving empty a conical region of about 20° angle with the bonding axis (molecules depicted with diffuse color of Figure 10 and green region of its scheme). Most of these CH_2Cl_2 molecules keep making $\text{H}_{\text{DCM}} \cdots \text{N}$ short contacts during the whole simulation, i.e., they are preserved in the first solvation shell (Figure S9).

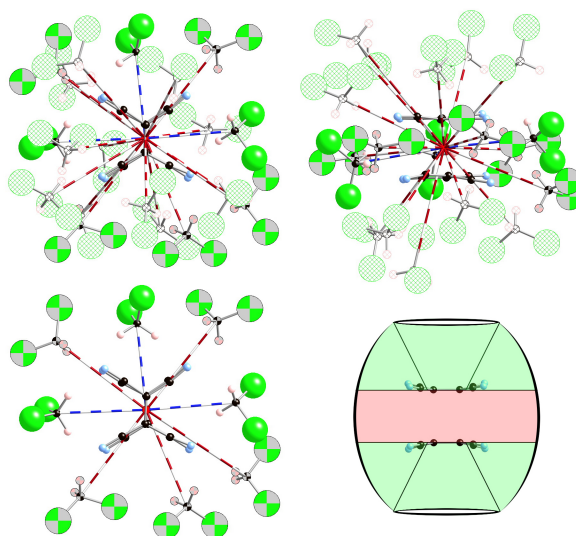


Figure 10. $[\text{TCNE}]_2^{2-}$ first solvation shell. The eight CH_2Cl_2 molecules are highlighted and its region is marked in red on the scheme (see text).

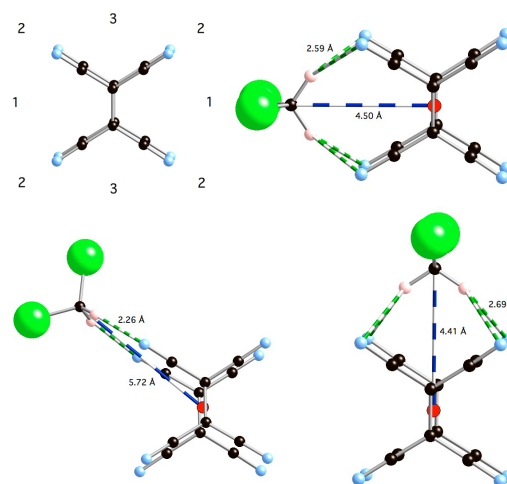


Figure 11. The three most stable positions where a CH_2Cl_2 molecule can be placed within the first solvation shell, obtained from static optimization calculations performed at PBE-D2/6-31+G(d) level.

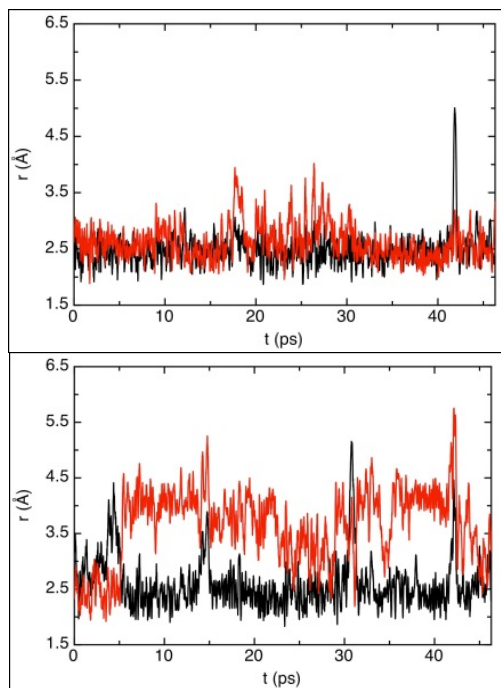


Figure 12. Time evolution of the distance between the two hydrogen atoms with their closest N atom of: (top) a CH_2Cl_2 molecule within the closest solvation shell, and (bottom) a CH_2Cl_2 molecule of the red region of Figure 10's scheme not belonging to the closest solvation shell.

The free energy profile at 175 K for the dissociation process for both in the gas phase and in solution is plotted in Figure 13. The gas phase profile shows a shallow metastable minimum at ca. 2.95 Å, with a small barrier towards dissociation of 0.85 $\text{kcal}\cdot\text{mol}^{-1}$. Given the fact that the curve is not yet stabilized, no estimation about the ΔA of the process can be made. Alternatively, static calculations (performed with G09 at PBE-D2/6-31+G(d) level) in the gas phase predicted a metastable minimum at 2.91 Å with a $\Delta A = 54.0 \text{ kcal}\cdot\text{mol}^{-1}$ at 175 K and a barrier of 0.59 $\text{kcal}\cdot\text{mol}^{-1}$. Therefore, MD simulations and static calculations provide very close results in the gas phase. Moreover, the free energy profile at 175 K has also been obtained in the full explicit solution environment by means of CPMD simulations. The curve exhibits a stable minimum at around 3.0 Å (Figure 13), with a barrier toward dissociation of 9.6 $\text{kcal}\cdot\text{mol}^{-1}$. Although the curve is not fully stabilized, it suggests the dimer formation to be stable, with ΔA (175 K) around -5.5 $\text{kcal}\cdot\text{mol}^{-1}$. On the contrary, static calculations predict a metastable minimum at 2.90 Å, with a ΔA (175 K) = 3.6 $\text{kcal}\cdot\text{mol}^{-1}$ and a barrier towards dissociation of 7.1 $\text{kcal}\cdot\text{mol}^{-1}$.

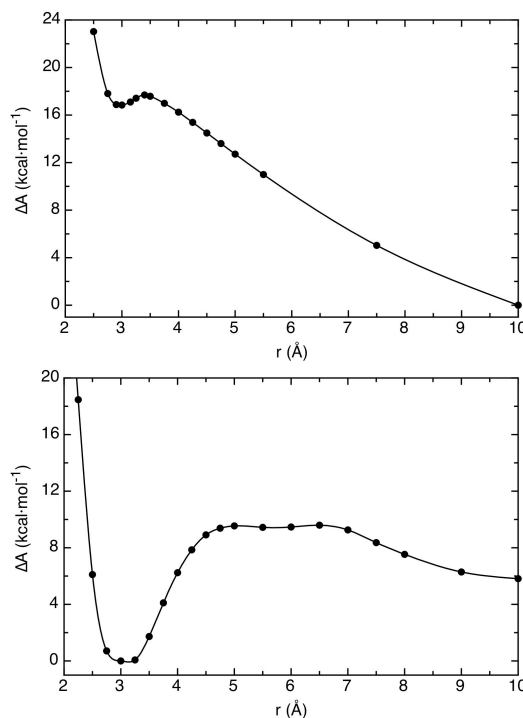


Figure 13. Free energy profiles of the $[\text{TCNE}]_2^{2-}$ dissociation process at 175 K obtained at the gas phase (top) and in CH_2Cl_2 solution (bottom). The distance r is defined as the intermonomer dynamic-distance reaction coordinate (see text).

CONCLUSIONS

The solvation and stability of the π - $[\text{TCNE}]_2^{2-}$ dimer in dichloromethane solution has been exhaustively studied by means of MD simulations. In the first part of this work, the precise role of the NBu_4^+ cations was analyzed using FFMD simulations. Simulations on $(\text{NBu}_4^+)[\text{TCNE}]^-$ single ion pairs and $(\text{NBu}_4^+)_2[\text{TCNE}]_2^{2-}$ aggregates showed that cations dissociate from the ion pair or the aggregate starting from a close initial configuration. Furthermore, when both NBu_4^+ cations are set ca. 16 Å away from the dimer as initial configuration, none of the cations approaches the dimer after 5 ns production run. Hence, the cations are not essential in the stabilization of π - $[\text{TCNE}]_2^{2-}$ in solution. The free energy profiles at 175 and 300 K obtained through the PMF approach showed that, while at 175 K a metastable minimum is found at the equilibrium distance range of the π - $[\text{TCNE}]_2^{2-}$ dimer, no bound minimum is found at room temperature, in good agreement with the experimental findings.

AIMD simulations on the π - $[\text{TCNE}]_2^{2-}$ dimer in CH_2Cl_2 at 175 and 300 K with no cations exhibited that the dimer preserves its structure at the lower temperature, whereas it dissociates at the higher temperature. RDF analyses of the trajectories revealed that the dimer is stabilized by $\text{N}(\text{TCNE})\cdots\text{H}(\text{CH}_2\text{Cl}_2)$ contacts, and the integration of the RDF first peak discloses 4 hydrogens around each N. The first solvation shell of the π - $[\text{TCNE}]_2^{2-}$ dimer consists of 20 CH_2Cl_2 molecules. This first solvation shell can be divided in three parts: three solvent molecules, which maximize the $\text{H}\cdots\text{N}$ contacts during the whole trajectory; five solvent molecules, which complete the surrounding region

equidistant from both monomers; and the remaining twelve molecules, that are located in the upper and lower parts of the solvation shell. The eight solvent molecules of the first two groups are the main responsible molecules for the dimer's stabilization. The twelve molecules located in the upper/lower regions leave empty a conical region of about 20° with the bonding axis in both sides.

The free energy profile of the π -dimer dissociation obtained through AIMD simulations at 175 K provides a stable dimer by $-5.5 \text{ kcal}\cdot\text{mol}^{-1}$, with an equilibrium distance of 3.0 Å, and a barrier toward dissociation of $9.6 \text{ kcal}\cdot\text{mol}^{-1}$.

ASSOCIATED CONTENT

Supporting information: Initial configuration of the $(\text{NBu}_4^+)(\text{TCNE}^-)$ single ion pair in FFMD simulations of Figure 1; Initial configuration of the $(\text{NBu}_4^+)_2(\text{TCNE}^-)_2$ aggregate in FFMD simulations of Figure 2; Initial configuration of the $(\text{NBu}_4^+)_2(\text{TCNE}^-)_2$ aggregate in FFMD simulations of Figure 3; Distances as a function of time on the $(\text{TCNE}^-)_2(\text{NBu}_4^+)_2$ aggregate in CHCl_3 at 175 K, starting from remote initial geometry; Snapshots of $(\text{TCNE}^-)_2(\text{NBu}_4^+)_2$ aggregate along the PMF of the dissociation process (Figure 4) at 175 K in CH_2Cl_2 ; PDFs of the $\text{H}_{\text{DCM}}\cdots\text{N}$ distance of both hydrogens of each CH_2Cl_2 molecule within the closest solvation shell; Time evolution of the distance between both hydrogen atoms of each CH_2Cl_2 molecule of positions 1, 2, and 3 with their closest N; Time evolution of the distance between both hydrogen atoms of each CH_2Cl_2 molecule within the first solvation shell with their closest N.

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Notes

The authors declare no competing financial interest.

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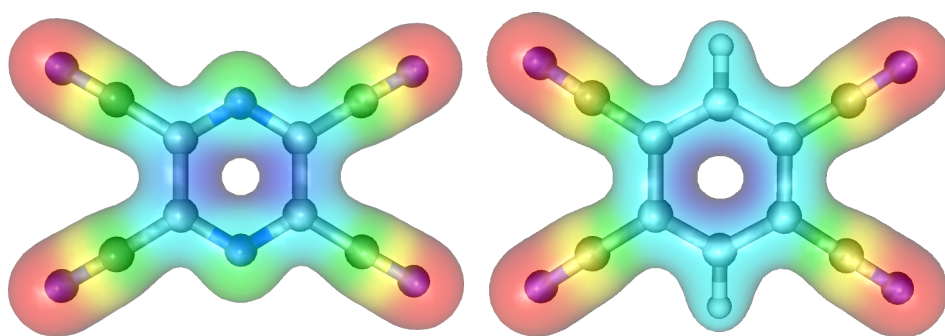
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3.4. Publication 3

The Importance of the Cation-Anion Interactions for the Orientational Preference of Long, Multicenter Bonds: A Study-Case Based on the $[\text{TCNB}]_2^{2-}$ (TCNB = Tetracyanobenzene) and $[\text{TCNP}]_2^{2-}$ (TCNP = Tetracyanopyrazine) Dimers



The Importance of the Cation-Anion Interactions for the Orientational Preference of Long, Multicenter Bonds: A study-case based on the $[\text{TCNB}]_2^{2-}$ (TCNB = Tetracyanobenzene) and $[\text{TCNP}]_2^{2-}$ (TCNP = Tetracyanopyrazine) Dimers

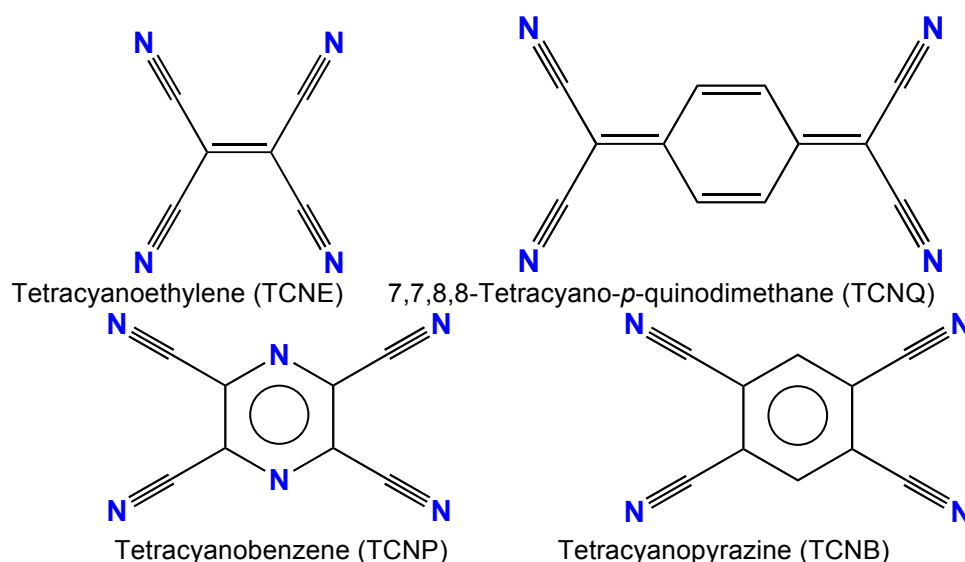
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Abstract: The orientational preference of the $\pi\text{-}[\text{TCNP}]_2^{2-}$ and $\pi\text{-}[\text{TCNB}]_2^{2-}$ dimers, which possess long, multicenter bonding, is assessed in the present work using RASPT2 and DFT calculations. The two reported crystal structures containing $\pi\text{-}[\text{TCNP}]_2^{2-}$ present $D_{2h}(\theta = 0^\circ)$ and $C_2(\theta = 30^\circ)$ orientations, while the single reported containing $\pi\text{-}[\text{TCNB}]_2^{2-}$ is a $C_2(\theta = 60^\circ)$ conformer. This orientational mismatch is the focus of the present study. Interaction energy decompositions as a function of the dihedral angle (θ) show the electrostatic nature of such interactions. By means of model $\text{K}_2[\text{TCNP}]_2$ and $\text{K}_2[\text{TCNB}]_2$ aggregates, their interactions energy curves as a function of θ , for several orientations of the K^+ cations are obtained, which reproduce the experimental orientations as absolute or local minima.

Introduction

The origin, physical manifestations, and energetic properties of long, multicenter bonds between dimers of neutral or charged π -radicals, first reported in $\pi\text{-}[\text{TCNE}]_2^{2-}$ dimers (TCNE = tetracyanoethylene) is well established.^{1,2} Long, multicenter bonds have been identified in a wide variety of radical...radical interactions: anionic,³ cationic dimers,⁴ anionic...cationic,⁵ and within π -dimers of neutral radicals.⁶ Despite the widespread occurrence of long, multicenter bonds between radical pairs, their orientational preferences^{7,8} are limited. While some studies focused on the orientational preference of specific radicals,⁷ a general procedure for rationalizing the angular dependence of neutral and charged radical...radical interactions has been shown to work well for 12 radicals, with 9 being N-containing radicals.⁸ The procedure, called the Maximin Principle, states that "the lowest energy conformation maximizes overlap of the frontier orbitals while simultaneously minimizing intermolecular contacts".⁸ In other words, by minimizing the sum of the intermolecular atom-atom electrostatic interactions that originate from the net electronic charge located on each atom of the radical, a value that presumed to be repulsive. In most of the 12 tested neutral and charged radicals, the Maximin Principle correctly predicted the most common dimer found in their crystals. However, in a few cases the predicted minimum is an observed geometry, but not the most common one. Importantly, the predicted geometry for $\pi\text{-}[\text{TCNE}]_2^{2-}$ (TCNE = tetracyanoethylene) with a displaced geometry has never been observed, and is a failure recognized by the authors.⁸ Note, as a general rule, that the eclipsed geometry becomes the most stable orientation only when the electrostatic atom-atom interactions are negligible, or when it is invariant with the relative orientation.



As illustrated in Figures 1 and 2, the Maximin principle also fails for π -[TCNP] $_2^{2-}$ and π -[TCNB] $_2^{2-}$ (TCNP = 1,2,4,5-tetracyanopyrazine; TCNB = 1,2,4,5-tetracyanobenzene). TCNP and TCNB are relatively poor electron cyanocarbons, and form numerous Mulliken donor-acceptor complexes,⁹ and in some cases form radical anions that are stabilized via delocalization. This is the basis for numerous stable electron transfer salts that have been characterized to exhibit technologically important properties,¹⁰ e.g. magnetic ordering,¹¹ metal-like electrical conductivity,¹² and even superconductivity.¹³ For instance, the reaction of $\text{V}(\text{CO})_6$ with TCNE,^{14,15} TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane),¹⁶ TCNB,¹⁷ and TCNP,¹⁸ form molecule-based bulk ferromagnets having magnetic ordering temperatures as high as room temperature. Among the electron poor cyanocarbons, TCNQ [E° (vs. $\text{SCE}(\text{MeCN}) = 0.14 \text{ V}$] and TCNE [$E^\circ = 0.17 \text{ V}$] are electrochemically easily and reversibly reduced. TCNB and TCNP, however, are far more difficult to reduce: they undergo a reversible one-electron reduction at -0.64 and -0.31 V, respectively.¹⁹

As TCNB and TCNP have a similar geometry, and the most stable geometry predicted for their π -dimers by the Maximin Principle should be similar, i.e. a slipped orientation with one of the radical anions laterally displaced relative to the other along its central C-C bond, Figures 1a and 2a. Instead, the known polymorphs of these two dimers have different orientations, Figures 1 and 2, with neither being the most stable orientation predicted by the Maximin Principle. Thus, the failure of the Maximin Principle is not an exceptional situation somewhat connected to the small size of the [TCNE] $^{\cdot-}$, but a general failure that reflects a common and deeper origin.

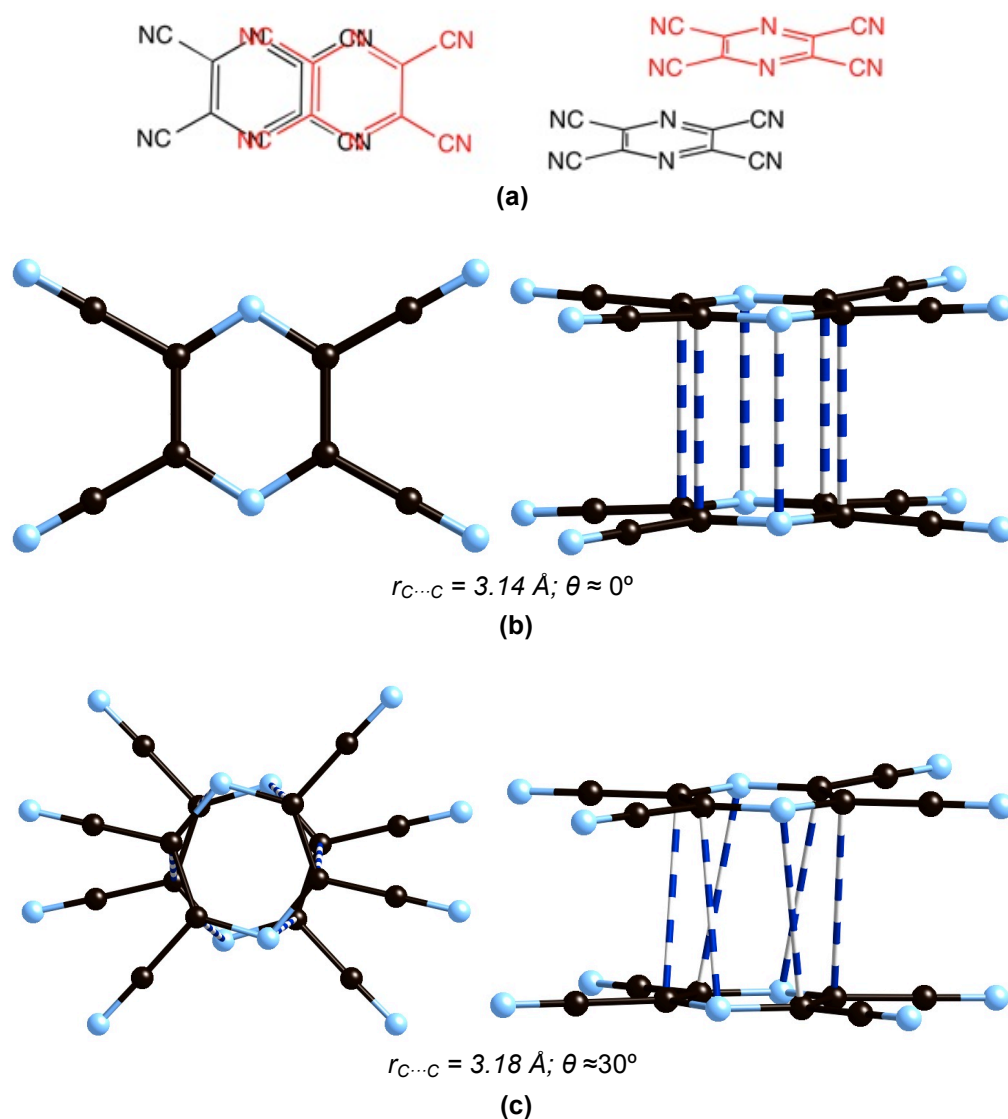


Figure 1. (a): Most stable geometry of $[\text{TCNP}]_2^{2-}$ predicted by the Maximin Principle. (b): Side (left) and top (right) views of the structure the $\pi\text{-}[\text{TCNP}]_2^{2-}$ present in $\{[\text{Cr}(\text{C}_6\text{H}_6)_2]^+\}_2[\text{TCNP}]_2^{2-}$. Note the local D_{2h} symmetry of the anion radical dimer. (c): Side (left) and top (right) views of the structure of $\pi\text{-}[\text{TCNP}]_2^{2-}$ present in $[\text{TDAE}]^{2+}[\text{TCNP}]_2^{2-}$ [TDAE = tetrakis(dimethylamino)ethylene]. The shortest $\text{C}\cdots\text{C}$ distance between adjacent fragments is indicated under each structure.

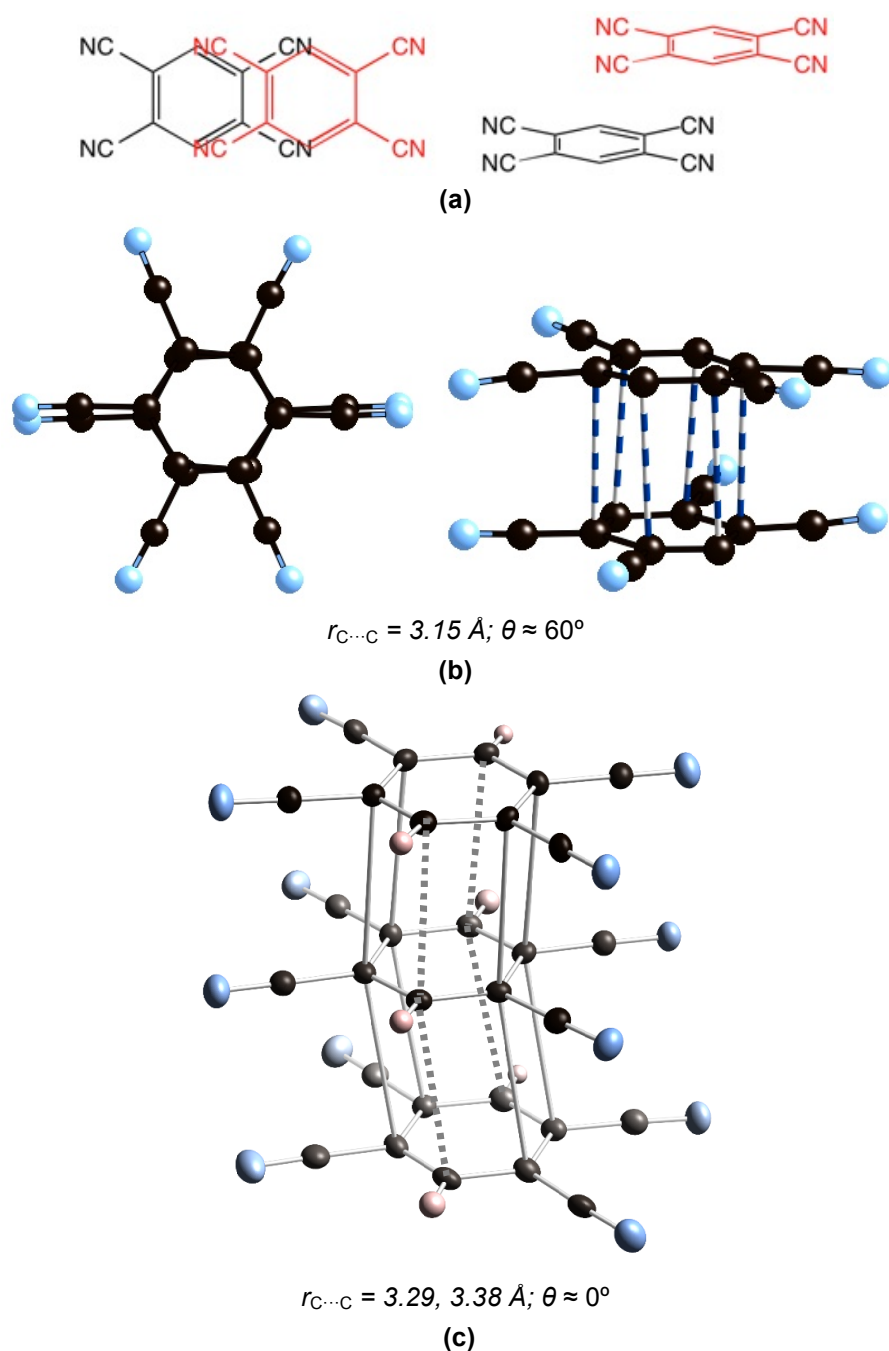


Figure 2. (a): Most stable geometry predicted by the Maximin Principle for $[\text{TCNB}]_2^{2-}$; (b): Side (left) and top (right) views if the structure of $[\text{TCNB}]_2^{2-}$ present in $[\text{YbCp}^*_2][\text{TCNB}]$; (c): Structure of the π - $[\text{TCNB}]_2^{2-}$ trimer found in $[\text{TDAE}][\text{TCNB}]_3 \cdot \text{MeCN}$ (i.e. $[\text{TDAE}]^{2+}[\text{TCNB}]_3^{2-}$). The shortest C $\cdots$ C distance between adjacent fragments is indicated under each structure.

Hereafter, the results of a computational study aimed at addressing the following key issues about these dimers are presented: (1) Do all the crystal structures of the π - $[\text{TCNB}]_2^{2-}$ and π - $[\text{TCNP}]_2^{2-}$ dimers present a long, multicenter bond? (2) Do the crystallographic structures correspond to minima in the potential energy surface of these dimers, as is presumed in most analyses? (3) What is the true orientational preference of these dimers and which one is its driving force? (4) How does such orientational preference compares with the orientation of these dimers in crystals where they are contained? In the following, each of these questions is sequentially addressed, which are also of general interest in relation to other radical $\cdots$ radical interactions.

Methodological details

The electronic structure and properties of the π -dimers were evaluated using the M06L density functional.²⁰ This density functional was shown to successfully reproduce the RASPT2 reference computations on π -[TCNB]₂²⁻ and π -[TCNP]₂²⁻ in a recent benchmark study, where other 22 density functionals were also considered.²¹ RASSCF/RASPT2 calculations²² based on the (30,28) active space were carried out for the interaction energy decomposition analyses (vide infra). The (30,28) active space results from considering the full π -space parallel to the bonding axis, and it also is the active space considered in the benchmark of ref. 21. All calculations were done using the 6-31+G(d) basis set.²³ All M06L calculations were performed using Gaussian-09,²⁴ whereas Molcas7.6 was used for the RASSCF and RASPT2 calculations.²⁵ The basis set superposition error (BSSE) was corrected using the counterpoise method.²⁶

The angular preference of these radicals was determined by examining the variation with the dihedral angle θ (Figure 3) of the dimer interaction energy (the optimum geometry of the dimer was computed for each value of θ).

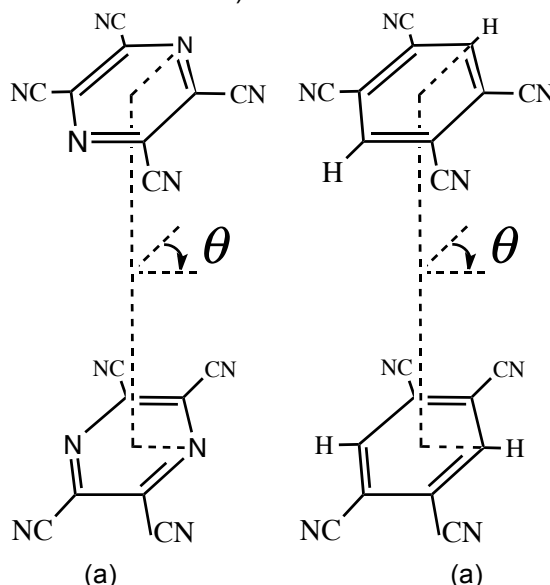


Figure 3. Definition of the dihedral angle, θ , in π -[TCNP]₂²⁻ (a) and π -[TCNB]₂²⁻ (b). θ defines the relative orientation of one radical anion respect to the other in both dimers, and the $\theta = 60^\circ$ conformation is depicted above.

The nature of the long, multicenter bond was established by considering the dominant components of the radical $\cdots$ radical pair, defined, for a given pair AB, as:

$$E_{\text{int}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}}. \quad (1)$$

According to the “InterMolecular Perturbation Theory” (IMPT)²⁷ perturbative method, the interaction energy between a pair of radicals (AB) can also be written as:

$$E_{\text{int}} = E_{\text{er}} + E_{\text{el}} + E_{\text{pol}} + E_{\text{ct}} + E_{\text{disp}} + E_{\text{bond}} \quad (2)$$

where E_{er} is the exchange repulsion energetic component (originating from the Pauli Exclusion Principle, which dominates at short distances and is the cause of the so-called repulsive wall), E_{el} is the electrostatic interaction component between two fragments whose multipolar distribution is taken as those for the isolated fragments, E_{pol} is the polarization energetic component (which accounts for the change in electrostatic component that the presence of each fragment causes in the other fragment multipolar distribution), E_{ct} is the charge transfer component (only relevant in donor-acceptor complexes), E_{disp} is the dispersion component (which accounts for the difference in the correlation energy of the AB complex and the isolated A and B fragment) and the E_{bond} component (which accounts for the gain in energy due to the pairing in AB of the unpaired electrons of the A and B fragments, only present when the interacting fragments are radicals).

Except for highly polarizable molecules, E_{pol} is much smaller than E_{el} and can be disregarded for a qualitative analysis of the dominant energetic components. The same applies to E_{ct} in radical pairs where the two interacting components are alike, as charge transfer cannot occur. In these cases, which include the dimers of interest here:

$$E_{int} \approx E_{er} + E_{el} + E_{disp} + E_{bond} \quad (3),$$

where each of the remaining components are estimated as follows:

$$E_{disp} = E_{int}[HF/CASSCF(min)] - E_{int}[Full-CI] \quad (4)$$

where $E_{int}(HF/CASSCF(min))$ is the energy obtained by the smallest CASSCF(min) active space needed to properly describe the multideterminantal electronic structure of the radicals. When only one determinant is needed, as is the case in most closed shell systems, it can be estimated from a HF calculation, and for open-shell systems it can be estimated from a UHF or ROHF computation. $E_{int}[Full-CI]$ is the energy computed when doing a Full-CI computations. However, as these computations are too demanding for extended monoelectronic basis sets, it is usually taken as the total energy from a CASPT2 or RASPT2 computation, preferably using a large active space, CASPT2(large), that is:

$$E_{disp} = E_{int}[HF/CASSCF(min)] - E_{int}[(AB)CASPT2(large)] \quad (5)$$

Except when a high accuracy is desired, where more accurate expressions can be employed,²⁸ the magnitude of E_{el} can be approximated as the sum of $-[q(i)q(j)]/r_{ij}$ for all unique pairs of atoms of A and B, with $q(i)$ and $q(j)$ being the net atomic charge on atoms i and j , while r_{ij} is their interatomic distance. The atomic charges in the radical anions were estimated using Kolman's CHelpG method.²⁹ The E_{bond} component (by definition the energy difference between a state where the electrons in the SOMO orbitals of AB are paired and unpaired) was estimated as the difference between the ground state singlet and the triplet states of AB.⁶ Finally, E_{er} can be obtained as:

$$E_{er} = (E_{AB} - E_A - E_B) - (E_{el} + E_{disp} + E_{bond}) \quad (6)$$

Results and discussion

- (1) *Do all the crystal structures of the π -[TCNB] $_2^{2-}$ and π -[TCNP] $_2^{2-}$ dimers present a long, multicenter bond?*

To date only two structures with π -[TCNP] $_2^{2-}$,^{7,30} and only one with π -[TCNB] $_2^{2-}$ have been reported.³¹ The two structures of π -[TCNP] $_2^{2-}$ have different relative orientations of this dimer, i.e. they are eclipsed ($D_{2h}(\theta = 0^\circ)$ for $\{[\text{Cr}(\text{C}_6\text{H}_6)_2]^+\}_2[\text{TCNP}]_2^{2-}$ (Figure 1b),³⁰ and rotated $C_2(\theta \approx 30^\circ)$ for $[\text{TDAE}]^{2+}[\text{TCNP}]_2^{2-} \cdot 2\text{MeCN}$ (Figure 1c).⁷ In both orientations the π -[TCNP] $_2^{2-}$ dimers exhibit the geometrical signatures common to all long, multicenter bonds: (a) a shortest C $\cdots$ C distance (3.135 and 3.181 Å) smaller than the sum of the two van der Waals C radii, and (b) a bending of the CN groups away from the radical-anion coplanarity, of 3.8° in $\{[\text{Cr}(\text{C}_6\text{H}_6)_2]^+\}_2[\text{TCNP}]_2^{2-}$ and 1.0° in $[\text{TDAE}]^{2+}[\text{TCNP}]_2^{2-} \cdot 2\text{MeCN}$.

The π -[TCNB] $_2^{2-}$ dimer present in $[\text{YbCp}^*_2][\text{TCNB}]$ ($\text{Cp}^* = \text{pentamethylcyclopentadienide}$)³¹ has the shortest interfragment C $\cdots$ C distance is 3.15 Å and the radicals are rotated by $\theta \approx 60^\circ$ (Figure 2b), and belong to the C_2 space group. Note that due to the dimer symmetry, in an isolated dimer a $\theta \approx 60^\circ$ rotation is equivalent to a $\theta \approx 120^\circ$ rotation. It should be mentioned that $[\text{TDAE}][\text{TCNB}]_3 \cdot \text{MeCN}$,³² obtained by reducing TCNB by TDAE (tetrakis(dimethylamino)ethylene), possesses $[\text{TCNB}]_3^{2-}$ from the analysis of its structure, magnetic, and spectroscopic properties, Figure 2c, with the two extra electrons distributed over three fragments. Besides noticing their eclipsed orientation, the structure and properties of these trimers will not be further considered in this work.

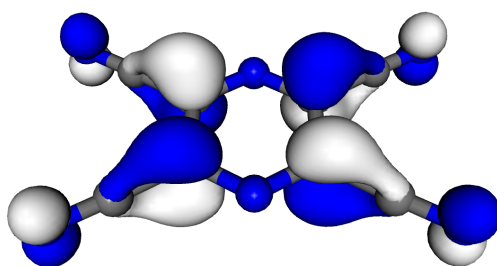
In addition to these geometrical features, the presence of a long, multicenter bond has an electronic structure similar to covalently-bonded molecules. The main differences between long, multicenter bonds and conventional $2e^-/2c$ covalent bonds are: (1) their much weaker interaction energy and greater equilibrium distance (long bonds have these two properties in the range of van der Waals minima, with which they were previously confused), and (2) their different energetic origin (the interaction energy in long bonds is not dominated by the electron-pairing energetic component, but by the electrostatic plus dispersion components of the interaction energy). In the following two subsections, we show that these π -[TCNB] $_2^{2-}$ and π -[TCNP] $_2^{2-}$ dimers each present a long, multicenter bond.

a. π -[TCNP] $_2^{2-}$ dimers in crystals

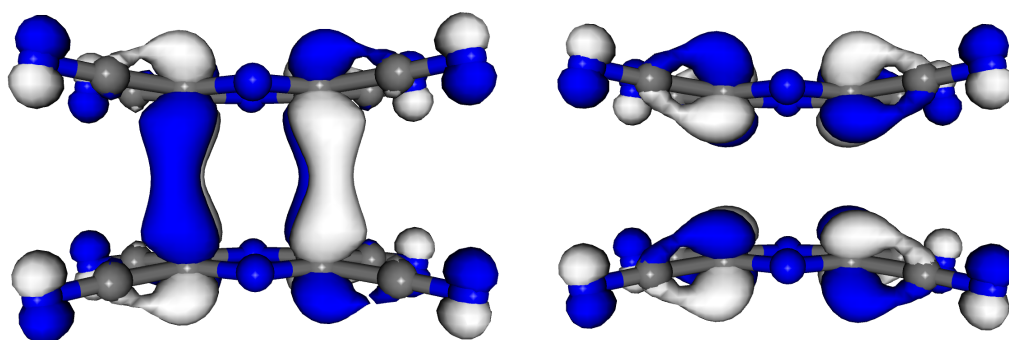
The electronic structures for the eclipsed $D_{2h}(\theta \approx 0^\circ)$, and rotated $C_2(\theta \approx 30^\circ)$ conformations of the π -[TCNP] $_2^{2-}$ dimer were analyzed at their crystal geometry in order to determine their electronic ground state. For completeness the $D_{2d}(\theta = 90^\circ)$ configuration (at its optimized geometry, as no experimental geometry exists for this conformation) was also included in the study.

The three conformations share the same electronic ground state, which can be rationalized as follows: due to the non-negligible overlap of the two radical anion orbitals, a bonding and antibonding combination of these orbitals are formed in the dimer (Figure 4). Of particular relevance is the combination that results from the two SOMOs. As shown in Figure

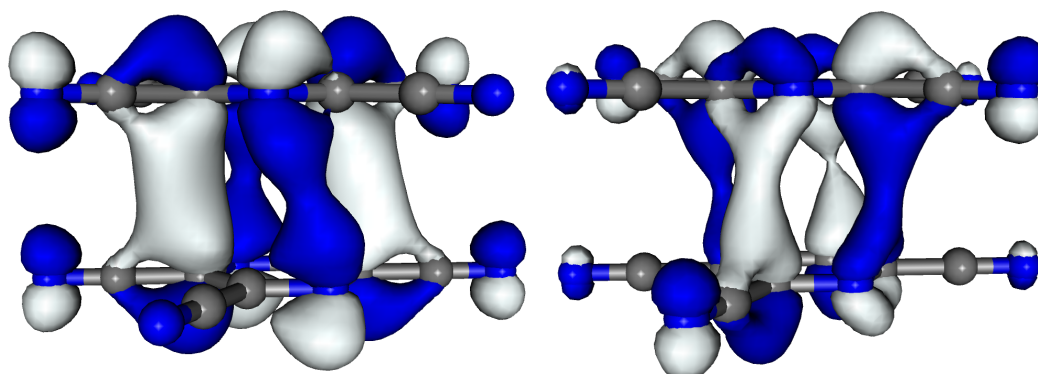
4a, the SOMO is a π^* orbital mostly located at pyrazene ring carbons, which has a small contribution over the nitriles. A natural population analysis of the M06L/6-31+G(d) wavefunction for the $D_{2h}(\theta \approx 0^\circ)$ conformer indicates that the HOMO, which is the bonding combination of the SOMOs, has an occupation of 1.72, while the occupation of the LUMO is 0.28. Thus, the ground state of the dimer has a dominant contribution of a diamagnetic closed-shell singlet state. The $C_2(\theta \approx 30^\circ)$ conformer exhibits a similar behavior (1.59 / 0.41), and the $D_{2d}(\theta = 90^\circ)$ has a fully closed-shell singlet nature (2.0 / 0.0). Consistent with this description of the ground state, the triplet state is higher in energy in all conformations.³³ Therefore, a long, multicenter bond is found in the two structures of π -[TCNP]₂²⁻, the $D_{2h}(\theta = 0^\circ)$ and $C_2(\theta \approx 30^\circ)$ conformations.



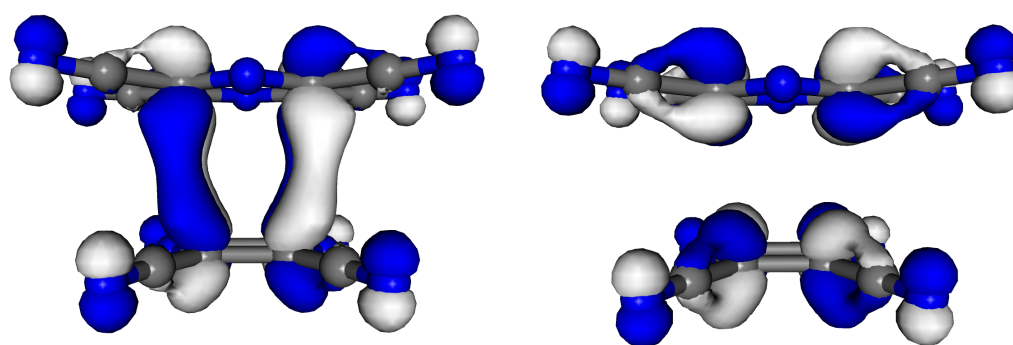
(a)

 $D_{2h}(\theta = 0^\circ)$

(b)

 $C_2(\theta \approx 30^\circ)$

(c)



$D_{2d}(\theta = 90^\circ)$

(d)

Figure 4. (a): SOMO of the $[\text{TCNP}]^{\cdot-}$ at its optimized M06L/6-31+G(d) geometry; (b): bonding and antibonding combinations of the SOMOs (left and right) for the $D_{2h}(\theta = 0^\circ)$ conformation of an isolated $\pi\text{-}[\text{TCNP}]_2^{2-}$; (c): same views for the $(\theta \approx 30^\circ)$; and (d): $D_{2d}(\theta = 90^\circ)$ conformations of $\pi\text{-}[\text{TCNP}]_2^{2-}$ at its optimized geometry.

b. $\pi\text{-}[\text{TCNB}]_2^{2-}$ dimers in crystals

As already mentioned, $\{[\text{Yb}(\text{C}_6\text{H}_6)_2]^+\}_2[\text{TCNB}]_2^{2-}$ is the only known crystal possessing $\pi\text{-}[\text{TCNB}]_2^{2-}$, which are in a $\theta \approx 60^\circ$ conformation. This conformation differs from the $\theta \approx 30^\circ$ conformation observed for $[\text{TCNP}]_2^{2-}$ (vide supra). The ground state electronic structure for the $C_2(\theta \approx 60^\circ)$ conformation of $\pi\text{-}[\text{TCNB}]_2^{2-}$ was analyzed. For completeness that for the $D_{2h}(\theta = 0^\circ)$ and $D_{2d}(\theta = 90^\circ)$ conformations were also performed (at their optimum geometry, as no experimental geometry exists for these conformations). The MO diagram for the three conformations were found to be similar to that described above for the $\pi\text{-}[\text{TCNP}]_2^{2-}$, i.e. all orbitals of the monomers, including their SOMOs (Figure 5a), combine forming a bonding and antibonding combination (Figures 5b-5d). Once again, the ground state is the closed-shell singlet state where the highest doubly occupied orbital of the dimer is the bonding combinations of the SOMOs and the antibonding combination is empty. The computational results from a natural orbitals analysis performed at the M06L/6-31+G(d) level confirmed this picture: the bonding and antibonding combinations of the SOMOs have occupation numbers 1.92 and 0.08 in the D_{2h} and the $C_2(\theta \approx 60^\circ)$ conformers, and 1.87 and 0.13 for the D_{2d} conformer (therefore, at the M06L/6-31+G(d) level, the ground state singlet has a dominant closed-shell character, although with a small contribution of the open-shell singlet). This results are validated by RASPT2 calculations, for which the D_{2h} , $C_2(\theta \approx 60^\circ)$, and D_{2d} conformers have occupation numbers of 1.57 / 0.43, 1.63 / 0.37, and 1.57 / 0.43, respectively. The triplet state is higher in energy than the singlet ground state for all conformations.³⁴ Therefore, the geometrical features combined with their ground state electronic structure are in accord with a long, multicenter bond for the $\pi\text{-}[\text{TCNB}]_2^{2-}$ for the $C_2(\theta \approx 60^\circ)$ conformer.

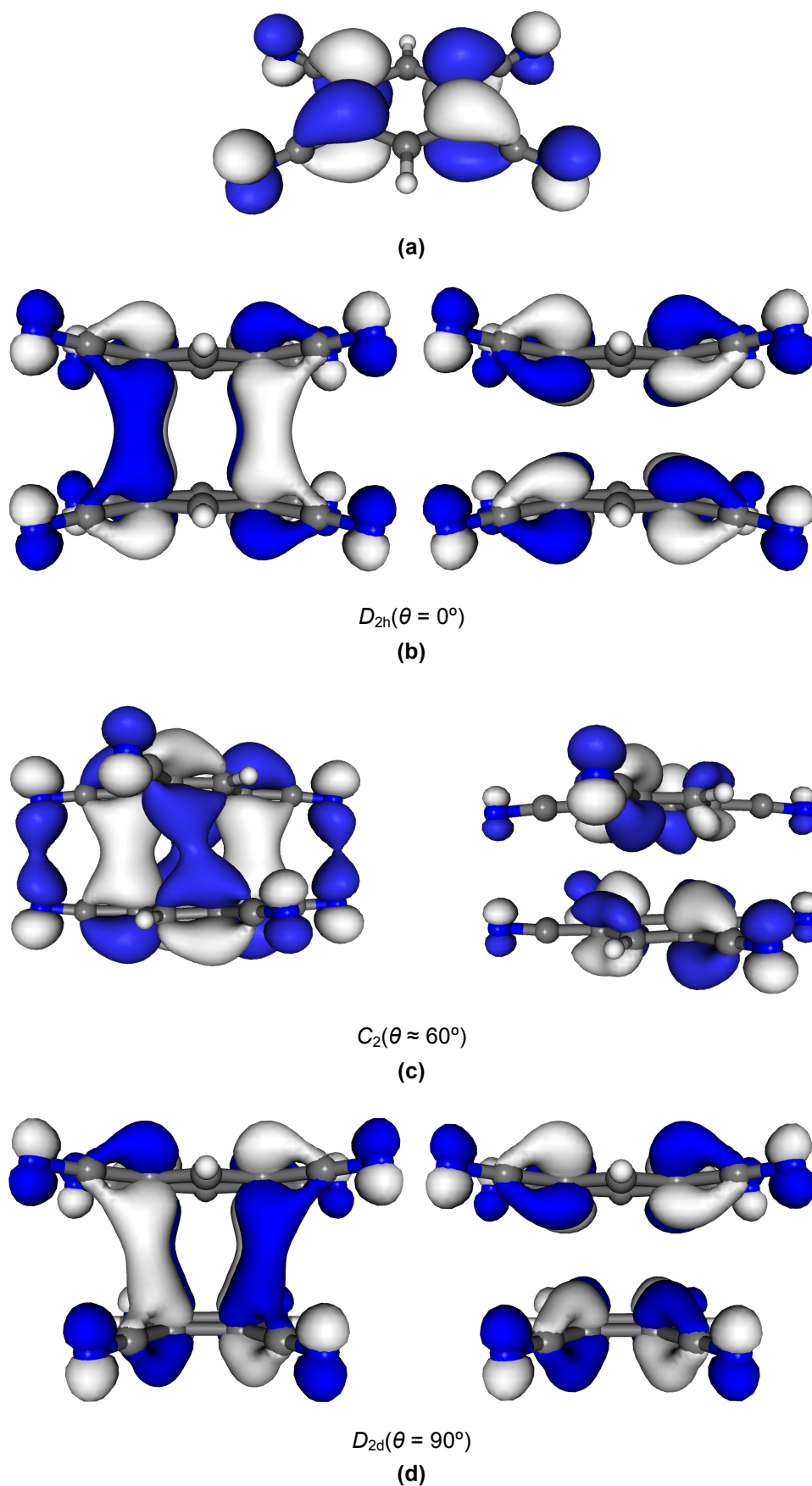


Figure 5. (a): SOMO of the $[\text{TCNB}]_2^{2-}$ at its optimized M06L/6-31+G(d) geometry. (b): bonding and antibonding combinations of the SOMOs (left and right pictures) for the $D_{2h}(\theta = 0^\circ)$ conformation of an isolated π - $[\text{TCNB}]_2^{2-}$; (c): equivalent views for the $(\theta \approx 60^\circ)$ and (d): $D_{2d}(\theta = 90^\circ)$ conformation.

- (2) Do the crystallographic structures correspond to minima in the potential energy of the π -[TCNP] $_2^{2-}$ and π -[TCNB] $_2^{2-}$ dimers?

In order to answer the question posed in the section title, the geometry of the crystalline $D_{2h}(\theta = 0^\circ)$ and $C_2(\theta \approx 30^\circ)$ conformations of π -[TCNP] $_2^{2-}$ and $C_2(\theta \approx 60^\circ)$ conformation of π -[TCNB] $_2^{2-}$ were fully optimized for the singlet ground state. The optimized $D_{2h}(\theta = 0^\circ)$ conformation of π -[TCNP] $_2^{2-}$ is slightly distorted geometry of the same symmetry (Figure 6a). However, this was not the situation in the $C_2(\theta \approx 30^\circ)$ conformation, which rotated to transform into the $D_{2d}(\theta = 90^\circ)$ conformation (Figure 6b), 3.0 kcal·mol $^{-1}$ more stable than the fully optimized $D_{2h}(\theta = 0^\circ)$ structure. Both fully optimized structures have the geometrical features and electronic structure of long, bonded dimers.

The fully optimized D_{2h} and D_{2d} structures of π -[TCNP] $_2^{2-}$ have total energies above their dissociated products, suggesting their metastable character, as occurs for [TCNE] $_2^{2-}$.^{1,2,3} This was confirmed by computing, at the M06L/6-31+G(d) level, the interaction energy curve of the dimer as a function of the inter-fragment distance (Figure 7, each point computed by relaxing the geometry of an isolated π -[TCNP] $_2^{2-}$ for the desired interfragment distance). Dissociation from the D_{2h} and D_{2d} minima requires overcoming a barrier of about 2.4 kcal·mol $^{-1}$ for the D_{2h} conformation, and 5.0 kcal·mol $^{-1}$ for the D_{2d} conformation. Both barriers have their origin in the addition of a repulsive electrostatic component and the attractive bonding and dispersion components.^{1,2,3,35}

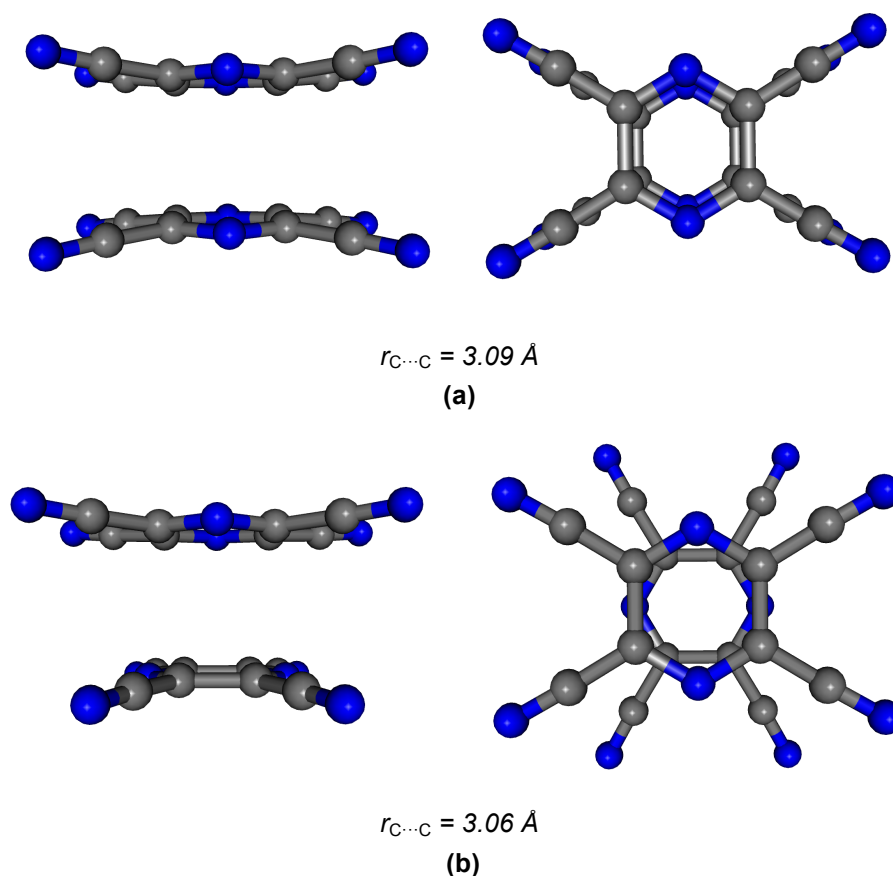


Figure 6. Fully optimum geometry of π -[TCNP] $_2^{2-}$ computed at the M06L/6-31+G(d) level. (a): D_{2h} conformer (shortest C $\cdots$ C = 3.09 Å, out-of-plane bending = 6.6°); (b): D_{2d} conformer (shortest C $\cdots$ C = 3.06 Å, out-of-plane bending = 4.2°).

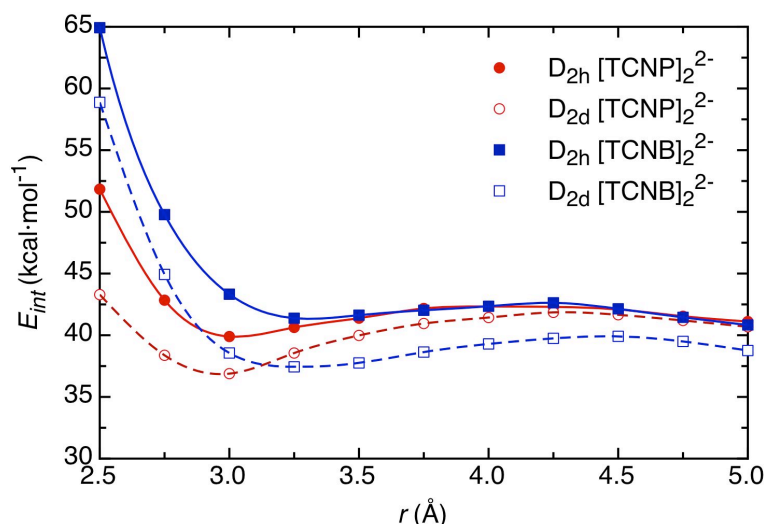


Figure 7. Interaction energy curves for the dissociation of π -[TCNP] $_2^{2-}$ and π -[TCNB] $_2^{2-}$ into two radical anion fragments, at the M06L level, for the D_{2h} and D_{2d} conformations. In all curves the 6-31+G(d) basis set was used and the basis set superposition error (BSSE) was corrected using the counterpoise method.

The geometry optimization of the $C_2(\theta = 60^\circ)$ crystal structure of π -[TCNB] $_2^{2-}$ also indicates that this structure is not a minimum in the potential energy surface of the dimer. Instead, it transforms into the $D_{2d}(\theta = 90^\circ)$ conformation (Figure 8b). A geometry optimization was also performed for π -[TCNB] $_2^{2-}$ in an hypothetical $D_{2h}(\theta = 0^\circ)$ conformation (Figure 8a). The $D_{2h}(\theta = 0^\circ)$ and $D_{2d}(\theta = 90^\circ)$ minima have energies above that for their dissociated fragments (the $D_{2h}(\theta = 0^\circ)$ conformation by $42.2 \text{ kcal}\cdot\text{mol}^{-1}$, and the $D_{2d}(\theta = 90^\circ)$ conformation by $41.5 \text{ kcal}\cdot\text{mol}^{-1}$), thus suggesting a metastable character of these minima, caused by the existence of a barrier toward their dissociation.³⁵ This metastable character is confirmed by the interaction energy curves for both conformations, Figure 7.

How can a metastable minima form for energetically exothermic crystals? As in all previously reported dimers found in crystals and presenting a long, multicenter bond,¹⁻³ this is attributed to [radical anion]...counterion interactions, whose sum, which is also helped by the also attractive dispersion and bonding energetic components of the [radical anion]...[radical anion] interaction, exceed the combined effect of the [radical anion]...[radical anion] plus the counterion...counterion repulsions. Such an energetic balance has already been demonstrated on small (radical ion) $_2$ (counterion) $_2$ aggregates present in the structure.³⁶ By running computations on small supramolecular aggregates, Table 1 demonstrates that such energetic balance also holds for the two π -[TCNP] $_2^{2-}$ crystals and the $([\text{YbCp}^*_2])_2[\text{TCNB}]_2^{2-}$ crystal.

Table 1. Interaction energy values between all pairs of molecules in the following (cation)₂(anion)₂ aggregates: [Cr(C₆H₆)₂]₂[TCNP]₂, [TDAE][TCNP]₂, and [YbCp*₂][TCNB]₂. The sum of all pairs is collected in E_{tot}, together with the interaction energy, E_{int}, relative to their dissociation into four fragments. All energies (in kcal·mol⁻¹) were computed at the M06L/6-31+G(d) level. Relativistic Stuttgart RSC ANO/ECP basis set and core potentials³⁷ were used for Yb atoms.

(cation) ₂ (anion) ₂ aggregate	Interaction	M06L
{[Cr(C ₆ H ₆) ₂] ⁺] ₂ [TCNP] ₂ ²⁻	E _{anion1...anion2}	42.2
	E _{cation1...cation2}	21.6
	E _{anion1...cation1}	-62.6
	E _{anion1...cation2}	-63.5
	E _{anion2...cation1}	-63.5
	E _{anion2...cation2}	-62.5
	E _{tot}	-188.3
	E _{int}	-144.6
[TDAE] ²⁺ [TCNP] ₂ ²⁻ ·2MeCN	E _{anion1...anion2}	41.5
	E _{anion1...cation²⁺}	-83.9
	E _{anion2...cation²⁺}	-104.8
	E _{tot}	-147.2
	E _{int}	-191.8
{[YbCp* ₂] ⁺] ₂ [TCNB] ₂ ²⁻	E _{anion1...anion2}	44.3
	E _{cation1...cation2}	27.5
	E _{anion1...cation1}	-93.0
	E _{anion1...cation2}	-94.4
	E _{anion1...cation1}	-95.7
	E _{anion1...cation2}	-96.1
	E _{tot}	-307.4
	E _{int}	-273.6

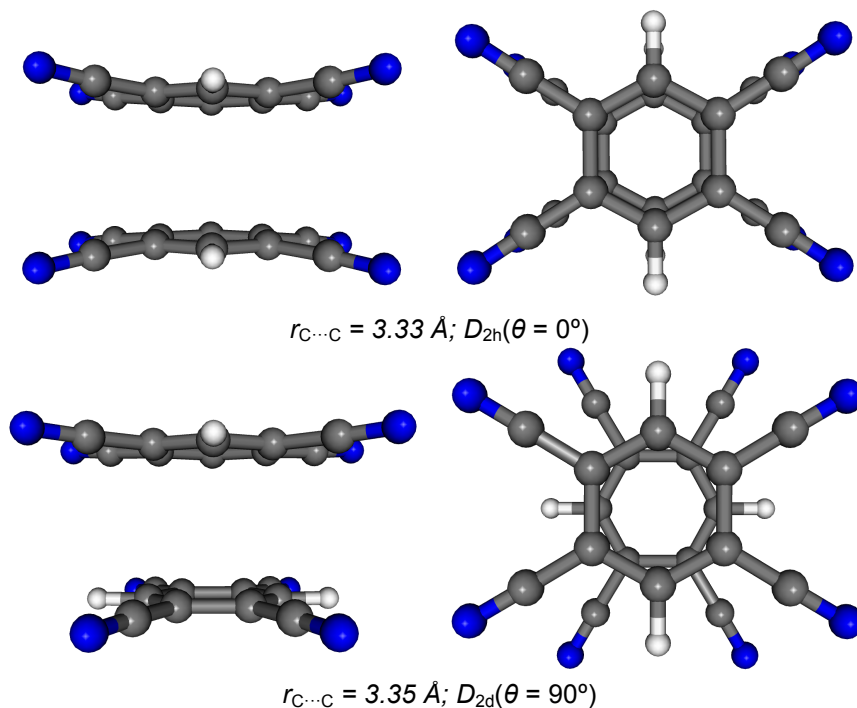


Figure 8. Fully optimized geometry of an isolated π -[TCNB]₂²⁻ dimer obtained computed at the M06L/6-31+G(d) level. (**top**) Hypothetical $D_{2h}(\theta = 0^\circ)$ conformation (shortest C $\cdots$ C distance = 3.33 Å, out-of-plane bending = 6.5°); (**bottom**), $D_{2d}(\theta = 90^\circ)$ conformation that results from the optimization of the $C_2(\theta \approx 60^\circ)$ conformation extracted from the {[Yb(C₆H₆)₂]⁺]₂[TCNB]₂²⁻ crystal (shortest C $\cdots$ C distance = 3.35 Å, out-of-plane bending = 3.0°).

(3) *Orientational preference of the π -[TCNP] $_2^{2-}$ and π -[TCNB] $_2^{2-}$ dimers*

The information on the orientational preference is limited and puzzling: i.e. (a) there are three relative orientations: $\theta = 0^\circ$ and 30° for π -[TCNP] $_2^{2-}$, and $\theta = 60^\circ$ for [TCNB] $_2^{2-}$; (b) the eclipsed $\theta = 0^\circ$ is computational a minimum in both dimers; (c) for π -[TCNP] $_2^{2-}$, the geometry optimization of the $\theta = 30^\circ$ conformation ends in a $\theta = 0^\circ$ minimum, while in π -[TCNB] $_2^{2-}$ the $\theta = 60^\circ$ conformation it ends in a $\theta = 90^\circ$ minimum; (d) both behaviors differ from the known orientational preference for π -[TCNE] $_2^{2-}$ dimers, where the dimers present a $D_{2h}(\theta \approx 0^\circ)$ conformation in all reported structures; and (e) all observed and optimized structures exhibit a long, multicenter bond.

In order to understand these observations, the orientational preference of isolated [TCNB] $_2^{2-}$ and [TCNP] $_2^{2-}$ dimers were evaluated in the $0 \leq \theta \leq 360^\circ$ range by computing the interaction energy curve as a function of the dihedral angle (Figure 3; due to the symmetry, the curve had only computed to be computed for $0 \leq \theta \leq 90^\circ$). Figure 9 shows the curves for the π -[TCNP] $_2^{2-}$ and π -[TCNB] $_2^{2-}$ computed at the RASPT2(28,32)/6-31+G(d) level (each point of this curve was obtained at the optimum M06L/6-31+G(d) geometry obtained by fixing θ while all other variables are allowed to be optimized). Note that the entire curves are positive everywhere. The variation of the interaction energy for an isolated π -[TCNP] $_2^{2-}$ and π -[TCNB] $_2^{2-}$ is similar: (a) both have a global minimum at 90° and a local minimum at 0° , slightly higher in energy than the absolute minimum (2.67 and 2.20 kcal·mol $^{-1}$ for [TCNP] $_2^{2-}$ and [TCNB] $_2^{2-}$, respectively); (b) both have a barrier separating the two minima, but in the [TCNP] $_2^{2-}$ dimer is located around $\theta = 30^\circ$, while in the [TCNB] $_2^{2-}$ dimer is found around $\theta = 45^\circ$ (the barrier height in the $90 \rightarrow 0^\circ$ direction is 6.93 and 4.63 kcal·mol $^{-1}$ for the [TCNP] $_2^{2-}$ and [TCNB] $_2^{2-}$, respectively). This change in the barrier position explains why the optimization of the rotated crystal structure in one dimer ends in the optimum D_{2h} conformation, while in the other dimer ends in the optimum D_{2d} conformation.

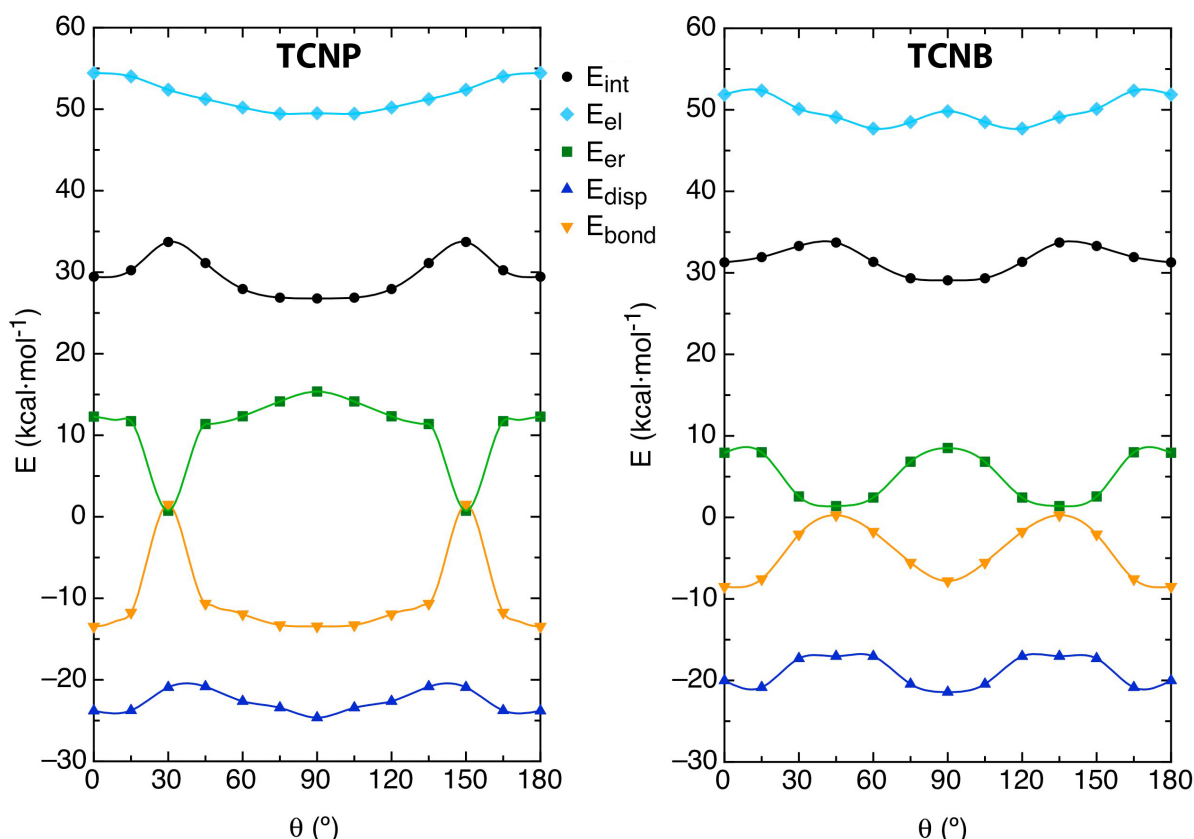


Figure 9. Variation of the intermolecular interaction energy of π -[TCNP]₂²⁻ and π -[TCNB]₂²⁻ as a function of θ , (Figure 2). Also shown is the variation of the energy components of the interaction energy (E_{er}, E_{el}, E_{disp} and E_{bond}) at each angle, thus allowing to define the nature of the interaction energy at each point.

The nature of the [radical anion]⋯[radical anion] interaction at the two minima can be quantitatively determined from the components of the interaction energy in these two points (Table 2). The investigation about the nature of the radical⋯radical interaction in these dimers can be completed by analyzing also how it changes when the inter-fragment orientation (defined by θ) is varied or when the inter-fragment distance, r , is increased (Figure 10). The interaction energy of the two dimers, at their optimum geometry, is strongly dominated by the destabilizing electrostatic component, followed, at large distance, by the stabilizing dispersion and a bonding components, Table 2. Thus, the nature of these three radical⋯radical interaction as *predominantly electrostatic, with small dispersion and bonding contributions*. Interestingly, the diamagnetic nature of these dimers is associated to the energetic preference of the small bonding contribution due to electron pairing, that is, for a closed-shell singlet ground state.

Table 2. Computed values of the E_{er}, E_{el}, E_{disp}, E_{bond} components of the interaction energy, E_{int}, for the π -[TCNP]₂²⁻ and π -[TCNB]₂²⁻. These components were computed according equations 1-6.

Dimer	Conformation	E _{er}	E _{el}	E _{disp}	E _{bond}	E _{int}
π -[TCNP] ₂ ²⁻	$D_{2h}(\theta = 0^\circ)$	12.3	54.4	-23.8	-13.5	29.5
	$C_2(\theta = 30^\circ)$	0.7	52.4	-20.9	1.5	33.7
	$D_{2d}(\theta = 90^\circ)$	15.4	49.5	-24.6	-13.4	26.8
π -[TCNB] ₂ ²⁻	$D_{2h}(\theta = 0^\circ)$	7.9	51.9	-20.0	-8.5	31.3
	$C_2(\theta = 60^\circ)$	2.4	47.7	-17.0	-1.7	31.3
	$D_{2d}(\theta = 90^\circ)$	8.5	49.8	-21.4	-7.8	29.1

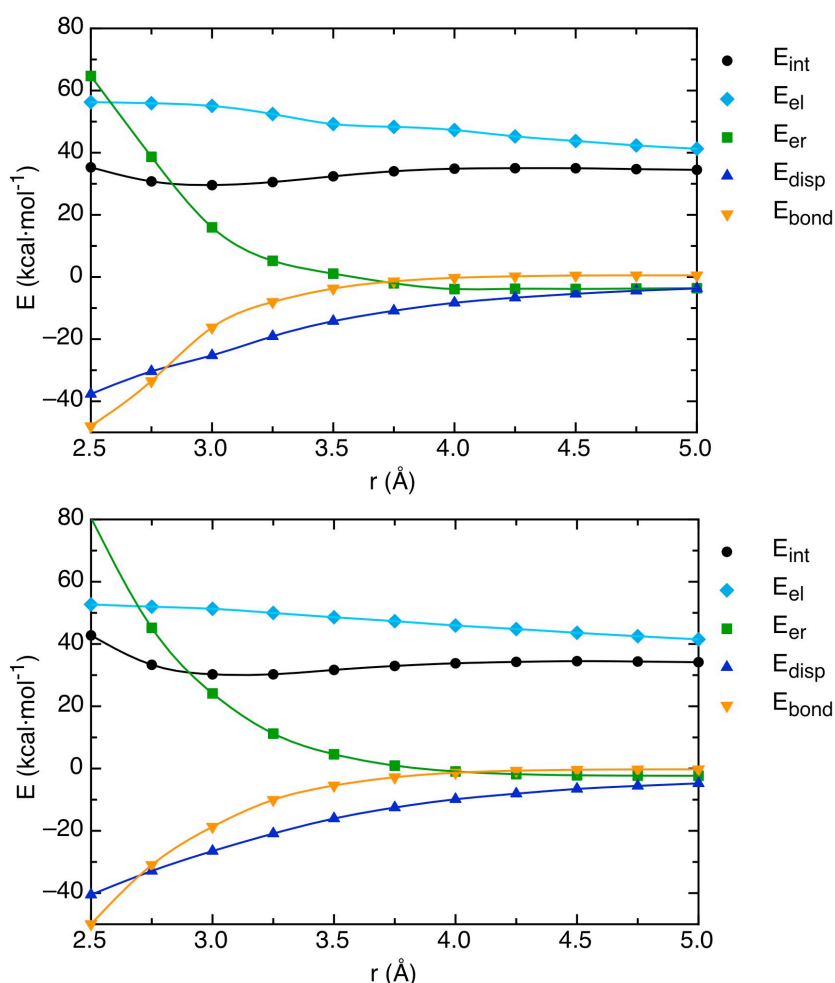


Figure 10. Variation with the fragments separation distance, r , for the components (E_{er} , E_{el} , E_{disp} , E_{bond}) of the interaction energy (E_{int}), computed at the RASPT2/RASSCF(30,28) level. **(top)** for the D_{2h} conformation of the $[\text{TCNP}]_2^{2-}$ dimer; **(bottom)** for the D_{2h} conformation of the $[\text{TCNB}]_2^{2-}$ dimer.

However, no component of the interaction energy reproduces well the angular dependence of the interaction energy (Figure 9): (a) the E_{el} curve has a strength close to the E_{int} curve, but it does not reproduce well the angular dependence; (b) the E_{disp} and E_{bond} components have a similar angular preference to E_{int} , but do not reproduce the E_{int} stability. The same conclusions hold when the variation of the components of the interaction energy is analyzed as a function of the inter-fragment separation (Figure 10). The two main features are the dominance of the electrostatic component at all distances, and the origin of the energy barrier toward dissociation (the electrostatic component presents no barrier, as it decreases as $1/r$, and only when the attractive E_{disp} or E_{bond} components are added a barrier is found), which is in good agreement with previous studies.^{1,2,3,35}

A good agreement with the angular orientation defined by E_{int} is obtained when the E_{el} and E_{bond} components are considered together ($E_{el} + E_{bond}$). Furthermore, the agreement improves when the dispersion component is also added ($E_{el} + E_{bond} + E_{disp}$ sum) (Figure 11). However, although E_{disp} is the strongest attractive component at all orientations of the dimer, its change with the θ is small, and, thus, has little impact on establishing the angular dependence of the π - $[\text{TCNP}]_2^{2-}$ and π - $[\text{TCNB}]_2^{2-}$. Other sums of components were also tested ($E_{el} + E_{disp}$, $E_{er} + E_{bond}$ and $E_{er} + E_{disp}$), but they were worse than the $E_{el} + E_{bond}$ sum. It is worth mentioning

that the latter sum is also that used in the Maximin Principle, a fact that guarantees the validity of such principle when defining the relative orientation observed for π -[TCNP] $_2^{2-}$ and π -[TCNB] $_2^{2-}$. The orientational preference by the results from the E_{int} computed in isolated dimers ($\theta = 0$ and 90°) does not necessarily agree with the orientation of the observed dimers ($\theta = 0, 30, \text{ and } 60^\circ$), Figure 11. This suggests that, at variance of what was previously assumed, such angular dependence also depends on the interaction of these dimers with their surrounding species, namely their counterions. This agrees well with the electrostatic component being dominant, and only after adding the counterions the resulting aggregate is energetically stable against dissociation (see Table 1), as previously found on other long-bonded dimers.³⁸

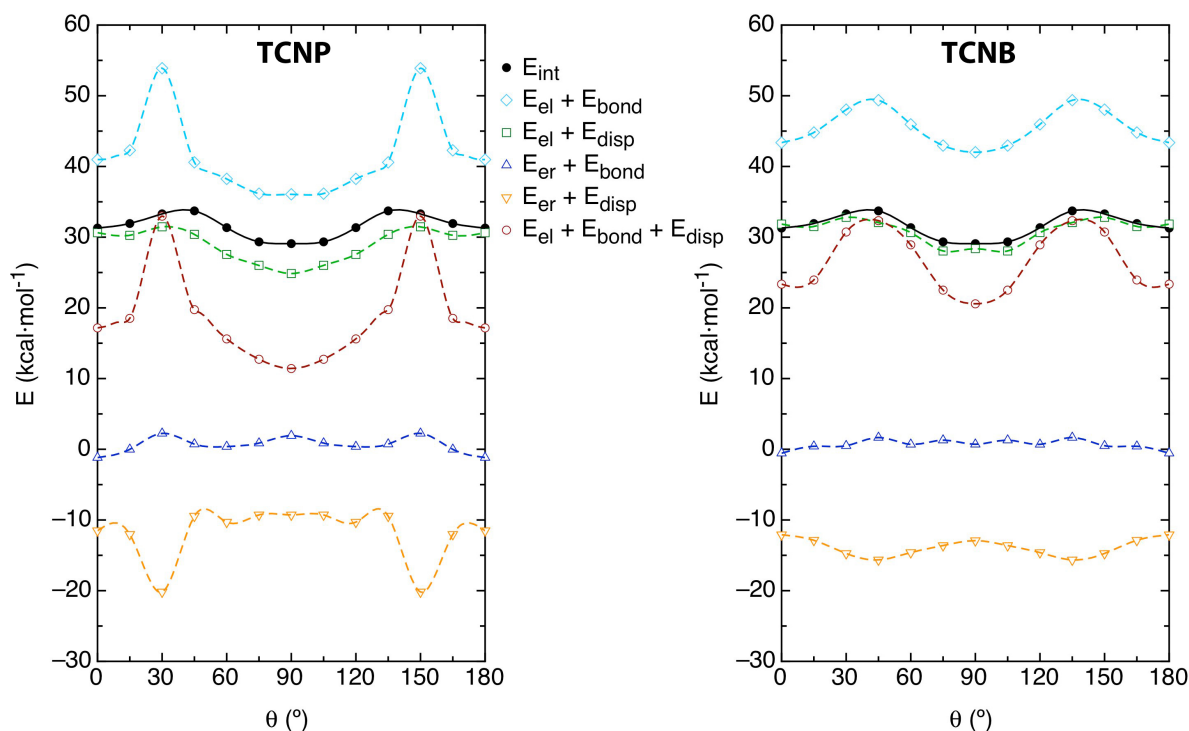


Figure 11. Different sums of the energy components for π -[TCNP] $_2^{2-}$ and π -[TCNB] $_2^{2-}$.

4. The true orientational preference of the [TCNB] $_2^{2-}$ and [TCNP] $_2^{2-}$ dimers.

As already pointed out the radical anion...radical anion interactions are not the dominant forces, as is already manifested in smaller aggregates, Table 1. The sum of all cation...anion electrostatic interactions exceeds the sum of the anion...anion plus cation...cation electrostatic interactions, and is the reason for the stability of the aggregates. If this is the case, it is also clear that cation...anion electrostatic interactions should also play a key role in defining the preferred orientation of the radical anion dimers.

This concept was investigated by computationally studying the impact of the counterions on the orientation of the radical anion dimers by evaluating how the $E_{\text{int}}(\theta)$ curves change as a function of the cation position for the four positions illustrated in Figure 12. Such variation is illustrated in Figure 13. Each point of the curves are obtained at each previously optimized π -[TCNP] $_2^{2-}$ or π -[TCNB] $_2^{2-}$ geometry, by allowing to relax the relative position of both K^+ cations given each fixed desired orientation (i.e., the desired **1**, **2**, **3**, or **4** positions). The four interaction energy curves

of both hypothetical $K_2[TCNP]_2$ and $K_2[TCNB]_2$ differ completely between them and the isolated dimer dianion ones (Figure 9). Therefore, the most stable orientation between $[TCNX]^{2-}$ moieties in $K_2[TCNX]_2$ aggregates highly depends on the position of both K^+ cations.

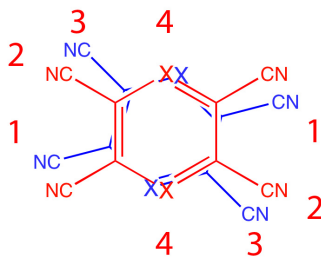


Figure 12. The four positions of the two K^+ cations in both $[TCNP]_2^{2-}$ and $[TCNB]_2^{2-}$ dimers, ($X = N, C-H$, respectively). The orientation of the cations in the dimer is fixed with respect to the red radical anion, while the blue radical anion is rotated.

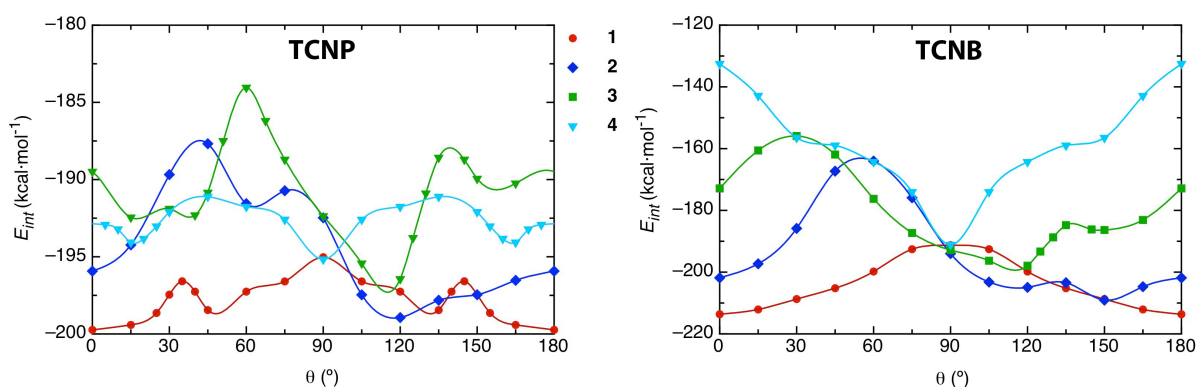


Figure 13. Interaction energy curves of $K_2[TCNP]_2$ (top) and $K_2[TCNB]_2$ (bottom) as a function of θ for the four positions of the K^+ cations shown in Figure 12.

The four curves differ dramatically in their shape, the number of most stable and position of their minima. They also differ from the curves computed for isolated dimers. In the $K_2[TCNP]_2$ dimer found in the $K_2[TCNB]_2$ aggregate each interaction energy curve presents three or even four local minima. The most stable one for each curve are the following: Position **1** curve has two minima at $\theta = \sim 135^\circ$ and $\theta = \sim 45^\circ$, Position **2** just one at $\theta = \sim 120^\circ$, Position **3** at $\theta = \sim 115^\circ$, and position **4** at $\theta = \sim 90^\circ$. All of them are within $5 \text{ kcal}\cdot\text{mol}^{-1}$ energy from the most stable minimum, which corresponds to the fully eclipsed D_{2h} conformation, with the cations placed in Position **1**. On the other hand, the $K_2[TCNB]_2$ curves the behavior is similar, although present only one or two minima is found in each curve and their energy differences are much higher. Their most stable minimum is again the fully eclipsed D_{2h} with K^+ cations in position **1**.

The most stable orientation of the $[TCNP]_2^{2-}$ dimers in $\{[Cr(C_6H_6)_2]_2[TCNP]_2\}$ crystal (the fully eclipsed and the two nearest $[Cr(C_6H_6)_2]^+$ cations are located in position **1**) correspond to the global minimum of Figure 13. In the $[YbCp^*_2][TCNB]$ crystal, $[TCNB]_2^{2-}$ dimers are rotated $\sim 120^\circ$ from the D_{2h} orientation, with both $[YbCp^*_2]^+$ cations located in position **2**. This orientation is also found to be a local minimum, although not the global one. The $[TCNP]_2^{2-}$ dimers in the $[TDAE][TCNP]_2\cdot 2\text{MeCN}$ crystal are rotated $\sim 30^\circ$ from the D_{2h} orientation. Since $[TDAE]^{2+}$ cations are 2+ charged, the model proposed in the present work does not apply for such aggregates.

Conclusions

The mismatch among the orientation of π -[TCNP] $_2^{2-}$ and π -[TCNB] $_2^{2-}$ dimers in their reported molecular crystals centered this work. The first part of this study showed that π -[TCNP] $_2^{2-}$ and π -[TCNB] $_2^{2-}$ form long, multicenter bonds in their reported crystal structures, as well as in the $D_{2d}(\theta = 90^\circ)$ orientation. However, when the two π -[TCNP] $_2^{2-}$ and the π -[TCNB] $_2^{2-}$ were optimized starting from their crystal geometry, only the $D_{2h}(\theta = 0^\circ)$ preserved its orientation. The $C_2(\theta = 30^\circ)$ of the π -[TCNP] $_2^{2-}$ and the $C_2(\theta = 60^\circ)$ π -[TCNB] $_2^{2-}$ optimizations led to both $D_{2d}(\theta = 90^\circ)$ conformations. Interaction energy curves as a function of the dihedral angle (θ) exhibited two only minima, the $D_{2h}(\theta = 0^\circ)$ and $D_{2d}(\theta = 90^\circ)$ orientations. Interaction energy decompositions manifest that the electrostatic component is the predominant term in the interaction energy, and is mainly responsible for the metastable character of these dimers. In addition, the electrostatic plus bonding terms are sufficient in order to qualitatively reproduce the shape of the interaction energy. The electrostatic effects are considered beyond the π -[TCNP] $_2^{2-}$ and π -[TCNB] $_2^{2-}$ dimers by taking into account K_2 [TCNP] $_2$ and K_2 [TCNB] $_2$ aggregates. When interaction energy curves as a function of θ are performed introducing K^+ in four different orientations, several minima arise. The reported crystal structure are successfully reproduced as absolute or local minima of these K_2 [TCNP] $_2$ and K_2 [TCNB] $_2$ interaction energy curves.

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- 34 At the M06L/6-31+G(d) level, the lowest energy triplet state has an energy above that for the singlet: 6.7 kcal·mol⁻¹ for the *D*_{2h} conformer, 6.5 kcal·mol⁻¹ for the *C*₂($\theta \approx 60^\circ$) conformer and 6.1 kcal·mol⁻¹ for the *D*_{2d} conformer of the [TCNB]₂²⁻ dimer.
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3.5. Publication 4

Unusually Long, Multicenter, Cation δ^+ ...Anion δ^- Bonding Observed for Several Polymorphs of [TTF][TCNE]



Unusually Long, Multicenter, Cation δ^+ ...Anion δ^- Bonding Observed for Several Polymorphs of [TTF][TCNE]**

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Abstract: The α , β , and δ polymorphs of [TTF][TCNE] (TTF=tetrathiafulvalene; TCNE=tetracyanoethylene) exhibit a new type of long, multicenter bonding between the [TTF] δ^+ and [TCNE] δ^- moieties, demonstrating the existence of long, hetero-multicenter bonding with a cationic δ^+ ...anionic δ^- zwitterionic-like structure. These diamagnetic π -[TTF] δ^+ [TCNE] δ^- heterodimers exhibit a transfer of about 0.5 e^- from the TTF to the TCNE fragments, as observed from experimental studies, in accord with theoretical predictions, that is, [TTF] δ^+ ...[TCNE] δ^- ($\delta \approx 0.5$). They have several interfragment distances < 3.4 Å, and a computed interaction energy of -21.2 kcal mol $^{-1}$, which is typical of long, multicenter bonds. The lower stability of [TTF] δ^+ [TCNE] δ^- with respect to typi-

cal ionic bonds is due, in part, to the partial electron transfer that reduces the electrostatic bonding component. This reduced electrostatic interaction, and the large interfragment dispersion stabilize the long, heterocationic/anionic multicenter interaction, which in [TTF] δ^+ ...[TCNE] δ^- always involves two electrons, but have ten, eight, and eight bond critical points (bcps) involving C–C, N–S, and sometimes C–S and C–N components for the α , β , and δ polymorphs, respectively. In contrast, γ -[TTF][TCNE] possesses [TTF] $_2^{2+}$ and [TCNE] $_2^{2-}$ dimers, each with long,

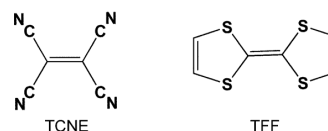
homo-multicenter $2e^-/12c$ (c =center, $2C+4S$) [TTF] $_2^{2+}$ cationic $^{2+}$...cationic $^{2+}$ bonds, as well as long, homo-multicenter $2e^-/4c$ [TCNE] $_2^{2-}$ anionic $^{2-}$...anionic $^{2-}$ bonding. The MO diagrams for the α , β , and δ polymorphs have all of the features found for conventional covalent C–C bonds, and for all of the previously studied multicenter long bonds, for example, π -[TTF] $_2^{2+}$ and π -[TCNE] $_2^{2-}$. The HOMOs for α -, β -, and δ -[TTF][TCNE] have 2c C–S and 3c C–C–C orbital-overlap contributions between the [TTF] δ^+ and [TCNE] δ^- moieties; these are the shortest intra [TTF...TCNE] separations. Thus, from an orbital-overlap perspective, the bonding has 2c and 3c components residing over one S and four C atoms.

Keywords: bond theory • charge transfer • molecular orbital calculations • multicenter bonding • radicals

Introduction

Our discovery that the tetracyanoethylene^[1] (TCNE)-electron-transfer salt of [Fe(C₅Me₅)₂], that is, [Fe(C₅Me₅)₂] $^{+}$ [TCNE] $^{-}$, was an organic-based magnet below 4.8 K,^[2] led us and others^[3,4] to explore numerous other TCNE-based electron-transfer salts. In addition, to identify additional magnets, we characterized the diamagnetic σ and π dimers of [TCNE] $^{-}$, that is, [C₄(CN)₈] $_2^{2-}$ ^[5] and π -[TCNE] $_2^{2-}$,^[6–8] respectively. The 2.89 Å intradimer separation for the eclipsed [TCNE] $_2^{2-}$ dimer was too long for a conventional C–C bond (≤ 1.54 Å), and too short for a van der Waals interaction (i.e., < 3.4 Å).^[9] This piqued our curiosity as to the nature of the intradimer bonding, and we experimentally and computationally characterized the bonding in π -[TCNE] $_2^{2-}$ dimers.

The unusual intradimer bonding present in [TCNE] $_2^{2-}$ originates from the SOMOs of the two [TCNE] $^{-}$ moieties



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**] TTF=tetrathiafulvalene, TCNE=tetracyanoethylene.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201100922>. The Supporting information contains X-ray crystallographic data in CIF format, a view of the interchain C–H...N contacts shorter than 2.9 Å in the β , δ , and γ phases, MO diagram for the interaction of the four SOMO orbitals or four radicals placed in an ABBA disposition when the AB overlap is stronger and weaker than the BB overlap, as well as a table collecting the properties of the bond critical points (bcps) in β , δ , and γ phases.

FULL PAPER

overlapping to form bonding/antibonding $[\text{TCNE}]_2^{2-}$ MOs (Figure 1). This radical results mostly from the electrostatic cation $^+$... $[\text{TCNE}]^-$ interactions exceeding the sum of the cation $^+$...cation $^+$ and anion $^-$...anion $^-$ repulsions enabling the

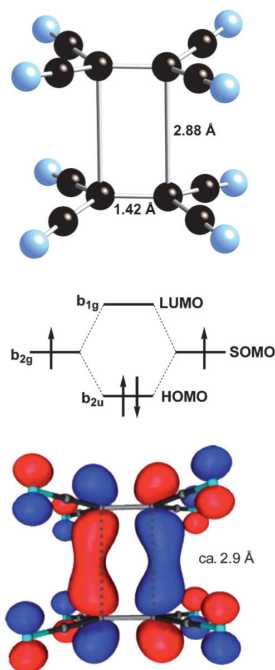


Figure 1. Stick-and-ball representation (top), MO diagram (middle), and b_{2u} HOMO (bottom) for π - $[\text{TCNE}]_2^{2-}$.

formation of energetically stable $[\text{cation}^+]_2[\text{TCNE}]_2^{2-}$ aggregates for which the SOMO orbitals of the two $[\text{TCNE}]^-$ moieties overlap. A doubly occupied bonding orbital and an empty antibonding orbital are generated by the combination of the overlapping SOMOs of the two $[\text{TCNE}]^-$ moieties. These orbitals are similar to those produced between the two moieties of a conventional covalent bond, and produce an attractive energetic component in addition to the electrostatic one. Additionally, dispersion also adds energetic stability to the $[\text{TCNE}]^-$... $[\text{TCNE}]^-$ interaction.^[10–12] The interaction between two $[\text{TCNE}]^-$ moieties is thus a long, multicenter C–C bond, because it differs from a conventional covalent bond in the genesis of the energetic stabilization, and longer equilibrium distances. Note that the $[\text{TCNE}]_2^{2-}$ dimers present in $[\text{cation}^+]_2[\text{TCNE}]_2^{2-}$ are diamagnetic, as they have a closed-shell singlet ground state, in good agreement with the experimental observations. Theoretical studies indicated that all $[\text{TCNE}]_2^{2-}$ dimers exhibit long, $2e^-/4c$ (c =center) C–C bonds, and are prototypes for long, multicenter C–C bonds between radical anions. More recently, long, multicenter C–C bonding has also been observed for $[\text{cyanil}]_2^{2-}$ ($2e^-/10c$ ($8C+2O$)),^[11] $[\text{TTF}]_2^{2+}$ (TTF =tetrathiafulvalene) ($2e^-/10c$ ($6C+4S$)),^[13] di(2,5,8-*tert*-butylphena-

lenyl) ($2e^-/14c$ ($14C$)),^[14,15] [tetracyanopyrazine] $_2^{2-}$ ($2e^-/8c$ ($8C$)),^[16] $[\text{TCNQ}]_2^{2-}$ (TCNQ =7,7,8,8-tetracyano-*p*-quinodimethane, $2e^-/20c$ ($12C+8N$)),^[17] and so forth.

As part of our previous analysis of the bonding present for π - $[\text{TCNE}]_2^{2-}$, two structural groups of dimers were identified; namely, eclipsed (L_c) and trans (L_T).^[7] L_c dimers are more prevalent. Only two examples of L_T -structured $[\text{TCNE}]_2^{2-}$ were found in the literature, and they were observed for α - and β - $[\text{TTF}][\text{TCNE}]$ (Figure 2).^[18] In addition

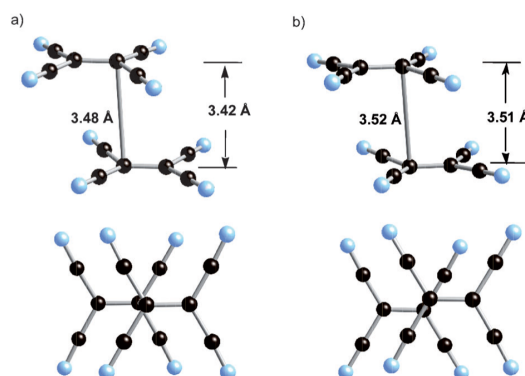


Figure 2. Side (top) and normal views (bottom) of the structure of L_T $[\text{TCNE}]_2^{2-}$ dimers present in a) α - and b) β - $[\text{TTF}][\text{TCNE}]$.^[18]

to not being eclipsed, each polymorph possesses TCNE moieties in which the nitriles bend toward each other and has a longer intradimer C–C separation of 3.50 ± 0.02 Å (the van der Waals limit), as opposed to the nitriles bending away from each other with about 2.9 Å intradimer C–C separations for the eclipsed structures. In addition, they were analyzed to possess three intra- $[\text{TCNE}]_2^{2-}$ bond critical points (bcps).^[7]

This unusual behavior prompted a systematic experimental and theoretical study of the bonding of π - $[\text{TCNE}]_2^{2-}$ in the L_T orientation observed for α - and β - $[\text{TTF}][\text{TCNE}]$, and identified a new class of long, multicenter bonding, which had not previously been observed, that is, for which the interacting ion radicals are of opposite charge. The α and β polymorphs of $[\text{TTF}][\text{TCNE}]$ have been reported previously,^[18,19] although we were only successful in isolating pure β - $[\text{TTF}][\text{TCNE}]$. During this study two new polymorphs, δ and γ , were discovered, the first one also presenting long, multicenter bonding between ion radicals of opposite charge. This new class of long bonds, for which the first example has π - $[\text{TTF}^{\delta+}\cdots\text{TCNE}^{\delta-}]$ bonding, is defined as the hetero class to distinguish it from previously known, long, multicenter bonds that involve ions of the same sign (i.e., homo-multicenter bonds). The existence of long bonds between ion radicals of opposite signs possess some intriguing problems concerning the stability of the interacting fragments, as ion radicals of opposite charge should form a conventional covalent bond. Finally, a comparative study of the long bond in the $[\text{TTF}][\text{TCNE}]$ polymorphs permits identifi-

cation of how the long, multicenter bonding between the ion radicals varies as a function of different orientations.

Experimental Section

TTF and TCNE were purchased and sublimed prior to use. Acetonitrile and CH_2Cl_2 were purified through an activated-alumina, dual-column, purification system under a positive pressure of dry N_2 , and all syntheses were performed in an inert DriBox (<1 ppm O_2) box. Infrared spectra were recorded with a Bruker Tensor 37 FTIR spectrophotometer ($\pm 1 \text{ cm}^{-1}$). The absorption spectra were taken in transmission mode by using a microscope glass slide as blank. A tungsten lamp was focused onto the sample and the transmitted light was captured by a lens system and guided through an optical fiber into an Ocean Optics USB4000 spectrometer in which the light was dispersed and recorded by a CCD detector. Magnetic susceptibilities were measured above 250 K in a 1000 Oe applied field on a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer as previously reported.^[20] The diamagnetic correction for $[\text{TTF}][\text{TCNE}]$ is $-168 \times 10^{-6} \text{ emu mol}^{-1}$.

α -[TTF][TCNE]: The α and β polymorphs of $[\text{TTF}][\text{TCNE}]$ ^[18,19] have been reported previously, but we were only successful in isolating pure β -[TTF][TCNE]. Thus, no further experimental studies were done for this phase, although, by using the already reported literature structure, it was included in our theoretical studies. The $\tilde{\nu}_{\text{CN}}$ IR absorptions have been reported previously to occur at 2218 (m), 2200 (s), 2186 (m), and 2177 cm^{-1} (w).^[19]

β -[TTF][TCNE]: The β polymorph of $[\text{TTF}][\text{TCNE}]$ was prepared by a literature procedure.^[18] IR (KBr): $\tilde{\nu}_{\text{CH}}=3100$ (m), 3084 (s), 3066 (m), 3028 (m), 2949 (m); $\tilde{\nu}_{\text{CN}}=2218$ (m), 2200 (s), 2194 (s), 2186 (s), 2178 (s); 1504 (m), 1449 (m), 1489 (m), 1390 (s), 1258 (s), 1102 (s), 826 (s), 811 (s), 805 (s), 747 (s), 737 (s), 683 cm^{-1} (s). The $\tilde{\nu}_{\text{CN}}$ IR absorptions were previously reported to occur at 2214 (m), 2198 (s), and 2179 cm^{-1} (s).^[19]

γ -[TTF][TCNE]: TTF (92.0 mg, 0.450 mmol) and TCNE (59.1 mg, 0.461 mmol) were each dissolved in MeCN (ca 3 mL), and the TCNE solution was dropwise added to the TTF solution with stirring. The yellow solution of TTF quickly turned black and a precipitate formed. The precipitate was collected by filtration. Yield: 92 mg (61%). Crystals for X-ray analysis were grown by dissolving this product in MeCN (ca 100 mL), and placing the solution in a freezer at -25°C for three days. Long needle-formed crystals were collected by vacuum filtration. IR (KBr): $\tilde{\nu}_{\text{CH}}=3113$ (w), 3086 cm^{-1} (m); $\tilde{\nu}_{\text{CN}}=2200$ (m), 2189 (m), 2170 (m), 2156 (s); 1505 (w), 1474 (w), 1362 (s), 1334 (s), 1246 (m), 1179 (w), 1085 (w), 827 (w), 744 (m), 682 (m), 548 (w), 433 cm^{-1} (s).

δ -[TTF][TCNE]: The remaining filtrate from the above-mentioned reaction was placed in the freezer for two more days, and small crystals, which were collected by vacuum filtration, formed. Yield: 15 mg (10%). IR (KBr): $\tilde{\nu}_{\text{CH}}=3093 \text{ cm}^{-1}$ (m), 3078 (s); $\tilde{\nu}_{\text{CN}}=2214$ (w), 2198 (m), 2180 (m), 2156 (m); 1391 (s), 1338 (m), 1255 (m), 1098 (s), 876 (m), 817 (m), 803 (m), 748 (m), 736 (m), 684 (m), 677 (m), 482 cm^{-1} (m).

X-ray crystallographic data collection and refinement: Crystals of the γ and δ polymorphs of $[\text{TTF}][\text{TCNE}]$ were mounted on a CryoLoop with Paratone oil. Intensity data for all structures were collected with a Bruker APEX CCD detector, and the data was integrated with the Bruker SAINT software program.^[21a,b] The intensity data were corrected for absorption with the SADABS program with multiscan data.^[21c] The structures were solved by direct methods^[22a] and refined by full-matrix least-squares methods with SHELXL-97.^[22c] The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. All hydrogen atoms were placed by using a riding model, and their positions were constrained relative to their parent atom with the appropriate HFIX command in SHELXL-97. The crystallographic data for α -, β -, γ -, and δ -[TTF][TCNE] are summarized in Table 1. CCDC-814909 (γ -[TTF][TCNE]) and -814910 (δ -[TTF][TCNE]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Summary of the crystallographic data for α -, β -, γ -, and δ -[TTF][TCNE].

	α	β	γ	δ
formula	$\text{C}_{12}\text{H}_4\text{N}_4\text{S}_4$	$\text{C}_{12}\text{H}_4\text{N}_4\text{S}_4$	$\text{C}_{12}\text{H}_4\text{N}_4\text{S}_4$	$\text{C}_{12}\text{H}_4\text{N}_4\text{S}_4$
M_r	332.47	332.47	332.47	332.47
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1$
a [Å]	13.310(6)	15.429(6)	6.962(4)	7.239(4)
b [Å]	15.475(5)	6.632(4)	12.835(7)	6.550(4)
c [Å]	6.864(3)	14.165(6)	15.279(8)	14.551(8)
α [°]	90	90	87.262(8)	90
β [°]	101.18(2)	104.32(3)	80.139(8)	97.917(8)
γ [°]	90	90	74.354(7)	90
V [Å ³]	1387(1)	1404.4(1.2)	1295.3(12)	683.3(7)
Z	4	4	4	2
ρ_{calcd} [g cm ⁻³]	1.591	1.571	1.705	1.616
T [K]	295	295	150(2)	150(2)
μ (Mo K α) [mm ⁻¹]	0.650	0.650	0.725	0.687
R_1 ^[a] (2σ data)	0.034	0.058	0.0754	0.0281
wR_2 ^[b] (2σ data)	0.030	0.056	0.0905	0.0616
reference	[18]	[18]	this work	this work

$$[a] R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|. [b] wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)]^{1/2}.$$

Computational methodology: The electronic structure and properties of π dimers, presumed to present long distance bonds, were initially evaluated at the B3LYP density functional^[23] level. This was followed by CASSCF(4,4), and MCQDPT/CASSCF(4,4) multireference calculations performed because previous B3LYP computations^[24] for $[\text{TCNE}]_2^{2-}$ dimers failed to reproduce the observed diamagnetic ground state, a property that is properly accounted by MCQDPT/CASSCF(4,4) calculations (a type of multiconfigurational perturbation calculation on a multi-configurational CASSCF(4,4) wavefunction, where the MCQDPT method^[25] is used). The MCQDPT/CASSCF(4,4) method provides an accurate evaluation of the dispersion component of the interaction energy and gives results similar to those obtained by using the CASPT2 method.^[26] In the CASSCF(4,4) and MCQDPT/CASSCF(4,4) calculations the (4,4) active space is made of HOMO and LUMO of the neutral TTF and TCNE, and holds a total of four electrons. In these CASSCF(4,4) calculations, both the closed-shell and open-shell singlet states, which can originate from the interaction of the two doublet $[\text{TTF}]^+$ and $[\text{TCNE}]^-$ radical ions, are properly described.

All B3LYP calculations were done with the 6-31+G(d) basis set^[27] and the Gaussian 03 suite of programs,^[28] whereas the CASSCF(4,4) and MCQDPT/CASSCF(4,4) calculations were done by using the GAMESS 06 suite of programs.^[29]

To fully characterize the bonds in the open-shell and closed-shell minima, we carried out an atoms-in-molecules (AIM) analysis^[30] of the electronic densities of these structures at the optimum geometries. According to the AIM methodology, an intermolecular bond presents a (3,−1) bcp in the electronic density of the complex. This bcp connects two bonded atoms, and can be characterized by the electron density (ρ) and Laplacian (∇^2 , the sum of the curvatures of the density at the bcp, obtained by adding the eigenvalues of the second derivative of the density at the bcp). In all known hydrogen bonds and van der Waals bonds the ρ at the bcp is very small, and the ∇^2 is positive. In conventional covalent bonds (e.g., C–C bond in ethane), ρ is very often one-order-of-magnitude larger and ∇^2 is negative. In ionic bonds, as NaCl, ρ is also small, but the ∇^2 is positive.

Results and Discussion

Synthesis and characterization: The reversible one-electron oxidation potentials of TTF and TCNE in MeCN are 0.30 and 0.15 V (vs. SCE), respectively;^[31] hence, $\text{TTF} + \text{TCNE} \rightarrow$

[TTF]⁺[TCNE]⁻ is not spontaneous ($E^0 = -0.15$ V) in solution. Nonetheless, a rapid precipitation of two polymorphs of [TTF][TCNE] occurs;^[18,19] this may either be a Mulliken donor-acceptor complex or an electron-transfer salt, as established for organic-based metal-like [TTF]^{0.54+}[TCNQ]^{0.54-} (TCNQ $E^0 = -0.17$ V^[31]). Studies of the spectroscopic and magnetic properties of α - and β -[TTF][TCNE] were sought, but we were only successful in isolating pure β -[TTF][TCNE]. However, two additional polymorphs of [TTF][TCNE] (γ and δ) were isolated. The preparations are solvent dependent, and mixtures of materials are frequently present, and except for the β phase, the preparations are not reproducible. [TTF][TCNE] decompose when exposed to air.

The IR spectra as well as powder X-ray diffraction data are sufficiently different from each other, hence, they were used to identify the phases present, and the γ and δ phases were identified. The visible region of the electronic absorption spectra of the β -, γ -, and δ -[TTF][TCNE] polymorphs are featureless and do not provide information to assist in the characterization. In contrast, each polymorph has a different IR spectrum, which can be used to identify them (Figure 3).

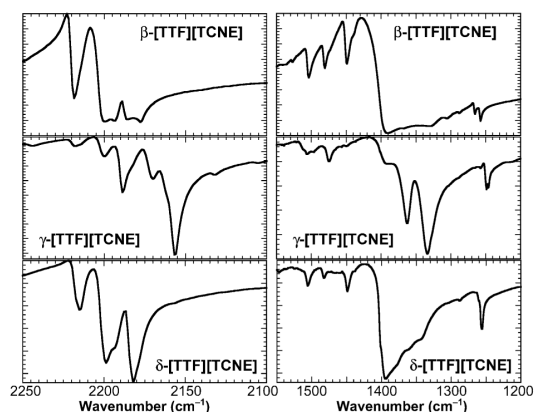


Figure 3. IR spectra of β -, γ -, and δ -[TTF][TCNE] in the $\bar{\nu}_{\text{CN}}$ region, and the 1200–1550 cm^{-1} region. The ordinate is transmittance (top = 100%, bottom 0% (= 100% absorption)).

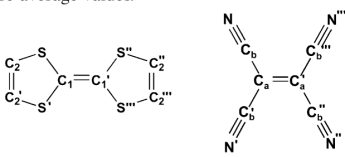
Crystallographic structures: The crystal structures of α - and β -[TTF][TCNE] have been determined by X-ray crystallography at room temperature by Clemente and Marzotto.^[18] Our attempts to prepare these phases led to the isolation of two materials whose IR spectra (and subsequent powder X-ray diffraction) indicated that they were neither α - nor β -[TTF][TCNE]. The structures of these two new compounds were determined and designated the γ - and δ -[TTF][TCNE] polymorphs. γ -[TTF][TCNE] was both rotationally and pseudomerohedrally twinned, but software enabled the solution of the structure.^[22d] The TTF and TCNE moieties are similar in each of these polymorphs, and each polymorph

possesses parallel chains. The key differences between the four polymorphs are in the chain stacking.

The nature of the TTF and TCNE moieties: In each of the four [TTF][TCNE] polymorphs, TTF is oxidized to [TTF]⁺. The central C–C bond is 1.387(2), 1.38(1), 1.39(1), and 1.385(2) Å, respectively, for the α -, β -, γ -, and δ -polymorphs. These values lie between 1.350 and 1.467 Å for TTF⁰ (bond order = 2)^[33a] and [TTF]²⁺ (bond order = 1) (Table 2).^[33b] This assessment is also in agreement with an analysis of the C–S bond lengths, concluding that α - and β -[TTF][TCNE] should be described as [TTF]^{0.54+}[TCNE]^{0.54-}.^[18,19] Likewise, TCNE is reduced to [TCNE]⁻. The central C–C bond is 1.397(3), 1.40(1), 1.41(3), and 1.404(3) Å, respectively, for the α -, β -, γ -, and δ -polymorphs. These distances lie between 1.346^[1,34a] and 1.488 Å^[1,34b] for TCNE⁰ (bond order = 2) and [TCNE]²⁻ (bond order = 1), and agree with 1.394 Å for [TCNE]⁻ (bond order = 1.5, Table 2). Furthermore, the TTFs and TCNEs in the four polymorphs are slightly twisted out of the planes, but not as twisted as expected, and observed for a bond order = 1 [TTF]²⁺^[33b] and [TCNE]²⁻.^[34b] The bond lengths for α -, β -, γ -, and δ -[TTF][TCNE] as well as for TTF⁰, [TTF]²⁺, TCNE⁰ and [TCNE]²⁻, and the average values are listed in Table 2. There are two unique TTF and TCNEs for γ -[TTF][TCNE], and, even though they are poorly refined, both are listed in Table 2 together with their average distances. Hence, the formal oxidation states for TTF and TCNE are about 0.5 and –0.5 for the α -, β -, and δ -[TTF][TCNE] polymorphs, and +1 and –1 for γ -[TTF][TCNE], similar to what has been reported for the α and β polymorphs.^[18,19]

Packing arrangement: All four polymorphs of [TTF][TCNE], possess parallel chains with different packing arrangements (Figure 4–7). The α and β polymorphs possess a ...AABBAABB... alternating sequence (A = TTF, B = TCNE), but different geometrical orientations (see below). In contrast, the δ polymorph possesses a ...ABABABAB... alternating sequence, whereas the γ polymorph possesses parallel segregated ...AAAA... and ...BBBB... chains. The specific details and differences are described below.

Each polymorph has a different local minimum in the free-energy potential energy surface;^[35] this makes each polymorph thermodynamically and kinetically stable against dissociation or transformation into another polymorph. In relation to the stability against dissociation, not all chains are energetically stable; this is elaborated in the following qualitative argument. As A and B are charged species, the main energetic component is the electrostatic cation^{δ+}...anion^{δ-} component, although the bonding component that originates from the SOMO–SOMO overlap and pairing of the bonding combination, and the dispersion energetic component also contribute to make the interaction between A and B energetically stable. An evaluation of the interaction energy of an isolated AB dimer confirms its stability. The same computations indicate that two dimers placed in an AB...BA or BA...AB disposition are energetically repul-

Table 2. Non-hydrogen intramolecular bond lengths (Å) for α -, β -, γ -, and δ -[TTF][TCNE] and related TTF, [TTF]₂²⁺, [TTF]²⁺, TCNE, [TCNE]⁻, [TCNE]₂²⁻, and [TCNE]²⁻. Values in angle brackets are average values.


	α ^[18]	β ^[18]	γ ^[a]	δ	[TTF] ₂ ²⁺	TTF ⁰ [33a]	[TTF] ²⁺ [33b]
C ₁ –C ₁ '	1.378(2)	1.38(1)	1.397(12) 1.380(13) <1.39(1)>	1.385(3)	1.400(13) 1.407(14) <1.40>	1.347(3)	1.467
C ₁ –S (average)	1.737(3)	1.719(2)	1.719(2) 1.728(15) <1.723(11)>	1.729(6)	1.71	1.760(2)	1.669
C ₂ –S (average)	1.726(9)	1.733(13)	1.725(13) 1.728(13) <1.726(12)>	1.730(13)	1.725	1.745(2)	1.691
C ₂ –C ₂ ' (average)	1.316(6)	1.325(7)	1.339(10) 1.327(7) <1.333(10)>	1.330(5)	1.31	1.329(2)	1.342

	α ^[18]	β ^[18]	γ ^[a]	δ	[TCNE] ₂ ²⁻ [1]	TCNE ⁰ [34a]	[TCNE] ²⁻ [34b]	[TCNE] ⁻ [1]
C _a –C _a '	1.397(3)	1.40(1)	1.426(14) 1.385(15) <1.41(3)>	1.404(4)	1.425	1.346	1.488	1.394
C _a –C _b (average)	1.426(9)	1.425(10)	1.418(9) 1.436(14) <1.427(14)>	1.421(12)	1.421	1.442	1.399	1.430
C _b –N (average)	1.142(4)	1.145(10)	1.152(8) 1.148(17) <1.150(12)>	1.146(4)	1.149	1.159	1.159	1.132

[a] 150 K.

sive, that is, AA or BB dimers. Consequently, only the ...ABABABAB... chains in the δ polymorph are energetically stable, whereas the existence of ...AABBAABB... chains in the β polymorph, and the segregated ...AAAA... and ...BBBB... chains in the γ polymorph are stabilized by inter-chain interactions. These interactions are of the C–H ^{δ} ...N ^{δ} -type (i.e., a C–H...N hydrogen bond for which the C–H donor group belongs to a cation and the acceptor atom to an anion). In the β , γ , and δ phases this separation is 2.485, 2.627, and 2.480 Å, respectively; these values are well below the sum of their H and N van der Waals radii of 2.75 Å^[36] (Figure S1 in the Supporting Information).

Structures of the four [TTF][TCNE] polymorphs:

α -[TTF][TCNE]: This polymorph has been described as [TTF]₂[TCNE]₂ with [TTF]₂²⁺ and [TCNE]₂²⁻ dimers,^[18] and subsequently [TCNE]₂²⁻ has been noted to represent an uncommon L_T orientation (Figure 2a).^[7] Similar to the TCNEs (Figure 2a), the TTFs form pairs with about 3.5 Å interplanar separation; however, they are slipped with respect to the short C₂ axis that resides in the plane of the TTF, and the CN groups are bent towards each other. Hence, pairs of these TTFs do not resemble previously reported [TTF]₂²⁺ dimers.^[13] There are essentially no sub van der Waals intrachain TTF...TTF and TCNE...TCNE interactions, but there are 13 C...C, C...S, C...N, and S...N sub van der Waals

TTF...TCNE intrachain interactions (Figure 4, Table 3). The shortest C–C interactions are between TCNE C9 and the equidistant to C3 and C6 atoms of the TTF molecule (3.122 Å). The shortest C–S (S2–C12) distance, 3.074 Å, is the shortest intradimer separation. The other C–C interactions shorter than 3.4 Å are: C3–C8 3.162, C6–C7 3.256, C2–C10 3.301, C6–C8 3.353, and C3–C12 3.385 Å, whereas the other C–S bonds shorter than 3.4 Å are: S2–C10 3.168, S3–C7 3.358, S1–C8 3.366 Å, C3–N5 is 3.228, and S1–N2 is 3.223 Å. The dimers form non-slipped chains. The central C–C bond of the TCNE is twisted 51.9° relative to the central C–C bond of TTF. The two fragments in these dimers are slightly bent to avoid each other, similar to the structure found in [TCNE]₂²⁻ dimers. In the TTF fragments the central S atoms are twisted in average 3.2° relative to the plane formed by the central C–C atoms and one of the S atoms. The same happens in TCNE with the C atoms of the CN groups, which are twisted off the plane by 5.4° relative to the plane formed by the central C–C atoms and one of the cyano C atoms. Hence, α -[TTF][TCNE] is best described as possessing charged fragments, that is, [TTF] ^{δ} ...[TCNE] ^{δ} -, with hetero-multicenter bonding in a ...ABBAABBA... stacking motif. This heterodimer is distinctly different to both [TTF]₂²⁺ and [TCNE]₂²⁻ homodimers previously reported. Whereas there are 13 sub van der Waals C...C, C...S, C...N, and N...S interactions that connect the TTF and

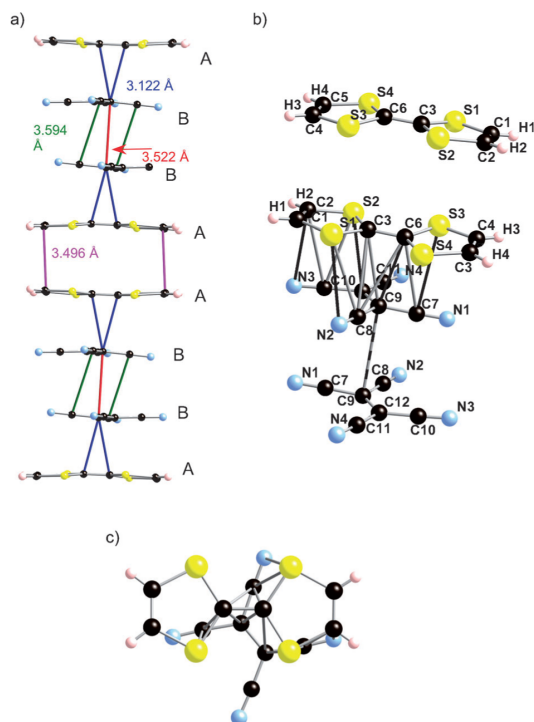


Figure 4. a) Side, b) atom-labeling, and c) normal chain views of α -[TTF]...[TCNE] showing 13 TTF...TCNE interactions < 3.4 Å, and the 3.52 Å-long C9-C9 TCNE...TCNE interaction (dashed line in b), see also Figure 2a). Atoms connected with bcps are connected with black lines in b) and c) (see text).

Table 3. [TTF]...[TCNE] distances < 3.4 Å for α -, β -, and δ -[TTF][TCNE], and the intradimer eclipsed distances for γ -[TTF][TCNE]. The atom numbering refers to the crystal structure determinations (cif files) and are given in Figures 4b, 5b, 6b, and 7b. Note that not all sub van der Waals contacts present a bond component (see text).

Contact no.	Contact	α ^[18] Distance [Å]	Contact	β ^[18] Distance [Å]	Contact	γ Distance [Å]	Contact	δ Distance [Å]
1	C3-C9	3.122	C3-C12	3.107	C9-C10	3.319	C3-C8	3.063
2	C6-C9 ^[a]	3.122	C6-C12	3.167	C9'-C10'	3.348	C4-C8	3.103
3	C3-C8	3.162	C3-C11	3.179	C8'-C11'	3.382	C3-C11	3.148
4	C6-C7	3.256	C6-C10	3.245	S1-S4	3.326	C4-C7	3.156
5	C3-C12	3.385	C2-C7	3.284	S1'-S4'	3.341	C3-C9	3.346
6	S2-C12	3.074	C3-C9	3.345	S2-S3	3.336	C4-C11	3.380
7	S2-C10	3.168	C1-N1	3.275	S2'-S3'	3.318	C2-N4	3.312
8	S3-C7	3.358	S2-C9	3.042	C2-C3	2.927	C6-N1	3.345
9	S1-C8	3.366	S2-C7	3.204	C2'-C3'	2.923	S2-C9	3.009
10	S1-N2	3.223	S1-C11	3.340	N1-N4	3.284	S2-C12	3.204
11	C2-N3	3.228	S3-C10	3.389	N2-N3	3.308	S4-C7	3.294
12	C2-C10	3.301	S1-N4	3.202	C1-C6	3.129	S1-C11	3.310
13	C6-C8	3.353			C4-C5	3.135	S1-N3	3.178
14					N1'-N4'	3.281	C2-C12	3.295
15					N2'-N3'	3.275	S4-N1	3.355
16					C1'-C6'	3.137		
17			S3-N3 ^[b]	3.456	C4'-C5'	3.110		

[a] Italicized values refer to bcp (see text). [b] > 3.4 Å.

TCNE moieties in this π -[TTF...TCNE] dimer, there are no interchain interactions (except for short C-H...N contacts).

β -[TTF][TCNE]: Similar to the α polymorph, the β polymorph has been described as [TTF]₂[TCNE]₂,^[18] and this [TCNE]₂²⁻ dimer has also been noted to represent an uncommon L_T orientation (Figure 2b).^[7] However, similar to the α polymorph, the crystal is better described as forming π -[TTF^{δ+}...TCNE^{δ-}] dimers (Figure 5b), which are slightly displaced sideways with respect to those found in the α polymorph (Figure 5b). The shortest C-C distance between TTFs of adjacent dimers of the same chain is 3.71 Å, whereas between TCNEs the shortest distance is 3.39 Å (the shortest intradimer distance is 3.107 Å). No short C-C intra-chain interactions are found between TTF and TCNE fragments of adjacent chains, but short C-H...N contacts are present. There are, however, 12 C...C, C...S, and S...N sub van der Waals interactions within the fragments of the π -[TTF...TCNE] dimer (Figure 5, Table 3). The shortest interaction is 3.042 Å between S2-C9, and the shortest C-C interaction is between TTF C3 and TCNE C12 (3.107 Å). The other interactions shorter than 3.4 Å are: C6-C12 3.167, C3-C11 3.179, C6-C10 3.245, C2-C7 3.284, C3-C9 3.345, N1-C1 3.275, N4-S1 3.202, S2-C9 3.042, S2-C7 3.204, S1-C11 3.340, and S3-C10 3.389 Å.

Similarly to that observed for the α polymorph, the two fragments in the π -[TTF...TCNE] dimers are slightly bent to avoid each other. In the TTF fragments the central S atoms are twisted in average 5.7° relative to the plane formed by the central C-C atoms and one of the S atoms. This also occurs for the TCNE moieties for which the C atoms of the CN groups are twisted 4.5° relative to the plane formed by the central C-C atoms and one of the cyano C atoms. Furthermore, the central C-C bond of the TCNE is twisted 50.7° relative to the central C-C bond of TTF.

γ -[TTF][TCNE]: The solid-state structure of γ -[TTF][TCNE] consists of parallel, segregated, nonuniform, 1D chains of eclipsed centrosymmetric π -[TTF]₂²⁺ and π -[TCNE]₂²⁻ dimers, (Figure 6) that is, segregated ...AA-AA... and ...BB-BB... chains. The unit cell has two unique centrosymmetric pairs of chains that are chemically equivalent. The intrachain intra- and interdimer separations are 2.925 ± 0.002 and 3.846 Å for [TCNE]₂²⁻ and 3.333 ± 0.015 and 3.553 Å for [TTF]₂²⁺. The average central C-C bonds is 1.41 Å for [TCNE]₂²⁻ and 1.40 Å for [TTF]₂²⁺, and are in accord

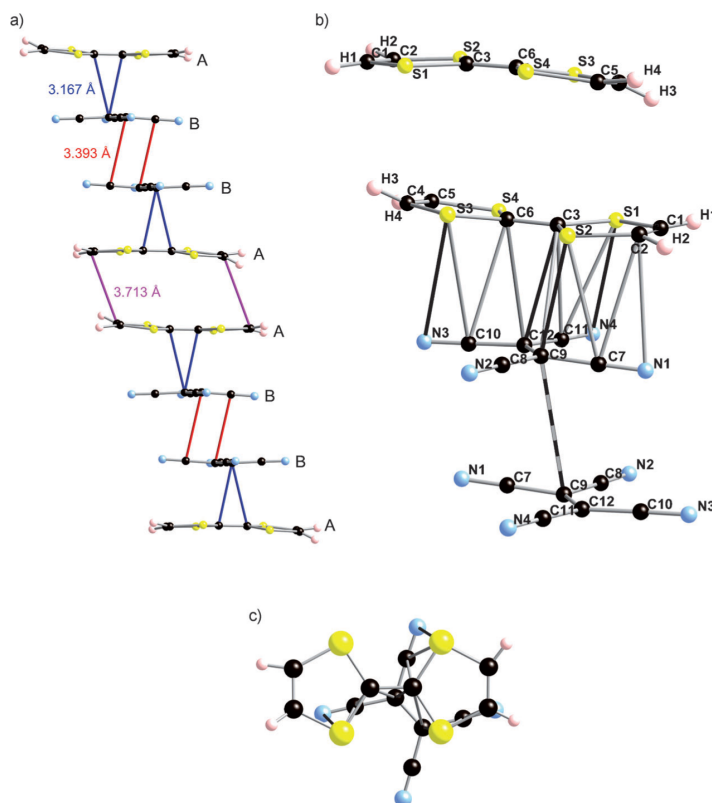


Figure 5. a) Side, b) atom-labeling, and c) normal chain views of β -[TTF][TCNE] showing the 12 TTF...TCNE interactions <3.4 Å, and the 3.48 Å-long C9–C9 TCNE...TCNE interaction (dashed line in b), see also Figure 2b). Atoms connected with bcps are connected with black lines in b) and c) (see text); one bcp exceeds 3.4 Å.

with that previously reported for $[\text{TCNE}]_2^{2-}$ and $[\text{TTF}]_2^{2+}$, and differ from what has been observed for TTF^0 , $[\text{TTF}]^{2+}$, TCNE^0 , $[\text{TCNE}]^-$, and $[\text{TCNE}]_2^{2-}$ (Table 2). (To the best of our knowledge the structure of isolated $[\text{TTF}]^-$ has yet to be reported.)

There are 17 C–C, S–S, and N–N sub van der Waals TTF...TTF and TCNE...TCNE interactions <3.4 Å (Figure 6b, Table 3). Short C–C interactions are: C9–C10 3.319, C9'–C10' 3.348, C8'–C11' 3.382 for TTF...TTF, and C2–C3 2.927, C2'–C3' 2.923, C1–C6 3.129, C4–C5 3.135, C1'–C6' 3.137, C4'–C5' 3.110 Å for TCNE...TCNE. S–S and N–N interactions <3.4 Å are: S1–S4 3.326, S1'–S4' 3.341, S2–S3 3.336, S2'–S3' 3.318, N1–N4 3.284, N2–N3 3.308, N1'–N4' 3.281, and N2'–N3' 3.275.

The presence of $[\text{TCNE}]_2^{2-}$ is also evident from its $\tilde{\nu}_{\text{CN}}$ absorptions at 2200, 2189, 2170, and 2156 cm^{-1} , which differ a bit from the 2191, 2174, 2169, and 2163 cm^{-1} absorptions observed for $[\text{MeNC}_5\text{H}_4]_2[\text{TCNE}]_2$.^[37] $[\text{TCNE}]_2^{2-}$ also has a characteristic antisymmetric combination of the intrafragment $\tilde{\nu}_{\text{CC}}$ stretches of each central C–C bond at 1362 cm^{-1} .^[1,6,8] This absorption is also present for $[\text{TTF}]_2^{2+}$ and is observed at 1355 cm^{-1} .^[13]

δ -[TTF][TCNE]: The solid-state structure of δ -[TTF][TCNE] consists of parallel 1D chains of alternating TTF and TCNE moieties in a ...ABABA-BAB... chain (Figure 7a). This is in contrast to the ...AAB-BAABBAA... chains present in each of the α and β polymorphs (Figures 4a and 5a). As noted, the central C–C bonds in these dimers are 1.385 and 1.404 Å for TTF and TCNE, respectively. The latter agrees well with the presence of $[\text{TCNE}]^-$ (cf. 1.394 Å), but is in poorer agreement with $[\text{TCNE}]_2^{2-}$ (cf. 1.435 Å), and even worse with TCNE^0 and $[\text{TCNE}]_2^{2-}$ (Table 2). The former agrees best with $[\text{TTF}]_2^{2+}$, which has the same oxidation state as $[\text{TTF}]^+$.

There are 15 C–C, C–N, C–S, and S–N sub van der Waals, intradimer, TTF...TCNE interactions <3.4 Å (Figure 7b, Table 3). The shortest interaction is S2–C9 (3.009 Å), followed by C3–C8 (3.063 Å). Other short C–C interactions (<3.4 Å) are: C2–C12 3.295, C4–C8 3.103, C3–C11 3.148, C4–C7 3.156, C3–C9 3.346, and

C4–C11 3.380 Å. N–C, S–N, and S–C interactions <3.4 Å are: N3–S1 3.178, S2–C12 3.204, S4–C7 3.294, S1–C11 3.310, N4–C2 3.312, N1–C6 3.345, and S4–N1 3.355 Å. Similarly to what was found in the α and β polymorphs, the two fragments in the π -[TTF...TCNE] dimers are slightly bent to avoid each other. The central S atoms are twisted in 3.3° relative to the plane formed by the central C–C atoms and one of the S atoms. For the TTF moieties, and similarly for the TCNE moieties, the C atoms of the CN groups twist 2.8° relative to the plane formed by the central C–C atoms and one of the cyano C atoms. Furthermore, the central C–C bond of the TCNE is twisted 64.6° relative to the central C–C bond of TTF. Hence, similar to both α - and β -[TTF][TCNE], δ -[TTF][TCNE] is best described as possessing a neutral π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] dimer, with multicenter bonding.

Thus, the shortest intermolecular distances within the chains for the α (3.1 Å C...C distance), β (3.1 Å C...C distance), and δ (3.0 Å C...C distance) polymorphs are found between A and B suggesting the presence of AB dimers. The shortest inter-AA C...C distance (between a pair of TCNE units) is 3.5, 3.4, and 3.4 Å for the α , β , and γ poly-

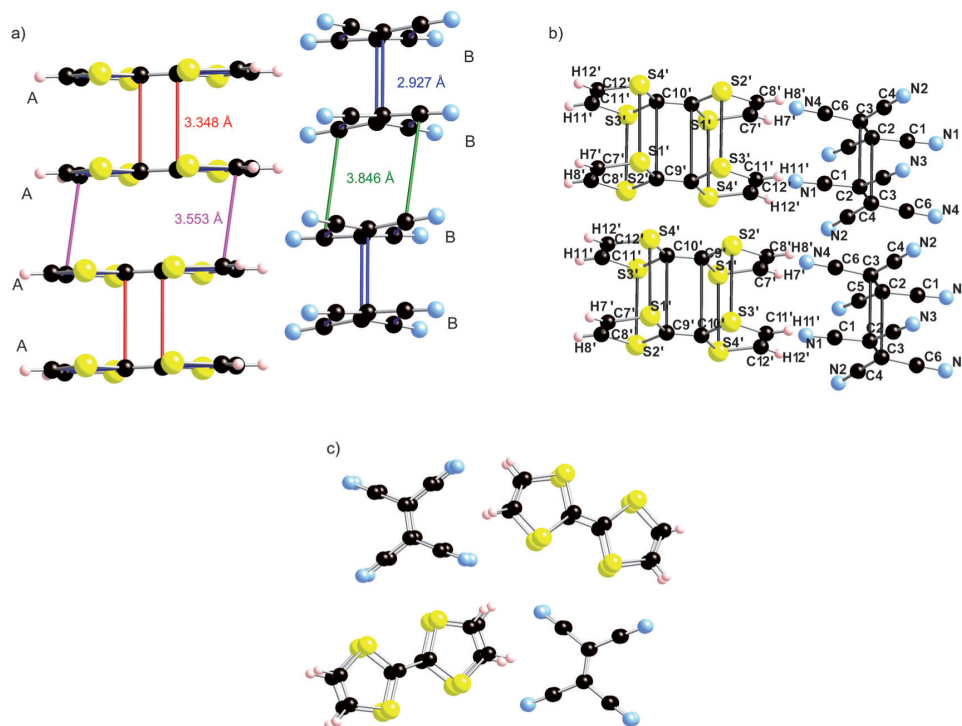


Figure 6. a) Side, b) atom-labeling, and c) normal views of γ -[TTF][TCNE] showing parallel, segregated, nonuniform, 1D chains of eclipsed centrosymmetric π -[TTF]₂²⁺ and π -[TCNE]₂²⁻ dimers. Only one crystallographically unique set of chains is shown in a).

morphs, respectively. Additionally, in the γ polymorph, the AA and BB dimers show short C...C distances of 3.3 and 2.9 Å, respectively. The shortest interdimer C...C distances are 3.6 and 3.8 Å, in the AA and BB chains, respectively.

Magnetic properties: The 250–300 K magnetic susceptibility, χ , was measured on polycrystalline samples of β - and δ -[TTF][TCNE]. Each exhibited a temperature-independent diamagnetic susceptibility. Because pure α -[TTF][TCNE] was not available, it was not measured, but due to the close structural similarity to β -[TTF][TCNE] it is assumed to also have a diamagnetic ground state. Hence, given the assignment of [TTF]⁺ and [TCNE]⁻ for each of the four polymorphs, each specie must have a $S=1/2$ doublet ground state. These doublet states must exhibit strong antiferromagnetic coupling, and bonding, such that the triplet excited state is not populated at room temperature, resulting in the diamagnetic behavior. Both of the dimers present in γ -[TTF][TCNE], that is, [TTF]₂²⁺^[13] and [TCNE]₂²⁻^[7,8] have independently shown to be diamagnetic. The magnetic properties of γ -[TTF][TCNE] are under investigation.

Bonding in β -[TTF][TCNE]: As described above, except for small changes in the geometry, based on the significant number of sub van der Waals separations, the α -, β -, and δ -[TTF][TCNE] polymorphs are presumed to possess π -

[TTF^{δ+}...TCNE^{δ-}] dimers, the optimal geometry of which is shown in Figure 8, with multicenter bonding, as evidenced by the significant number of sub van der Waals interactions. This hetero-multicenter, zwitterionic bonding is distinctly different than the homo-multicenter bonding for [TTF]₂²⁺^[7,8] and [TCNE]₂²⁻^[13]. Therefore, a detailed analysis of the nature of the bonding present in [TTF^{δ+}...TCNE^{δ-}] dimers seemed necessary, starting with those found in the β -[TTF][TCNE]. This analysis was complemented with a description of the main differences found for the α and δ polymorphs.

The MO diagram computed at the UB3LYP/6-31+G(d) level for the π -[TTF^{δ+}...TCNE^{δ-}] dimers of the β -[TTF][TCNE], based on the crystal geometry (Figure 5), is shown in Figure 9. A natural population analysis indicated that the population of the HOMO and LUMO was 2.0 and 0.0, respectively, whereas at the CASSCF(4,4) level the occupation of the four active orbitals (HOMO–1, HOMO, LUMO, and LUMO+1) is 1.90, 1.92, 0.10 and 0.08 e⁻, respectively, (the (4,4) active space is made of HOMO and LUMO of TTF and TCNE, and holds a total of four electrons), values that confirm the validity of the UB3LYP results. Therefore, the B3LYP and CASSCF(4,4) ground state is a closed-shell singlet, in good agreement with the experimental magnetic data. The lowest energy triplet state at the UB3LYP level is 22.9 kcal mol⁻¹ above the closed-shell singlet, that is, too

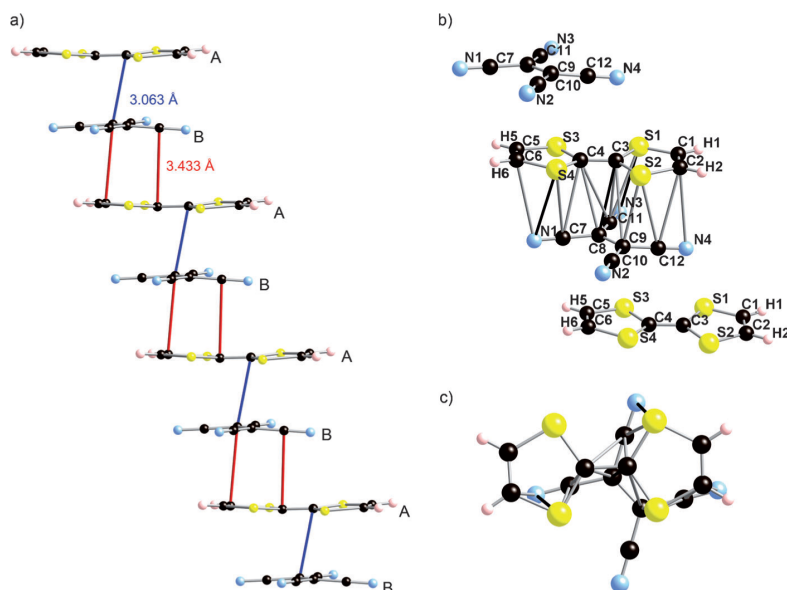


Figure 7. a) Side, b) atom-labeling, and c) normal views of π -[TTF^{δ+}...TCNE^{δ-}] dimers in δ -[TTF][TCNE] showing the 15 TTF...TCNE interactions <3.4 Å with adjacent dimers within the chains. Atoms connected with bcps are connected with black lines in b) and c) (see text).

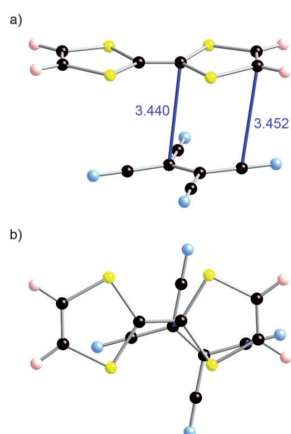


Figure 8. Optimized geometry of the π -[TTF^{δ+}...TCNE^{δ-}] dimer computed at the UB3LYP/6-31+G(d) level: a) side and b) top views. The Cartesian coordinates for the dimers and the values of the intramolecular distances are given in Table S1 and Figure S2 in the Supporting Information, respectively.

high to be thermally populated at room temperature, in accord with the magnetic data.

The MO diagram has all of the features observed for all of the previously studied long bonds, for example, π -[TTF]₂²⁺ and π -[TCNE]₂²⁻ dimers, and also found in conventional covalent C–C bonds.^[12] The HOMO for β -[TTF][TCNE] (Figure 9b,c) has orbital-overlap contributions between the [TTF]^{δ+} and [TCNE]^{δ-} moieties that are most

significant for 2c C9–S2 (atom labeling from Figure 5b) and 3c C12–C3/C6 interactions (C3 and C6 are the two atoms at which the π -bonding orbitals resides), with 3.107 and 3.167 Å separations, respectively. These separations are the shortest intra-[TTF]...[TCNE] distances for β -[TTF][TCNE] (Table 3).

A detailed analysis of the nature of the bonding can be done through an AIM analysis^[30] of all (3,–1) bcps in the electron density between bonded atoms between the [TTF]^{δ+} and [TCNE]^{δ-} moieties, for the optimum geometry, and the dimers found in α -, β -, and δ -[TTF][TCNE]. This is shown in Figure 10, and the characteristic properties of all bcps in the optimized and the β -[TTF][TCNE] dimer are collected in Table 4. The number and characteristics of their bcps varies due to small variations in

the geometry of these dimers (Table 5); this affects the way the total densities overlap.

The AIM analysis for β -[TTF][TCNE] indicates four critical points (C3–C12 (3.107 Å), C9–S2 (3.042 Å), S1–N4 (3.202 Å), and S3–N3 (3.456 Å), Figure 10d, Table 3 and Table 4). The number of bcps is less than that expected for a C_{2v} symmetry (six bcps, two C–C, and four C–S, see Figure 10b) due to the 50.7° twist of the two central C–C bonds, caused by the antibonding nature of the SOMO–SOMO overlap in the C_{2v} symmetry, the electrostatic forces, and the exchange-repulsion component, in an proportion that requires additional studies, which are out of the main focus of this work.

Also note that whereas HOMO shows a 3c C12–C3/C6 interaction, the AIM analysis only has a bcp between C12–C3. This is probably due to the lack of C_{2v} symmetry of the C12 atom position relative to the C3–C6 bond.^[38] From an AIM perspective [TTF^{δ+}...TCNE^{δ-}] can be considered as having a long, 2e⁻/8c bond with C–C, C–S, and two N–S components over the 3C, 3S, and 2N atoms. This differs from a 2e⁻/5c bond with C–S and C...C–C components over an S- and 4C-atoms description obtained from the aforementioned orbital-overlap analysis, although, as shown below, the SOMO–SOMO overlap is only one of the dominant components of the interaction (the dispersion component is the other one, and the electrostatic one is much smaller). Neither S–N bcps have significant orbital overlap, and the latter 3.456 Å S3–N3 exceeds the sum of the van der Waals radii (3.35 Å; Table 4). Thus, distances shorter than the sum of the van der Waals radii is not always a good

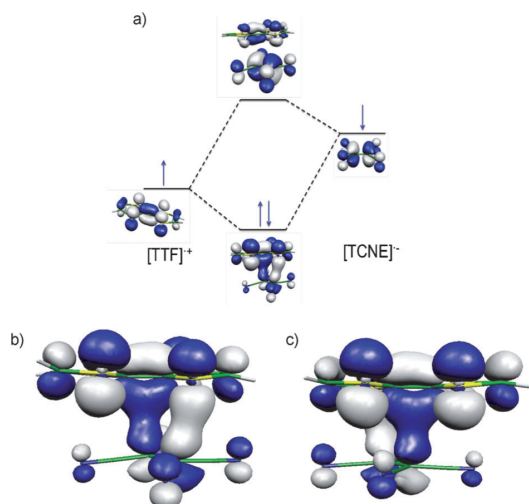


Figure 9. a) MO diagram computed at the UB3LYP/6-31+G(d) level for the π -[TTF]^{δ+}...[TCNE]^{δ-} dimers present in β -[TTF][TCNE]. Detailed b) front and c) back views of the HOMO. The MO diagrams for optimized [TTF][TCNE], α -, and δ -[TTF][TCNE] are very similar (see the Supporting Information, Figure S3, and their HOMOs and LUMOS are shown in Figure S4 and S5, respectively).

criterion to define the presence of a bonding interaction, as occurs for hydrogen bonds, by the AIM methodology.^[39] Attributing a bonding component to atoms that lack orbital overlap is counterintuitive, but has been reported for the central carbons on each 2,5,8-tri-*tert*-butylphenalenyl in di(2,5,8-tri-*tert*-butylphenalenyl) due to a node.^[12] In this case this bonding component is ascribed to dispersion forces, and this C–C separation is 3.20 Å, which is shorter than the other sub van der Waals C–C separations that are ≥ 3.30 Å.

This 3.456 Å S3–N3 bcp can be attributed to the combination of dispersion and electrostatic contributions. A detailed analysis of the impact of these components is, in any case, out of the scope of this work and will be left for future investigation. To the best of our knowledge, the ability of the AIM methodology to properly describe the properties of multicenter bonding has not been fully explored, and may be another “bonding quandry”.^[40] Finally, also note that controversy exists as to whether the existence of a (3,–1) bcp is a sufficient condition or just a necessary condition for the presence of a bond; disputes arise as to if only (3,–1) bcps associated to energetically stable interactions can be considered as bonds in the literature.^[41]

The charge distribution on the TTF and TCNE fragments (graphically depicted in Figure 11) was also analyzed with a Mulliken population analysis, which indicated that

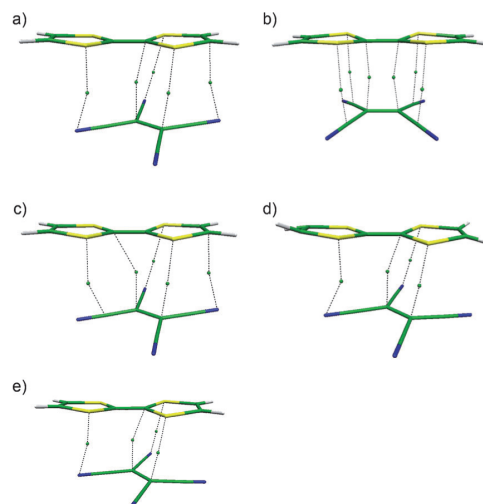


Figure 10. The bcps found in the UB3LYP/6-31+G(d) wavefunction at a) the optimum geometry of [TTF][TCNE] (five bcps with C–C, two N–S, N–C, and C–S components), b) the optimized [TTF][TCNE] imposing C_{2v} symmetry (six bcps with two C–C and four C–S components), c) the α - (five bcps with C–C, N–S, N–C, and two C–S components), d) β - (four bcps with C–C, C–S, and two N–S components), and e) δ -[TTF][TCNE] (four bcps with C–C, C–S, and two N–S components) polymorphs. The C=C...C=C dihedral angle is 136.0°.

Table 4. Properties of the four bcps that connect the two fragments of the π -[TTF]^{δ+}...[TCNE]^{δ-} dimers present for the β polymorph and the optimized [TTF][TCNE].^[a]

Atoms involved	r [Å]	Density [a.u.]	Laplacian [a.u.]
crystal geometry			
C3–C12	3.107	0.012	0.029
S3–N3	3.456	0.008	0.025
S1–N4	3.202	0.011	0.032
S2–C9	3.042	0.017	0.042
optimum UB3LYP/6-31+G(d) geometry			
C3–C12	3.440	0.007	0.015
S3–N3	3.657	0.005	0.015
S1–N4	3.521	0.006	0.017
S2–C9	3.329	0.010	0.025
C2–N1 ^[b]	3.397	0.006	0.015

[a] For each bcp, the atoms involved, the density, and the Laplacian at the critical point (both in atomic units) are noted. The atom numbering is also indicated in the top of the table (C3–C9 is the shortest interfragment C–C distance). See Figure 5b for the atom labeling. [b] This critical point appears when the crystal geometry is fully optimized (see text).

Table 5. Values of the most relevant parameters that define the relative disposition of the π -[TTF]^{δ+}...[TCNE]^{δ-} dimer, at the optimum geometry, and values found for the α , β , and δ polymorphs.

Polymorph	C12–C3 [Å]	C9–S22 [Å]	C6–C3–C12–C9 [°]	N17–C2 [Å]	C2–S21–S22–C3 [°]	C4–S24–S23–C6 [°]	S22–C3–C6–S23 [°]
optimized	3.440	3.329	–136.0	3.397	178.6	–179.6	3.0
α	3.121	3.075	–130.4	3.228	–179.5	178.9	7.4
β	3.107	3.042	–131.8	3.275	178.3	179.2	7.7
δ	3.064	3.008	–130.8	3.312	179.4	179.2	7.5

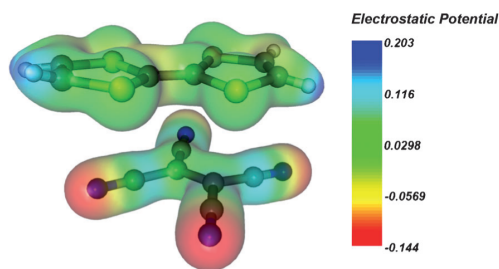


Figure 11. Computed charge distribution of π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] found for the β -[TTF][TCNE] crystal. The charge distribution is visualized by projecting the electrostatic potential onto the isosurface of 0.05 atomic units of electron density. Red regions indicate regions of negative charge, whereas blue represent regions of positive charge.

Table 6. Degree of electron transfer (ionicity) for α -, β -, γ -, and δ -[TTF][TCNE].

Polymorph	Method	z^+ , [TTF] $^{2+}$	z^- , [TCNE] $^{2-}$	Ref.
α	X-ray	0.54	-0.54	[18] ^[a]
α	IR	0.5	-0.5	[19]
α	MO Mulliken	0.5	-0.5	this work
α	ESP	0.4	-0.4	this work
β	X-ray	0.54	-0.54	[18] ^[a]
β	IR	0.5	-0.5	[18]
β	MO Mulliken	0.5	-0.5	this work
β	ESP	0.3	-0.3	this work
γ	MO Mulliken	1	-1	this work
γ	ESP	1	-1	this work
γ	X-ray	1	-1	this work ^[b]
δ	MO Mulliken	0.6	-0.6	this work
δ	ESP	0.4	-0.4	this work
δ	X-ray	0.76	-0.76	this work ^[b]

[a] Based on the C-S bond length. [b] Using the method described in reference [18].

the net charge on each fragment is $+0.53 e^-$ for TTF and $-0.53 e^-$ for TCNE (Table 6). This reflects a formal charge transfer from TTF to TCNE. The magnitude of the shift is also confirmed by computing electrostatic potential (ESP) charges fit to reproduce the ESP around the molecule by using Kollman's method,^[42] which indicated a net charge of $0.32 e^-$, in absolute value. This result is consistent that obtained from infrared spectroscopy and an analysis of the crystallographically determined bond lengths.^[18,19]

As graphically indicated in Figure 11, the net positive charge is mostly located on the H atoms of the TTF fragment, although a net positive charge is also found near the central C=C bond of the TCNE fragment. Regions of net-negative-charge localization are only found on the CN groups.

In contrast to the repulsive nature of the intrafragment interactions reported for both [TTF] $_2^{2+}$ ^[13] and [TCNE] $_2^{2-}$,^[7,8] the intrafragment interaction is attractive for the π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] dimers by $-74.7 \text{ kcal mol}^{-1}$ with respect to the [TTF] $^{2+}$ and [TCNE] $^{2-}$ fragments, and just by $-8.9 \text{ kcal mol}^{-1}$ relative to the neutral TTF and TCNE fragments, all through UB3LYP/6-31+G(d) calculations

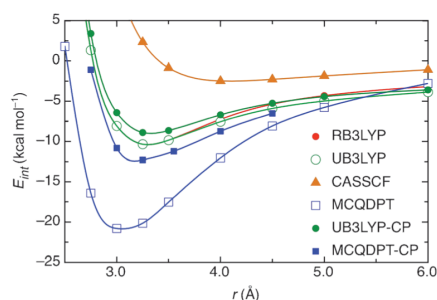


Figure 12. Potential energy curves computed at the UB3LYP/6-31+G(d) and RB3LYP levels when the two fragments of π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] are separated by stretching the shortest C-C interfragment distance (C3...C9), and maintaining the relative orientation of the dimer and the fragment geometry as occurs for β -[TTF][TCNE]. The CASSCF(4,4) and MCQDPT/CASSCF(4,4) curves computed with the 6-31+G(d) basis set are also given for comparison. The -CP curves indicate those for which the interaction energy has been counterpoise corrected.

(Figure 12). The RB3LYP- and UB3LYP-computed interaction energy curves for the dissociation of π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] into neutral TTF and TCNE is shown in Figure 12 (the small differences ($>4 \text{ \AA}$) are due to spin contamination of the UB3LYP wavefunction). MCQDPT/CASSCF(4,4) with the 6-31+G(d) basis set (the (4,4) active space was built as above) confirm the stability of the complex. The MCQDPT/CASSCF(4,4) curve is attractive by about 21 kcal mol^{-1} (BSSE not corrected value), with a minimum located at about $3.1 \text{ \AA}$, close to the experimental crystallographic value and about $0.3 \text{ \AA}$ shorter than the computed UB3LYP value, whereas the BSSE corrected MCQDPT/CASSCF(4,4) curve is attractive by $12.3 \text{ kcal mol}^{-1}$. Because a relatively small basis set was used, BSSE is overestimated, so by using a larger basis set, interaction-energy values would be between both noncorrected and corrected values.^[43] The higher stability of the MCQDPT-computed curve reflects the better description of the dispersion component of the interaction energy. A UB3LYP/6-31+G(d) full-geometry optimization of π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] confirms the stability to be the optimum geometry (Figure 8) that is similar to that observed in the crystal. A vibrational analysis confirmed the nature of the minimum in the potential energy surface.

The nature of the interaction energy in π -[TTF...TCNE] was also computed by using the same analysis as for [TCNE] $_2^{2-}$ and phenalenyl dimers,^[12] that is, the interaction energy (E_{int}) can be expressed as the sum of the exchange-repulsion (E_{er}), electrostatic (E_{ele}), dispersion (E_{disp}), and bonding (E_{bond}) components:

$$E_{\text{int}} = E_{\text{er}} + E_{\text{ele}} + E_{\text{disp}} + E_{\text{bond}} \quad (1)$$

By using the same procedure previously described,^[12] E_{bond} is $-22.9 \text{ kcal mol}^{-1}$ from the CASSCF(4,4) and from MCQDPT/CASSCF(4,4) $E_{\text{disp}} = -28.5 \text{ kcal mol}^{-1}$, $E_{\text{ele}} =$

−9.0 kcal mol^{−1} (after evaluating the Coulomb interaction by using the ESP charges for the atoms of the dimer), and $E_{\text{int}} = -21.2$ kcal mol^{−1}, by subtracting $E_{\text{er}} = +39.2$ kcal mol^{−1} in Equation (1). Thus, the dominant attractive force in the formation of the π -[TTF...TCNE] dimers are the bonding and dispersion, and the electrostatic component is less relevant, probably due to the large charge shift from π -[TTF^{δ+}...TCNE^{δ-}] for which $\delta=1$ to π -[TTF^{δ+}...TCNE^{δ-}] for which $\delta=0.5$.

The intrafragment interaction energy for π -[TTF^{δ+}...TCNE^{δ-}] is much weaker than that found for ionic bonds. For instance, the UB3LYP/6-31+G(d) interaction energy for a NaCl dimer to dissociate into Na+Cl or Na⁺+Cl[−] is −91.0 and −130.1 kcal mol^{−1}, respectively. The low value of π -[TTF^{δ+}...TCNE^{δ-}] is attributed to the previously mentioned TCNE to TTF charge transfer, which reduces the Coulombic energy with respect to NaCl. This can be shown by comparing the UB3LYP/6-31+G(d) potential-energy curves for π -[TTF^{δ+}...TCNE^{δ-}] and NaCl with the Coulomb potential energy, $E_{\text{Coul}} = q_i q_j / (4\pi\epsilon_0 r_{ij})$, for various values of the net charge (q_i) (Figure 13). Above the minimum, the UB3LYP curve for the dissociation of NaCl into Na⁺ and Cl[−] is nearly identical to the Coulomb potential for two fragments that have net charges of +1 and −1. However,

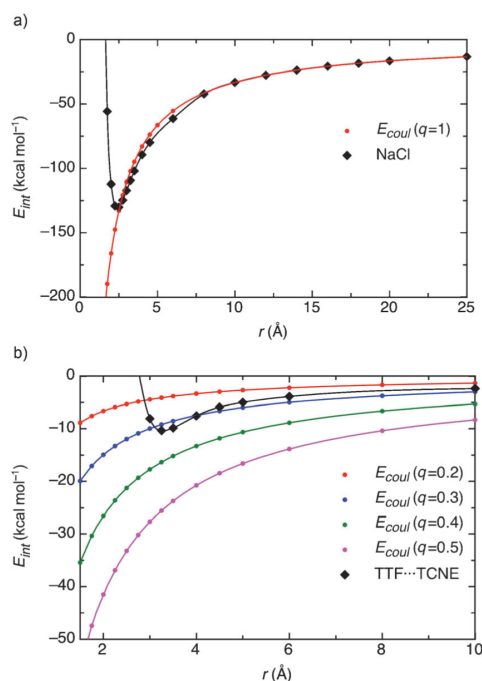


Figure 13. a) Potential-energy curve for a NaCl dimer computed at the UB3LYP/6-31+G(d) level, and (1+)...(1−) Coulomb potential-energy curve. b) Potential-energy curve of the π -[TTF^{δ+}...TCNE^{δ-}] dimer computed at the UB3LYP/6-31+G(d) level, and the $q_i = 0.5, 0.4, 0.3$, and 0.2 Coulomb potential-energy curves. The Coulomb potential-energy curves were computed by substituting q_i and q_j by the net charge in $E_{\text{Coul}} = q_i q_j / (4\pi\epsilon_0 r_{ij})$.

the π -[TTF^{δ+}...TCNE^{δ-}] curve, above its minimum, is close to the (+0.3)...(−0.3) curve (note that this curve is much less stable than the (+1)...(−1) curve).

It is also interesting to investigate computationally the reasons for the lack of formation of a classical covalent C–C bond for these TTF...TCNE dimers. UB3LYP/6-31+G(d) calculations show that two sigma dimers at a C–C distance of about 1.6 Å (Figure 14a) are stable. However, their

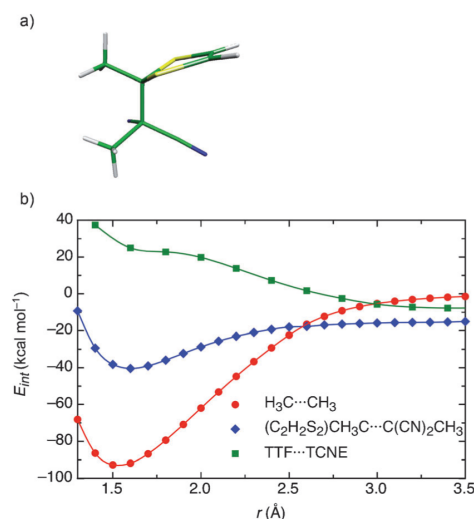


Figure 14. a) Geometry of (C₂H₂S₂)CH₃C and C(CN)₂CH₃ fragments used in the computation of the interaction energy, and b) potential-energy curves computed at the UB3LYP/6-31+G(d) level, for the interaction of two CH₃ fragments, a TTF and a TCNE fragment, and a (C₂H₂S₂)CH₃C and a C(CN)₂CH₃ fragment.

energy is 23 and 33 kcal mol^{−1} higher than that for the π conformation. This explains why these dimers are not spontaneously formed. The reason is attributed to the overlap between the non-bonding pairs of electrons of the CN and S atoms. This is seen by comparing the UB3LYP/6-31+G(d) potential-energy curves for the C–C separation in ethane (Figure 14b), a substituted ethane designed to mimic the local environment found in the σ -[TTF...TCNE] dimers (Figure 14b), and a [TTF...TCNE] dimer. Whereas the curve for ethane has a minimum with σ symmetry at 1.532 Å with an energy of −93.1 kcal mol^{−1}, and that for the substituted ethane has a minimum with σ symmetry at 1.601 Å and −40.4 kcal mol^{−1}, and a shoulder at the position of the π dimer due to the CN... (five-membered ring) interaction complemented by a C–H...S hydrogen bond. The [TTF...TCNE] dimer does not have a minimum at 1.6 Å, only a small bump in this region, and its only minimum is located at 3.440 Å, with an interaction energy of −7.8 kcal mol^{−1} (a weaker value than the MCQDPT/CASSCF(4,4) result reported above, due to the lack of proper accounting of the dispersion, in contrast to the B3LYP method). The instability of the σ -[TTF...TCNE] conformations can be attrib-

uted to the cost of bending the central C–C bonds and to larger steric effects.

The stability of the π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] is also in accord with the computational results of full-geometry optimization. The optimum UB3LYP/6-31+G(d) geometry (Figure 8) is similar to that observed in the crystal, although the shortest interfragment C...C distance of 3.440 Å is slightly longer than the 3.167 Å found in the β phase. The central C–C twist of the two bonds in the optimum geometry is 135.7°, but 50.7° in the β polymorph. A vibrational analysis confirmed the nature of the minimum in the potential energy surface.

The nature of π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] dimers in the stacks: As mentioned above, β -[TTF][TCNE] possesses π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] dimers that are not isolated, but stacked, forming ...ABBAABBA... chains and affecting the electronic structure of nearby AB or BA dimers, and an isolated AB dimer was evaluated.

The key point of interest is whether the electronic structure of two adjacent π -AB dimers, that is, ABAB in β -[TTF][TCNE] can be considered as two nearly independent A–B complexes or, instead, should be considered as an ABBA aggregate. This question was resolved by analyzing the electronic structure of the ground state for an ABBA aggregate (at the geometry present in the β polymorph) and comparing such a structure with that expected for A–B...B–A and A...B–B...A complexes. (This study could also have been done by making a similar comparison for the electronic structure of BAAB, but we choose ABBA to do the analysis.)

The MO diagram for the A–B...B–A complex, that is, for the interaction of two weakly interacting AB radicals in ABBA is qualitatively depicted in Figure S6 in the Supporting Information. The diagram assumes that the AB overlap is stronger than the BB overlap, as is the case in the β phase, due to the larger separation between BB than AB. The relative orientation of the two AB dimers is a consequence of all intermolecular interactions, and particularly of the dominant electrostatic interactions. This diagram can be compared with that predicted for an A...B–B...A complex (see the Supporting Information, Figure S7), which can be generated similarly to that of Figure S6 in the Supporting Information, but assuming that the AB overlap is weaker than the BB overlap and so are the orbital splittings. The main difference between the A–B...B–A and A...B–B...A diagrams is found in the nature of the HOMO orbital, as a crossing is produced in Figure S6 relative to Figure S7 between the AB(antibonding)+AB(antibonding) and AB(bonding)–AB(bonding) orbitals in the two diagrams.

The MO diagram computed at the UB3LYP/6-31+G(d) level for the singlet ground state of the ABBA aggregate present in β -[TTF][TCNE] is shown in Figure 15. When compared with those of Figure S6 and S7 in the Supporting Information, it is clear that the diagram closely resembles that shown in Figure S6, that is, the ABBA aggregate has an AB...BA type electronic structure. This conclusion is rein-

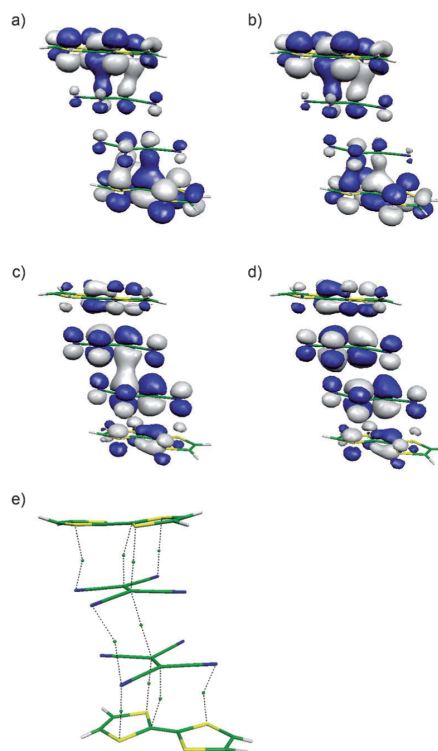


Figure 15. a) HOMO–1, b) HOMO, c) LUMO, and d) LUMO+1 molecular orbitals of an ABBA aggregate found in β -[TTF][TCNE], and e) ten bcps found in the wavefunction of the ABBA aggregate, computed at the UB3LYP/6-31+G4 level, connecting each AB pair and two that connect the BB pair.

forced by the bcps of the ABBA aggregate (Figure 15e and Table 4), as each AB dimer in ABBA presents the same four bcps found in an isolated AB dimer. The ABBA aggregate also presents two B...B bcps connecting the TCNE fragments. Note, however, that 1) the AB...BA interaction is repulsive by 6.8 kcal mol $^{-1}$ (UB3LYP/6-31+G(d)) and, consequently, there is no bond between the AB and the BA dimers (the aggregate in a crystal arises from interaction of the aggregate with nearby surrounding ions)^[44], and 2) the B...B overlap just produces a minor change in the MO diagram of the isolated AB dimer (Figure S7 in the Supporting Information). Therefore, the bcp analysis quantitatively confirms that the electronic structure of the ABBA complex (and thus, its electronic spectra) can be properly described by using isolated AB dimers.

Bonding in α - and δ -[TTF][TCNE]: The intradimer bonding for α - and δ -[TTF][TCNE] is essentially identical to that discussed for β -[TTF][TCNE], because the same π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] dimers found in β -[TTF][TCNE] are observed for α - and δ -[TTF][TCNE]. The interaction energy of the π -[TTF...TCNE] dimer is attractive by –8.8 kcal mol $^{-1}$

for both the α and δ polymorphs, for the dissociation in its neutral fragments, and by -72.0 and -72.8 kcal mol⁻¹ for dissociation into [TTF]²⁺ and [TCNE]²⁻. The MO diagrams for α - and δ -[TTF][TCNE] (Figure S3 in the Supporting Information) are nearly identical to those shown in Figure 9. However, the bcps found in the AIM analysis (Figure 10c and e) differ from those found in the β polymorph, as the α polymorph shows five bcps with C–C, N–S, N–C, and two C–S components, and β - and δ -[TTF][TCNE] each have four bcps with C–C, C–S, and two N–S components. Therefore, long, multicenter bonding occurs in the π -[TTF^{δ+}...TCNE^{δ-}] dimer found in the α and δ polymorphs. However, whereas the multicenter bond is $2e^-/8c$ for the β and δ polymorph, it is a $2e^-/10c$ (Figure 10c) for α -[TTF]-[TCNE].

The AB dimers in α -, β -, and δ -[TTF][TCNE] also exhibit a significant charge transfer from TCNE to TTF, that is, π -[TTF^{δ+}...TCNE^{δ-}]. The absolute value of the net charge on each fragment is 0.5 from a Mulliken analysis, and 0.4 according to an ESP calculation for the α polymorph, 0.5 and 0.3 for the β polymorph, and 0.6 and 0.4, respectively, for the δ polymorph (Table 6). The charge transfer is in accord with a lower interaction energy than that for NaCl dimers, and is -8.8 kcal mol⁻¹ in α - and δ -[TTF][TCNE] for neutral dissociation.

To complete the study of the π -[TTF...TCNE] dimers in the δ polymorph, the influence on the electronic structure of AB dimers induced by the presence of adjacent AB dimers placed in an ABAB sequence, instead of the ABBA sequence found in the β polymorph, was investigated. Hence, the electronic properties of an ABAB aggregate found in δ -[TTF][TCNE] (Figure 16) are similar to those for an ABBA aggregate found in β -[TTF][TCNE]. This is validated by comparing the bcp properties of an isolated AB aggregate in δ -[TTF][TCNE] (Table S2 in the Supporting Information) to an ABBA aggregate (Table S3 in the Supporting Information), and 1) the number of bcps of the ABAB aggregate are twice those found in isolated AB dimers, plus three interfragment points, and b) the density and Laplacian of these points are similar.

Finally, note that the ABAB aggregate is also unstable with respect to dissociation into two AB dimers by 1.0 kcal mol⁻¹, and, therefore, the existence in crystals is a consequence of the net attractive nature of interactions with nearby dimers.

Bonding in γ -[TTF][TCNE]: The packing motif present in γ -[TTF][TCNE] (Figure 6) consists of segregated chains of [TTF]₂²⁺ and [TCNE]₂²⁻ dimers, and hence differs significantly from the π -[TTF...TCNE] dimers found in α , β , and δ polymorphs (Figure 4 5, and 7). Note that the dimers of one chain are slightly interlocked with those of the adjacent chain (Figure 6) enabling efficient σ - σ , σ - π and π - π orbital overlap.

The structure and bonding of both [TTF]₂²⁺[13] and [TCNE]₂²⁻[6–11] dimers has been reported to have $2e^-/10c$, and $2e^-/4c$ bonds, respectively; however, this is the first

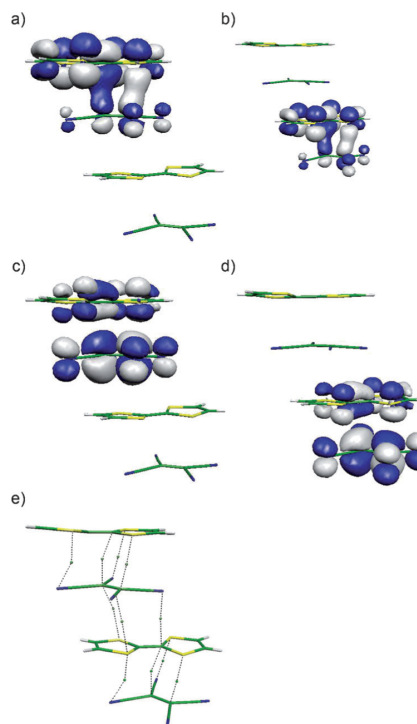


Figure 16. a) HOMO–1, b) HOMO, c) LUMO, and d) LUMO+1 molecular orbitals of an ABAB aggregate found in the δ phase, and e) nine bcps found in the wavefunction of the ABAB aggregate computed at the UB3LYP/6-31 + G(d) level.

structure possessing two types of π -dimers with long multicenter bonding. Hence, γ -[TTF][TCNE] is best formulated as [TTF]₂²⁺[TCNE]₂²⁻, that is, an AABB aggregate.

As a consequence of the shape of the SOMO1 and SOMO2 orbitals there is an important charge transfer from the [TCNE]₂²⁻ dimers into the [TTF]₂²⁺ dimers of $0.8 e^-$ (the shift is similar in Mulliken and ESP charge calculations). This shift is also observed in AB pairs placed at the same geometrical disposition as they have in the AABB aggregate. Such a charge shift has never been observed before in any other crystals of [TTF]₂²⁺[13] or [TCNE]₂²⁻[7,8] dimers and is thus a characteristic of the electronic structure of the AABB dimers.

The interaction energy of AABB with respect to dissociation into two double-charged [AA]²⁺ and a [BB]²⁻ is -242.1 kcal mol⁻¹. This is about three times the energy of the dissociation of an AB dimer into the ionic fragments and explains why the four TTF...TCNE interactions are present within each AABB aggregate. Dissociating the four constituent fragments in the neutral state requires 2.8 kcal mol⁻¹, whereas dissociation into two isolated [TTF]²⁺ and two isolated [TCNE]²⁻ fragments requires 43 times more energy (120.0 kcal mol⁻¹). Further computational and experimental studies are in progress.

Conclusion

The original assignment that α - and β -[TTF][TCNE] possesses [TCNE]₂²⁻ dimers with L_c orientation (Figure 2) has been revised, as this structural arrangement is reformulated to have only multicenter intradimers between TTF and TCNE moieties, that is, π -[TTF]^{δ+}[TCNE]^{δ-}. Likewise, a new polymorph, δ -[TTF][TCNE], also can be described as π -[TTF]^{δ+}[TCNE]^{δ-}. These zwitterionic heterodimers are diamagnetic, and exhibit an approximate transfer of 0.5 e⁻ (δ) from the TTF to the TCNE fragments, and are better described as [TTF^{δ+}...TCNE^{δ-}] ($\delta \approx 0.5$). This is observed from experimental studies, and agrees with theoretical predictions. The interfragment C...C distances are <3.4 Å and an interaction energy of -21.2 kcal mol⁻¹, which is typical of long, multicenter bonds. [TTF]^{δ+}[TCNE]^{δ-} has a reduced stability with respect to Na⁺Cl⁻ due to the partial, not full, electron transfer that reduces the electrostatic component of the bonding. This reduced electrostatic component and the large interfragment-dispersion interactions stabilize the long-bond formation.

The long, zwitterionic, hetero-multicenter bonding present in the α , β , and δ polymorphs of [TTF]^{δ+}[TCNE]^{δ-} has five, four, and four bcps, respectively, and thus always involves two electrons with ten, eight, and eight bonding atoms for these polymorphs, respectively (Table 7). These involve C-C, C-S, N-S, and sometimes C-N components. Optimized [TTF][TCNE], similarly to α -[TTF][TCNE], has five bcps, but some differ (Table 7) and whereas the observed structure has 13 sub van der Waals contacts shorter than 3.40 Å, the optimized structure has only two. These phases have small geometrical differences that lead to either the disappearance or appearance of bcps components. This indicates that these are not robust, and it is best to consider the average of the similar optimized and observed structures of the α -, β -, and δ -[TTF][TCNE] polymorphs, as well as the very similar bonding overlaps present in the respective HOMOs (Figure 9a, Figure S3 in the Supporting Information). The most pronounced overlaps for each of these HOMOs are virtually identical, and have a 2c C_{TCNE}-S_{TTF} and a 3c C_{TCNE}-(C_{TTF}-C_{TTF}) components; thus, they present a 2e⁻/5c intra-[TTF]^{δ+}[TCNE]^{δ-} bond, and this best describes the bonding.

In contrast, the γ -[TTF][TCNE] polymorph possesses long, homo-multicenter [TTF]₂^{2+ [13]} cationic⁺...cationic⁺ and

[TCNE]₂^{2- [6-8]} anionic⁻...anionic⁻ bonding, as previously reported.

Finally, it is interesting to compare [TTF][TCNE] to [TTF][TCNQ], which forms uniform 1D chains and exhibits high metal-like conductivity.^[32] TCNE is a slightly poorer electron acceptor^[31] and the spin distribution of its radical anion is more localized; hence, [TTF][TCNE] does not form uniform 1D chains exhibiting high metal-like conductivity, and forms nonconductive, diamagnetic heterodimers possessing multicenter interactions.

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Table 7. Summary of the bcps components to the bonding of α -, β -, γ -, δ -[TTF][TCNE], [TTF]₂²⁺, and [TCNE]₂²⁻.

Compound	Contacts <3.4 Å	Orbital overlap components	Number of bcps	Type of bcps	Figure
[TTF][TCNE] optimized	2 ^[a]	2c+3c	5	C-C, C-S, N-C, 2×N-S	8, 10a
α -[TTF][TCNE]	13	2c+3c	5	C-C, 2×C-S, N-C, N-S	4, 10d
β -[TTF][TCNE]	12	2c+3c	4	C-C, C-S, +2×N-S	5, 10e
δ -[TTF][TCNE]	15	2c+3c	4	C-C, C-S, 2×N-S	7, 10f
[TTF] ₂ ^{2+ [13]}		6×2c	8	4×C-C, 4×S-S	6
[TCNE] ₂ ^{2- [7,8]}	10	2×2c	2	2×C-C	1 (top), 6

[a] This number is much smaller than that detected experimentally because the DFT method tend to separate the fragments more than the experimental geometry, due to its well-known failure to properly describe the dispersion component.

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3.6. Summary

Fundamental aspects of long, multicenter bonding were the focus of this chapter. The nature of this bonding type was thoroughly analyzed in the gas phase. The CASSCF/RASSCF description of the π -[TCNE] $_2^{2-}$ and π -[TCNP] $_2^{2-}$ dimers shows that although the wavefunction is qualitatively well described by the minimal (2,2) active space, the direct π -space has to be included to obtain quantitative energies. Furthermore, the full π -space parallel to the bonding axis has also to be included in order to quantitatively describe the dissociation process. Density functionals also provide a qualitatively good description of long, multicenter bonding whenever dispersion terms are included. This is in accordance with the interaction energy decompositions performed on the π -[TCNB] $_2^{2-}$ and π -[TCNP] $_2^{2-}$ dimers, which reveal the dispersion as the main stabilizing term (although not the ultimately dominant, which is the repulsive electrostatic term).

In addition to the gas phase analyses, the behavior of π -[TCNE] $_2^{2-}$ in solution was also exhaustively analyzed. The MD simulations showed that cations are not essential in the stabilization of the π -[TCNE] $_2^{2-}$ in a CH₂Cl₂ solution. These simulations also unveiled that the dimer preserves its geometry in solution, presenting only small fluctuations and being almost identical than in the solid state. The first solvation shell of π -[TCNE] $_2^{2-}$ is composed by 20 CH₂Cl₂ molecules. Among them, 8 molecules are mainly responsible for the dimer's stabilization. CH₂Cl₂ molecules stabilize the π -[TCNE] $_2^{2-}$ principally through N $\cdots$ H contacts. The free energy profile shows that at 175 K the dimer is stable by -5.5 kcal·mol⁻¹, with an energetic barrier toward dissociation of 9.6 kcal·mol⁻¹.

The analysis of the reported crystal structures presenting π -[TCNP] $_2^{2-}$ or π -[TCNB] $_2^{2-}$ dimers showed that the rationalization of their relative orientation by no means can be deduced from calculations on the isolated dimer. Instead, the addition of two point charges (modeled by K⁺ cations) exhibits a great dependence of the dimer's preferred orientation with the relative orientation of the K⁺, arising the prominence of electrostatic interactions in this bonding type.

Finally, the study of the four polymorphs of [TTF][TCNE] discarded the existence of parallel displaced π -[TCNE] $_2^{2-}$ dimers (the so-called L_c orientation), as previously suggested. In contrast, the α - and β -polymorphs were reformulated as stacks of π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] entities. This long, multicenter bonded π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] does not collapse forming a σ -bond due to the high exchange-repulsion term of the interaction energy, albeit the attractive nature between the fragments. It is worth mentioning that B3LYP can reproduce MCQDPT results concerning this bonding type, due to its intrinsically stable nature.

CHAPTER FOUR

Room-temperature long, multicenter bonding

4.1. Introduction

In the previous chapter it has been evidenced how weak long, multicenter bonded dimers between radical ions are in solution. The MD simulations of π -[TCNE] $_2^{2-}$ in a dichloromethane solution showed that the dimer dissociates at room temperature and it can only be preserved at low temperature solutions. Despite this general behavior, there are some exceptional cases where π -dimers still preserve at room temperature. This extraordinary stabilization is obtained in two categories: oligomeric donors or acceptors and supramolecular aggregations.

As outlined in chapter 1, a large investigation on π -dimerization of oligothiophenes emerged during the 90s concerning alternative routes to explain electrical conductivity in polymers.¹ Oligothiophenes of different lengths and with different substituents were synthesized and challenged to dimerize in various conditions (solvent, temperature, concentration). In the course of such quest, some authors realized that larger conjugated systems induce higher stabilization and thus these π -dimers ultimately dissociate at higher temperatures.^{2,3} Long alkylic chains in terminal positions also induce stabilization, whereas substitution of the central monomeric units dramatically decreases the π -dimer's stability.^{2,4} As a consequence of such stabilization, long, multicenter dimers of oligothiophene radical cations are preserved even at room temperature in some cases.^{3,5} Oligopyrrole radical cations have also been synthesized and observed to exhibit this behavior.⁶⁻⁸ Recently, oligothiienoacenes (i.e., oligothiophenes with complete ring fusion) are being intensively studied for electronic applications due to their rigid planar structure,⁹ and they have also been found to form π -dimers preserved at room temperature.¹⁰

The second family of compounds that permit to maintain long, multicenter bonded dimers in solution at room temperature involves supramolecular aggregates. The first example where π -dimerization ever manifested via supramolecular aggregation was the formation of a host-guest complex between a TTF derivative and a cucurbit[8]uril (CB[8]), Figure 4.1.¹¹ CB[8] is a macrocyclic compound well-known to stabilize the inclusion of neutral and positively charged molecules in its cavity.¹² The EPR signal given by [TTF] $^{+}$ radical cations completely vanishes upon the addition of CB[8] at room temperature, thus evidencing that stabilization induced by the host-guest complex formation is remarkably enough to have the equilibrium mostly shifted to the π -dimer formation.

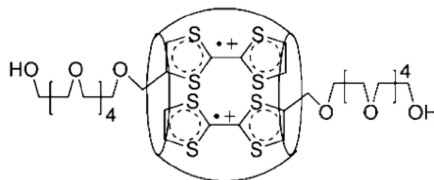


Figure 4.1. Schematic representation of a functionalized π -[R-TTF] $_2^{2+}$ dimer included in the cavity of a CB[8], according to ref. 11.

Subsequently, long, multicenter bonded dimers of oxidized TTF, oligothiophenes, and 4,4'-bipyridinium (BIPY) derivatives were characterized in several supramolecular aggregates. These aggregates involve calix[4]arenes,^{13,14} molecular clips,¹⁵ [n]rotaxanes,¹⁶⁻¹⁹ and [n]catenanes²⁰⁻²³ (Figure 4.2). Although the cases involving calix[4]arenes are intramolecular bond formation (and thus not due to supramolecular aggregation), they have been grouped in this category due to their similarity to the other compounds. Oxidized TTF-functionalized molecular clips can self-

aggregate leading to (molecular clip)₂ dimers where four [TTF]^{•+} are cofacially oriented, which form two diamagnetic π -[TTF]₂²⁺ dimers. Mechanically-interlocked molecular complexes such as [n]rotaxanes and [n]catenanes (and even a [3]rotacatenane)²⁴ also permit the formation long, multicenter bonded dimers in solution at room temperature. This fact arises when TTF or BIPY are considered as building blocks of at least two of the moieties that form the interlocked complex and both are mono-oxidized. In particular, it was found that π -dimerization is reversible in such complexes upon redox processes, being able to achieve different conformations.^{17,24} Given their novelty, these complexes were suggested as promising candidates for their potential application in molecular recognition processes and molecular switches.²⁵

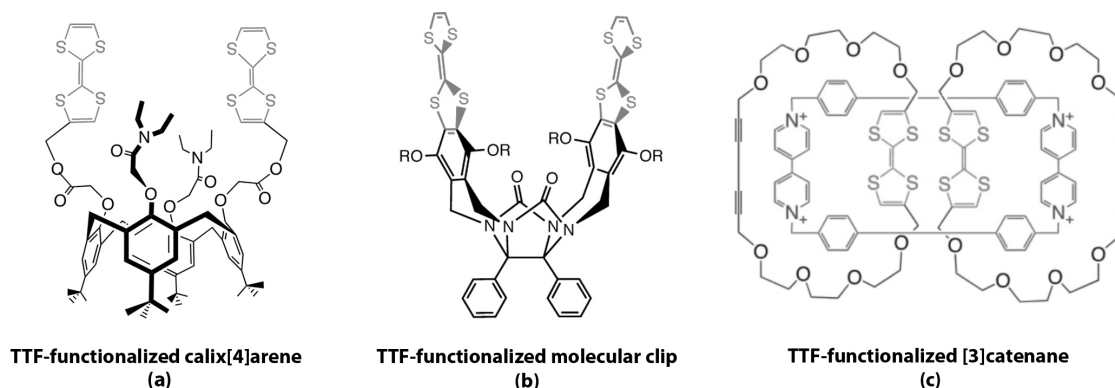


Figure 4.2. Examples of reported supramolecular aggregates that form long, multicenter bonding at room temperature.

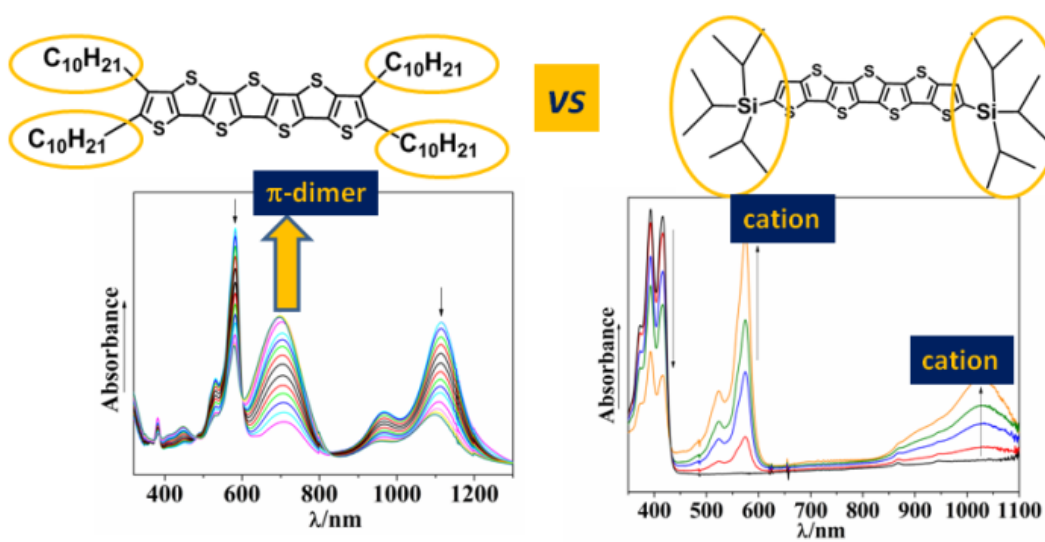
The present chapter focuses in the analysis of some examples of both categories of room temperature long, multicenter bonding. The dimerization of oxidized α,β -substituted heptathienoacene, [D4T7]^{•+} is investigated, as well as the effect of adding bulky substituents. Furthermore, the room-temperature formation of π -[TTF]₂²⁺ involving its inclusion in the cavity of a CB[8], and being considered as a building block of a molecular clip and a [3]catenane are also carefully studied.

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4.2. Publication 5

Substituent and Counterion Effect on the Formation of π -Dimers Dications of End-Capped Heptathienoacenes

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COMMUNICATION

Substituent and counterion effects on the formation of π -dimer dications of end-capped heptathienoacenes^{†‡}Cristina Capel Ferrón,^a M. Carmen Ruiz Delgado,^a Víctor Hernández,^a
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We have investigated the impact of the functionalization and the chemical nature of counterions on the π -dimer dications formation in two end-capped heptathienoacenes. Radical cations of an α -substituted heptathienoacene with triisopropylsilyl groups do not π -dimerize, while those of an α,β -substituted heptathienoacene with four *n*-decyl side chains show a high propensity toward π -dimerization, increased by PF_6^- counterions.

Organic semiconducting materials are attractive for application in electronic devices, due to many fundamental advantages over their inorganic counterparts in achieving low-cost and mechanically flexible electronics.¹ Thienoacenes, *i.e.*, oligothiophenes with completed ring fusion, are of particular interest due to their fully planar structure avoiding conformational disorder. However, the structural rigidity of these molecules leads to their lower solubility compared to the α -linked derivatives. To solve this problem, some synthetic strategies have been reported in the literature over the past few years, which incorporate the solubilizing triisopropylsilyl (TIPS) or *n*-decyl substituents in the α and/or β terminal positions of the oligothiophenyl backbones.^{2–4} The end-capping strategy leads to increased solubility and hindered irreversible polymerization under oxidative conditions. On the other hand, the attached bulky groups may cause steric interactions preventing a sizeable π -orbital overlap (dimerization) between the oxidized thienoacene chains. The close intermolecular contacts are, however,

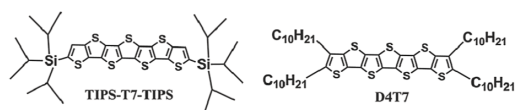


Chart 1 Chemical structure of TIPS-T7-TIPS and D4T7.

highly desirable in order to achieve a good p-type charge carrier mobility.⁵

For oligothiophenes, the reversible π -dimerization of the radical cations can conveniently be controlled by the attachment of bulky substituents in the β -positions at the inner rings.^{6–8} On the other hand, oxidized oligothiophenes with the substituents attached exclusively in the terminal α -positions tend to form π -bound dimers regardless of the diversity of the substituents employed, particularly at low temperature or in polar solvents like acetonitrile.^{7,9,10,11} The formation of a polaron-pair structure in an oxidized cyclic oligothiophene has also been recently investigated.¹²

In this work, we report on two different α - and α,β -substituted heptathienoacenes, the fully fused analogues of α -quinquethiophene, prepared with two TIPS and four *n*-decyl solubilizing side groups and referred to as **TIPS-T7-TIPS** and **D4T7**, respectively (see Chart 1). We have carried out a comparative experimental and theoretical study of the impact of the different functionalization on their electrochemical and spectroelectrochemical behaviour. The UV-Vis-NIR data for one-electron-oxidized **TIPS-T7-TIPS** and **D4T7** collected in the course of the *in situ* spectroelectrochemical monitoring and chemical doping with the thianthrenium radical cation PF_6^- salt (TAPF_6) are reported and compared.

A conventional cyclic voltammogram of **TIPS-T7-TIPS** in dichloromethane shows two reversible anodic waves at $E^0 = +0.58$ and $+0.99$ V vs. Ag/Ag^+ (see ESI[†]), revealing a significant stability of the corresponding single chain radical cation and dication. Fig. 1 displays the UV-Vis-NIR spectral changes recorded in the course of the $1e^-$ oxidation of **TIPS-T7-TIPS** within an OTTE cell in the presence of a large excess of the Bu_4NPF_6 electrolyte (Fig. 1b) and upon the stepwise addition of TAPF_6 (Fig. 1a). In both cases, two sharp and well resolved composed peaks emerged at 572 and 1039 nm, being associated with gradual formation of the isolated radical cations of this sterically hindered heptathienoacene.¹³

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[†] In Memoriam of Prof. Dr Rafael Suau (1945–2010).

[‡] Electronic supplementary information (ESI) available: Additional experimental data (cyclic voltammograms), topologies of the frontiers MO's of **D4T7** and **TIPS-T7-TIPS** and π -dimer dication of **D4T7**, side and top views of selected optimum structures of the π -dimer dication, calculated vertical one-electron excitations of **D4T7**^{•+} and **[D4T7^{•+}]₂(CH₂Cl₂)₈** and **[D4T7^{•+}]₂(PF₆[−])₂** aggregates as well as experimental and computational details. See DOI: 10.1039/c1cc14566e

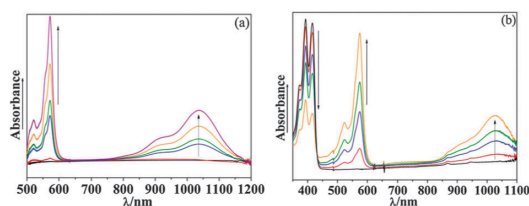


Fig. 1 UV-Vis-NIR spectral changes at room temperature accompanying $1e^-$ oxidation of **TIPS-T7-TIPS** with TAPF_6 in pure dichloromethane (a) and within an OTTE cell in dichloromethane containing 0.1 M Bu_4NPF_6 (b).

Thus, the bulky TIPS end groups hinder the π -dimerization of the radical cations, which was not observed under the experimental conditions employed in this study. A similar situation was found for the corresponding TIPS-T5-TIPS pentathienoacene derivative.¹⁴

The α,β -*n*-decyl-substituted **D4T7** shows only a single reversible anodic wave at $E^0 = +0.45$ V vs. Ag/Ag^+ , i.e., shifted to a lower energy by -0.13 eV compared to **TIPS-T7-TIPS**, most likely due to a positive inductive effect caused by the four *n*-decyl side chains. This result is consistent with the destabilization of the HOMO when going from **TIPS-T7-TIPS** (-4.60 eV) to **D4T7** (-4.35 eV), see ESI.† Fig. 2a–c displays the UV-Vis-NIR spectra of **D4T7** recorded *in situ* during the stepwise chemical oxidation with TAPF_6 .

From the early stages, the UV-Vis absorption of the parent neutral species progressively vanished in time (with a clear isosbestic point at ca. 430 nm) and two characteristic subgap absorptions due to the isolated radical cations appeared at 582 and 1116 nm (see Fig. 2a), i.e., at a slightly lower energy compared to the radical cation of **TIPS-T7-TIPS** (see above). At the same time, during the addition of the solution of TAPF_6 to the solution of **D4T7** in CH_2Cl_2 at rt, we also observed the progressive appearance of a third broad and structureless subgap absorption at ca. 700 nm, which is indicative of the formation of the corresponding π -dimer dication, see Fig. 2a and b. Note in this regard that the π -dimer dication in an α -substituted pentathienoacene with trimethylsilyl groups, **TMS-T5-TMS**, has been previously ascribed to a similar absorption at 596 nm.¹⁴ In the presence of a high excess of Bu_4NPF_6 , however, the broad absorption due to the π -dimer dication rapidly gains up in intensity relative to the Vis-NIR subgap peaks due to the isolated radical cation at 582 and 1116 nm (see Fig. 2c). This observation clearly reveals that a high excess of PF_6^- counterions facilitates the coupling between the radical cations of **D4T7**, thus promoting the formation of π -dimer dications at room temperature. Similar enhancements due to counterion effects were previously reported.¹⁵ Fig. 2d shows the evolution of the UV-Vis-NIR spectrum of **D4T7** during its potential-step electrochemical oxidation in the presence of a high excess of Bu_4NPF_6 at a low concentration of **D4T7** (around 10^{-5} M, comparable with the chemical doping, Fig. 2a–c) in a thin-layer (ca. 0.2 mm) OTTE cell (see Experimental, ESI.†). In this case, similar to Fig. 2c, the π -dimer was formed from the very beginning of the monitoring sequence, as evidenced by the progressive upsurge of the main visible absorption band at ca. 650 nm. This π -dimerization process is fully reversible as the back reduction

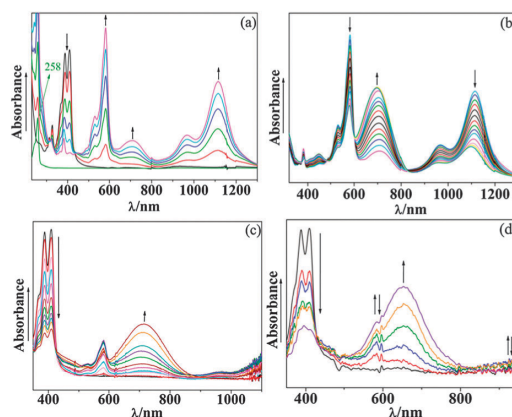


Fig. 2 UV-Vis-NIR spectral changes recorded in the course of the $1e^-$ oxidation of **D4T7** with 1 equiv. TAPF_6 in pure dichloromethane at room temperature, leading in the early stages to the main formation of isolated **D4T7** $^{+\bullet}$ together with a small fraction of π -dimer dications (a), during the subsequent conversion of **D4T7** $^{+\bullet}$ into π -dimer dications (b), and the same experiment but conducted in dichloromethane containing 0.1 M Bu_4NPF_6 (c). UV-Vis-NIR spectral monitoring of the *in situ* potential-step electrochemical oxidation of **D4T7** within an OTTE cell ($T = 293$ K, $\text{CH}_2\text{Cl}_2/0.3$ M Bu_4NPF_6) (d). The UV-Vis spectrum of neutral thianthrene (commercial sample) in CH_2Cl_2 is depicted at the bottom of Fig. 2a ($\lambda_{\text{max}} = 258$ nm).

of the ultimate π -dimer dication reversibly recovers the neutral form of the parent **D4T7** compound.

In order to get further insight into the structure of **[D4T7 $^{+\bullet}$] $_2$** and the role of the PF_6^- anions, DFT quantum chemical calculations were performed at the M06L/6-31G(d) level of theory. We first studied the optimum structure and stability of a **[D4T7 $^{+\bullet}$] $_2(\text{CH}_2\text{Cl}_2)_8$** aggregate, taken as a model system to explore the possible structure of the π -dimers of **D4T7 $^{+\bullet}$** mediated by a discrete number of solvent molecules (such theoretical data should be compared with the experimental results collected in solution at a low PF_6^- concentration). Then, an additional set of calculations was run on another **[D4T7 $^{+\bullet}$] $_2(\text{PF}_6^-)_2$** model, aimed at investigating the role played by the counterions upon high PF_6^- concentrations.

There are more than one M06L optimum structure for the **[D4T7 $^{+\bullet}$] $_2(\text{CH}_2\text{Cl}_2)_8$** aggregate, differing from each other in the spatial position (hereinafter called configurations) of the two radical cations (i.e., parallel or antiparallel) and the relative orientations of the eight *n*-decyl side groups relative to the rings plane. Table 1 collects the data for some of the most significant optimum structures for **[D4T7 $^{+\bullet}$] $_2(\text{CH}_2\text{Cl}_2)_8$** and **[D4T7 $^{+\bullet}$] $_2(\text{PF}_6^-)_2$** , indicating also their shortest C $\cdots$ C intermolecular distance, and their C=C $\cdots$ C=C dihedral angle that describes the disposition of the π -conjugated skeletons of the two radical cations. Side and top views of these optimum structures are provided in the ESI.† These results indicate that the *n*-decyl side chains play a key role in the stabilization of the π -dimers. These configurations may co-exist in solution, their relative probability of existence depending on their relative energetic stability, according to the Boltzmann distribution. Our theoretical results indicate that the antiparallel configurations are also slightly more stable than the parallel ones. For simplicity

Table 1 Shortest C...C distance, central C=C...C=C dihedral angle (θ) and interaction energy of some relevant conformations of the antiparallel (AP) and parallel (P) $[\text{D4T7}^{\bullet+}]_2$ dimers at their optimum M06L/6-31G(d) geometries. The $[\text{D4T7}^{\bullet+}]_2(\text{CH}_2\text{Cl}_2)_8$ and $[\text{D4T7}^{\bullet+}]_2(\text{PF}_6^-)_2$ energy is computed for the dissociation into two $[\text{D4T7}^{\bullet+}](\text{CH}_2\text{Cl}_2)_4$ and $[\text{D4T7}^{\bullet+}](\text{PF}_6^-)$ radical cations. The symbols u (up) and d (down) refer to the mutual orientation of the *n*-decyl side group (see ESI)

Dimer dication conformation	<i>R</i> /Å	$\theta/^\circ$	<i>E</i> _{int} /kcal mol ⁻¹
u-u-u-u AP $[\text{D4T7}^{\bullet+}]_2(\text{CH}_2\text{Cl}_2)_8$	3.29	0.2	-45.6
u-u-u-u P $[\text{D4T7}^{\bullet+}]_2(\text{CH}_2\text{Cl}_2)_8$	3.33	179.3	-41.4
u-d-u-d AP $[\text{D4T7}^{\bullet+}]_2(\text{CH}_2\text{Cl}_2)_8$	3.26	0.6	-77.4
u-d-u-d P $[\text{D4T7}^{\bullet+}]_2(\text{CH}_2\text{Cl}_2)_8$	3.29	171.5	-70.9
u-u-u-u AP $[\text{D4T7}^{\bullet+}]_2(\text{PF}_6^-)_2$	3.24	0.7	-67.0
u-u-u-u P $[\text{D4T7}^{\bullet+}]_2(\text{PF}_6^-)_2$	3.29	179.5	-61.7

reasons, only the u-u-u-u spatial orientations will be further considered in this study. It is also interesting to note that $[\text{D4T7}^{\bullet+}]_2(\text{PF}_6^-)_2$ aggregates of the same configuration are about 21 kcal mol⁻¹ more stable than the equivalent $[\text{D4T7}^{\bullet+}]_2(\text{CH}_2\text{Cl}_2)_8$ aggregates (see Table 1). The closest intermolecular C...C distance between the π -conjugated skeletons in the $[\text{D4T7}^{\bullet+}]_2(\text{PF}_6^-)_2$ aggregates is also shorter by ca. 0.3–0.4 Å; this fact would impact the UV-Vis-NIR absorption spectra of these two aggregates in solution.

Finally, Fig. 3 displays the potential energy curves for the dissociation of both $[\text{D4T7}^{\bullet+}]_2(\text{CH}_2\text{Cl}_2)_8$ and $[\text{D4T7}^{\bullet+}]_2(\text{PF}_6^-)_2$ antiparallel π -dimers into two separated $[\text{D4T7}^{\bullet+}](\text{CH}_2\text{Cl}_2)_4$ and $[\text{D4T7}^{\bullet+}](\text{PF}_6^-)$ radical cations, computed at the M06L/6-31G(d) level. These two plots further illustrate the higher stability of $[\text{D4T7}^{\bullet+}]_2(\text{PF}_6^-)_2$ with respect to $[\text{D4T7}^{\bullet+}]_2(\text{CH}_2\text{Cl}_2)_8$. That is, the theoretical data reported in this study strongly support the stabilizing role played by the PF_6^- anions with regard to the unusually high propensity towards π -dimerization showed by this **D4T7** heptathienoacene, in full agreement with our experimental findings.

As inferred from our preceding study of the family of TIPS end-capped oligothienoacenes,¹⁶ TDDFT provides a reliable description for the electronic absorption spectra of $\text{D4T7}^{\bullet+}$. TDDFT/M06L calculations predict two intense electronic transitions for $\text{D4T7}^{\bullet+}$ at 524 and 967 nm which are experimentally observed at 582 and 1116 nm (see ESI†). On the other hand, TDDFT/M06L fails to closely reproduce the absorption spectra of the π -dimer dication, the data calculated for the

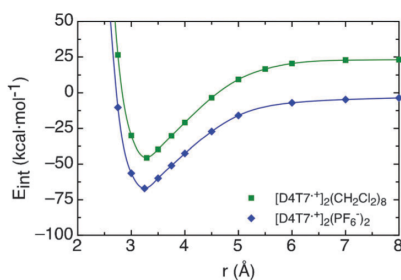


Fig. 3 Potential energy curves, computed at the M06L/6-31G(d) level, for the dissociation of the u-u-u-u $[\text{D4T7}^{\bullet+}]_2(\text{CH}_2\text{Cl}_2)_8$ and $[\text{D4T7}^{\bullet+}]_2(\text{PF}_6^-)_2$ π -dimers into two $[\text{D4T7}^{\bullet+}](\text{CH}_2\text{Cl}_2)_4$ and $[\text{D4T7}^{\bullet+}](\text{PF}_6^-)$ radical cations.

$[\text{D4T7}^{\bullet+}]_2(\text{PF}_6^-)_2$ aggregates giving the best fit (see ESI†). The theoretical electronic transitions obtained at the CIS/6-31G(d) level are much less reliable. This method has not provided acceptable transition energies and intensities even for the separate radical cation (see ESI†). Therefore, more accurate theoretical methods, such as CASPT2, are required to allow full description of the electronic absorption in the whole UV-Vis-NIR region for both the $\text{D4T7}^{\bullet+}$ monomer and π -dimer; however, in our case, the size of the systems presents a clear limitation.

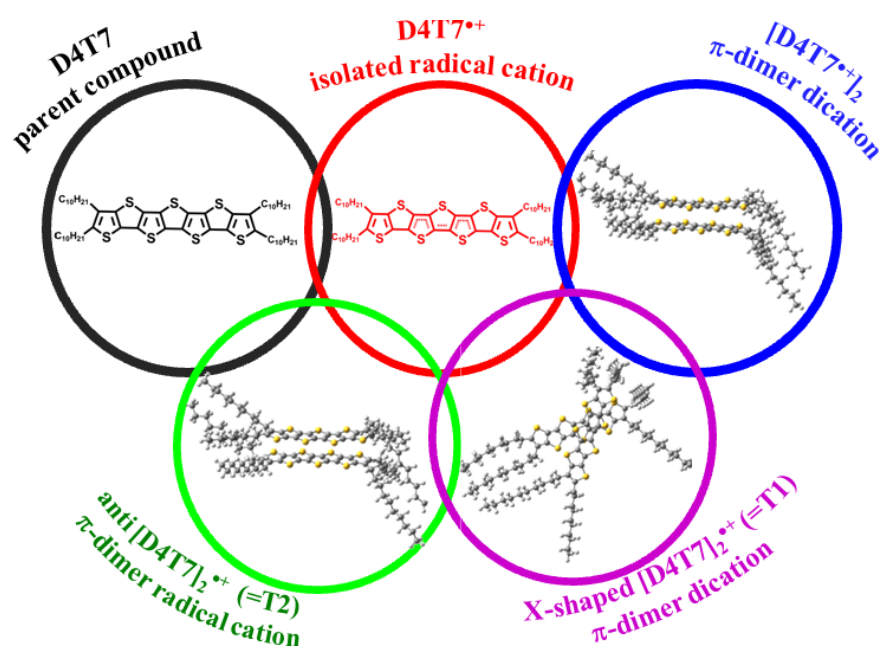
In situ UV-Vis-NIR data collected during the 1e⁻ chemical and electrochemical oxidation of **D4T7**, supported by quantum chemical M06L/6-31G(d) molecular geometry optimizations, indicate that $\text{D4T7}^{\bullet+}$ in CH_2Cl_2 undergoes π -dimerization already at room temperature, as evidenced by the progressive appearance of a Vis-NIR absorption band at ca. 700 nm, due to the formation of $[\text{D4T7}^{\bullet+}]_2(\text{CH}_2\text{Cl}_2)_n$ aggregates. Furthermore, in the presence of a high excess of PF_6^- counterions, the propensity of $\text{D4T7}^{\bullet+}$ toward the π -dimerization increases remarkably, due to the formation of $[\text{D4T7}^{\bullet+}]_2(\text{PF}_6^-)_2$ aggregates. In contrast, radical cations of **TIPS-T7-TIPS**, upon the replacement of the *n*-decyl chains by bulky triisopropylsilyl side groups, do not π -dimerize at room temperature, probably due to the sizeable steric hindrance.

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4.3. Publication 6

**Multistate π -Dimerization of Tetrakis(n-decyl)-heptathienoacene Radical Cations:
A Combined Experimental and Theoretical Study**



FULL PAPER

DOI: (to be filled in by the editorial staff)

Multistep π -Dimerization of Tetrakis(*n*-decyl)-heptathienoacene Radical Cations: A Combined Experimental and Theoretical Study

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Abstract: Radical cations of a heptathienoacene α,β -substituted with four *n*-decyl side groups (**D4T7**^{•+}) form exceptionally stable π -dimer dications already at ambient temperature (*Chem. Comm.* **2011**, 47, 12622). This extraordinary π -dimerization process is investigated here with focus on the ultimate [**D4T7**^{•+}]₂ π -dimer dication and yet unreported transitory species formed during and after the oxidation. To this end, we use a joint experimental and theoretical approach that combines cyclic voltammetry, in situ spectrochemistry and spectroelectrochemistry, EPR spectroscopy and DFT calculations.

The impact of temperature, thienoacene concentration and nature and concentration of counteranions on the π -dimerization process is also investigated in detail. Two different types of transitory species were detected in the course of the one-electron oxidation: (i) a different transient conformation of the ultimate [**D4T7**^{•+}]₂ π -dimer dications whose stability is strongly affected by the applied experimental conditions, and (ii) intermediate [**D4T7**]₂^{•+} π -dimer radical cations formed prior to the fully oxidized [**D4T7**]₂^{•+} π -dimer dications. Thus, this exhaustive work demonstrates the formation of peculiar

supramolecular species of heptathienoacene radical cations and their stability, nature and structure are successfully analyzed. We therefore believe that this study leads to a deeper fundamental understanding of the mechanism of dimer formation between conjugated aromatic systems.

Keywords: π -Dimers • Supramolecular chemistry • Oligothienoacenes • UV-Vis-NIR Spectroelectrochemistry • EPR • DFT calculations.

Introduction

In recent years, there has been a growing interest in the study of the π -dimerization of conjugated radical cations^[1-17] with a dual purpose: (i) elucidation of the nature of the charge-transport phenomena in p-doped semiconducting polymers and (ii) development of supramolecular bonding ideas for applications in material science, such as actuators.^[18-23] In particular, π -dimers of oligothiophene radical cations were proposed two decades ago to play a key role in electronic conduction of p-doped polythiophenes.^[24] Investigations into the mechanism of the interaction between oligothiophene radical cations^[1-8, 25-30] deepen the understanding of the chemistry of this particularly attractive building block for organic electronics. For instance, it has been found that the tendency for intermolecular π -dimerization can be attenuated and, in some cases, shut down when bulky groups are inserted in the β -positions at thiophene rings^[31-34]; note the evidence from X-ray crystallography that the closest intermolecular contact in the π -dimer of non-hindered systems takes place at the central rings.^[25-26, 29] As a result of the attachment of bulky side groups, unfavorable steric interactions may occur, preventing π -oligomers

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from close intermolecular contacts leading to a sizeable π -orbital overlap upon oxidation; an arrangement that is however highly desirable in order to achieve a good p-type charge carrier mobility.^[35] On the other hand, the steric hindrance of dimerization of cationic π -conjugated oligothiophenes provides valuable information on the intrinsic properties of positively charged π -systems in a segregated state and can be considered as an important technique for fabrication of “insulated molecular wires” in molecular devices.

Although oligo/polythiophenes are key ingredients in the development of π -extended optoelectronic materials, deviation from planarity may decrease conjugation through the torsion of single bonds or S-syn defects.^[36] Such defects do not arise in fully fused conjugated oligomers, such as pentacene, that however lacks of environmental stability. In this context, oligothienoacenes, the fused-ring analog of α -linked oligothiophenes, emerge as a promising new class of conjugated materials.^[37-39] Their rigid and planar molecular structures tend to form densely packed solid-state structures resulting in high charge carrier mobilities.^[35, 38] However, fused thiophenes lead to lower solubility compared to the α -linked analogs. To solve this problem, some synthetic strategies have been reported in the literature over the past few years, which incorporate the solubilizing tris(isopropyl)silyl (TIPS) or *n*-decyl substituents in the α and/or β terminal positions at the oligothieryl backbones^[38, 40]. Despite the large number of studies available on the π -dimerization of oligothiophene radical cations, only few examples are devoted to study the supramolecular arrangement of oligothienoacene radical cations. For instance, some of us recently demonstrated the formation of π -dimer dications in oxidized tetrathienoacenes,^[41] pentathienoacenes^[42] and heptathienoacenes.^[43] When compared to α -linked oligothiophenes, the high propensity towards π -dimerization of oligothienoacenes radical cations can be attributed to the rigid and planar structure which can maximize the intermolecular orbital overlap upon oxidation. Specifically, radical cations of a heptathienoacene α,β -substituted with four *n*-decyl side groups (**D4T7**, see Chart 1) are shown to exhibit an exceptional capability for π -dimer formation even at room temperature.^[43] Note that π -dimerization of planar conjugated radical cations in solution is scarce and usually encountered at low temperatures.^[44-46]

With aim at improving the understanding of the mechanism of π -dimer formation in oligothienoacenes, we focus here on the π -dimerization process of radical cations of **D4T7**. The properties of the ultimate $[\text{D4T7}^{\bullet+}]_2$ π -dimer dication and yet unreported transitory species formed during and after the oxidation are analyzed as a function of the temperature, the concentration of the heptathienoacene itself, and the concentration and nature of counterions; for instance, note that the stabilization of the radical cations is found to be strongly affected by the nucleophilic character of the counterions, which ultimately alters the dimer formation.^[47] To this end, we use a combined experimental-theoretical approach that links cyclic voltammetry, in situ spectroelectrochemistry and chemical doping methods (in particular UV-Vis-NIR and EPR monitoring) with density functional theory (DFT). TD-DFT/ ω B97XD calculations successfully provide a reliable assignment of the electronic absorption spectra of the ultimate π -dimer dication $[\text{D4T7}^{\bullet+}]_2$ and also the transitory species formed in the course of the **D4T7** oxidation. In turn, this approach greatly aids the identification of their nature and structure.

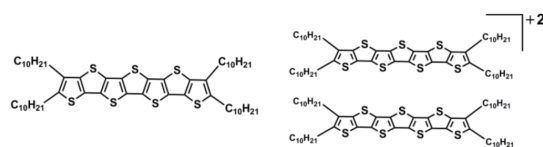


Chart 1. A molecular structure of **D4T7** (left) and a schematic structure of $[\text{D4T7}^{\bullet+}]_2$ π -dimer dication (right).

Results and Discussion

Experimental evidence of transitory oxidized species

1. Different conformations of $[\text{D4T7}^{\bullet+}]_2$ π -dimer dications

1.1 Oxidations performed at low concentration of **D4T7**: an influence of different oxidants, excess of counterions and their nature, and temperature variation

At the early stages of the UV-vis-NIR spectral monitoring of the stepwise oxidation of ca 10^{-5} M **D4T7** ($E_{1/2} = +0.34$ V vs Fc/Fc^+) with 1 equiv. $\text{TA}^{\bullet+}$ (TAPF_6 , $E_{1/2} = +0.82$ V vs Fc/Fc^+) the spectra show the appearance of two characteristic subgap absorptions at 582 and 1116 nm due to isolated radical cations **D4T7** ^{$\bullet+$} (Figure 1a). During the further addition of the solution of TAPF_6 , a third broad and structureless subgap absorption appears at ca 700 nm (Figure 1b), which is indicative of the formation of the ultimate π -dimer dication $[\text{D4T7}^{\bullet+}]_2$.^[43] A similar spectral evolution towards π -dimer dication formation is encountered when using the TASbCl_6 oxidant (Figures 1c,d).

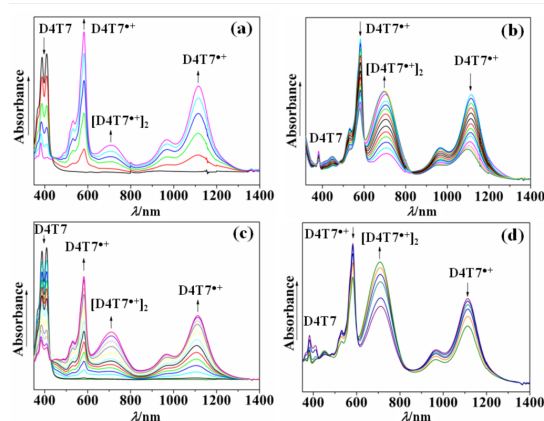


Figure 1. UV-Vis-NIR spectral changes recorded (i) in the course of the $1e^-$ oxidation of ca 10^{-5} M **D4T7** with 1 equiv. TAPF_6 (a) or TASbCl_6 (c) in dichloromethane at room temperature, leading at the early stages to the dominant formation of isolated **D4T7** ^{$\bullet+$} together with a small fraction of $[\text{D4T7}^{\bullet+}]_2$, and (ii) during the subsequent conversion of the radical cations into the π -dimer dications stabilized with PF_6^- (b) and SbCl_6^- (d).

The impact of the counterions on the formation of the $[\text{D4T7}^{\bullet+}]_2$ π -dimer dication has been analyzed by inspecting the spectral changes recorded in the course of the one-electron oxidation of **D4T7** with TAPF_6 in the presence of the supporting electrolytes tetrabutylammonium hexafluorophosphate, Bu_4NPF_6 , or tetrakis-

(pentafluorophenyl)borate, $\text{Bu}_4\text{N}\{\text{B}(\text{C}_6\text{F}_5)_4\}$. In the presence of the counterions, as seen in Figures 2a-c, the broad absorption due to the π -dimer dication gains up rapidly in intensity relative to the Vis-NIR subgaps of the isolated radical cations. While a similar upsurge of the $[\text{D4T7}^{+\cdot}]_2$ band is found at low PF_6^- concentrations (Figure 2a) and high $\text{B}(\text{C}_6\text{F}_5)_4^-$ concentrations (Figure 2c), this effect is more pronounced in the presence of a high excess of PF_6^- counterions (Figure 2b). Note that $\text{B}(\text{C}_6\text{F}_5)_4^-$ anions are considered as weakly coordinating (nucleophiles) and weakly ion-pairing^[48]; thus, they tend to stabilize the radical cations and prohibit the dimer dication formation due to steric hindrance caused by their bulky structure.^[49-50] Nonetheless, the formation of π -dimer dications is favored in the presence of both counteranions, the impact being more pronounced at high concentrations of PF_6^- . Identical behavior (*i.e.*, the formation of the π -dimer dications from the very beginning of the monitoring sequence) has been observed for the *in situ* UV-Vis-NIR spectroelectrochemical oxidation of low concentration (ca 10^{-5} M) **D4T7** in the presence of a high excess of Bu_4NPF_6 as supporting electrolyte (see Figure S1 in Supporting Information). Similar pairing enhancement effects caused by counterions were previously reported.^[51-52]

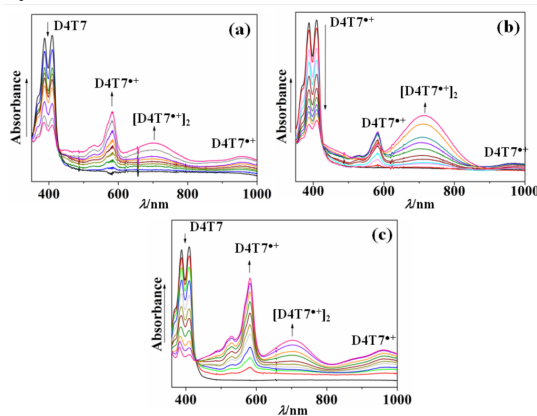


Figure 2. UV-Vis-NIR spectral changes recorded in the course of the stepwise $1e^-$ oxidation of ca 10^{-5} M **D4T7** with 1 equiv. TAPF_6 in dichloromethane at room temperature in the presence of 5×10^{-2} M Bu_4NPF_6 (a), 10^{-1} M Bu_4NPF_6 (b) and 10^{-1} M $\text{Bu}_4\text{N}\{\text{B}(\text{C}_6\text{F}_5)_4\}$ (c).

Figure 3 shows the UV-Vis-NIR spectra recorded upon *in situ* chemical doping of **D4T7** with TAPF_6 at various temperatures. As also found in the literature for non-fused oligothiophenes,^[3, 53] the tendency toward π -dimerization of $\text{D4T7}^{+\cdot}$ increases with decreasing temperature. Upon cooling, the intensity of the two subgaps related to the radical cations decreased and three new absorption bands appeared at 490, 681 and 876 nm; note that the band at 681 nm belonging to the ultimate π -dimer dication is the only one observed at room temperature (cf. Figure 1a). These experiments have revealed the presence of a transient oxidized species **T1** absorbing at 490 and 876 nm that is stabilized at sufficiently low temperature. It could be assigned to a different conformation of the $[\text{D4T7}^{+\cdot}]_2$ π -dimer dication, based on evidence from concentration-dependent chemical and electrochemical oxidation experiments and TD-DFT calculations described in the following sections.

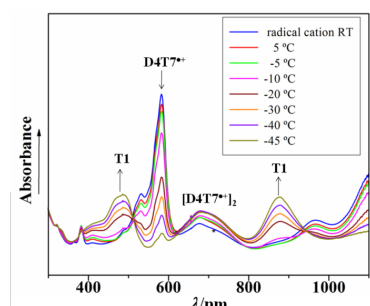


Figure 3. UV-Vis-NIR spectral changes recorded after the $1e^-$ oxidation of ca 10^{-5} M **D4T7** with 1 equiv. TAPF_6 in dichloromethane at room temperature, followed by rapid cooling of the solution containing reactive $\text{D4T7}^{+\cdot}$. The absorption bands denoted as **T1** belong to a transient π -dimer dication slowly converting to the ultimate $[\text{D4T7}^{+\cdot}]_2$ conformation.

Chemical oxidation of **D4T7** in dichloromethane with TAPF_6 under the experimental conditions corresponding to Figure 1a and 1b was also monitored with EPR spectroscopy. Only the signal of $\text{D4T7}^{+\cdot}$ was observed at $g = 2.0026$ as a 1:4:6:4:1 quintuplet with $a_H = 0.33$ mT (Figure 4). This hyperfine splitting pattern corresponds to the interaction of the unpaired electron with the proton nuclei of the two $-\text{CH}_2-$ groups attached to the terminal C_α atoms bearing significant spin density, unlike the C_β carbons (Figure 5). The EPR signal of $\text{D4T7}^{+\cdot}$ (black line) slowly diminished in the course of its conversion to the $[\text{D4T7}^{+\cdot}]_2$ π -dimer dication (blue line). No other signal was detected in the course of the dimerization in this low concentration region, not even upon cooling (cf. Figure 3), which proves that transient **T1**, much like the ultimate dimeric product $[\text{D4T7}^{+\cdot}]_2$, is a diamagnetic specie.

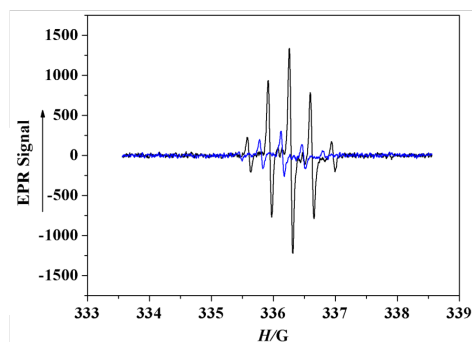


Figure 4. EPR spectrum of $\text{D4T7}^{+\cdot}$ ($g = 2.0026$) recorded after the chemical oxidation of ca 10^{-5} M **D4T7** with TAPF_6 in dichloromethane. Experimental conditions: $T = 293$ K, microwave power of 4.0 mW, modulation frequency of 9.42 GHz.

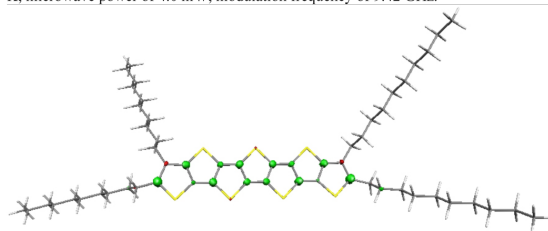


Figure 5. Spin electron density distribution of $\text{D4T7}^{+\cdot}$ calculated at the M06L/6-31G* level. Note the negligible spin density at the terminal C_β atoms.

1.2 Oxidations performed at high concentration of **D4T7**

To resolve the nature of the transient species **T1** absorbing at 490 and 876 nm (Figure 3) observed during the low temperature doping experiments, we investigated the concentration-dependent spectral changes accompanying the formation of $[\text{D4T7}^{\bullet+}]_2$. Figure 6a shows the UV-Vis-NIR spectra recorded in situ directly after the rapid chemical oxidation of 1.84×10^{-4} M **D4T7** (considering $>10^{-4}$ M as the high concentration limit) with 1 equiv. TASbCl_6 . The subgap absorption of $\text{D4T7}^{\bullet+}$ at 582 nm is diminished and the UV-Vis spectrum reveals the three dominant absorption bands at 490, 681 and 876 nm, in compliance with Figure 3. The band at 681 nm due to the ultimate π -dimer dication gains intensity in time at the expense of the absorption of the transient species. That is, the π -dimer dication is mainly formed from **T1** while the remaining radical cation absorbing at 582 nm is reacting more slowly and incompletely.

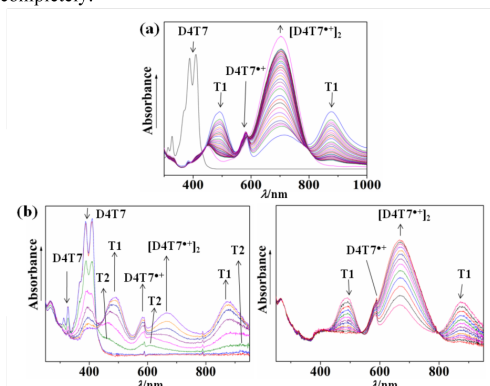


Figure 6. Rapid UV-Vis-NIR spectral changes recorded on the time scale of seconds directly after (a) complete $1e^-$ oxidation of **D4T7** (1.84×10^{-4} M) in dichloromethane with TASbCl_6 , and (b) rapid potential-step electrochemical oxidation of **D4T7** (1.84×10^{-4} M) within an OTTE cell ($T = 293$ K, $\text{CH}_2\text{Cl}_2/3 \times 10^{-3}$ M Bu_4NPF_6) in the early (left) and later (right) stages of the monitoring sequence.

The spectral changes monitored upon the chemical oxidation were reproduced after rapid (potential-step) electrochemical oxidation of **D4T7** in the high concentration regime (around 2×10^{-4} M, comparable with the chemical doping, Figure 6a) in the presence of a high excess of PF_6^- in a thin-layer (ca. 0.2 mm) spectroelectrochemical cell, (see Figure 6b). Similar to Figure 6a, both the ultimate π -dimer dication and the transient species **T1** are observable from the very beginning of the monitoring sequence; later on, **T1** transforms rapidly to the π -dimer dication. The conversion of **T1** and $\text{D4T7}^{\bullet+}$ to the π -dimer dication is moderately faster in the presence of the excess Bu_4NPF_6 electrolyte than that observed for the chemical doping with TASbCl_6 .

On the other hand, the more bulky $\text{Bu}_4\text{N}\{\text{B}(\text{C}_6\text{F}_5)_4\}$ electrolyte causes somewhat slower conversion of the transient species **T1** and the radical cation to the π -dimer dication (see Figure S2 in Supporting Information); that is, the weakly coordinated $\text{B}(\text{C}_6\text{F}_5)_4^-$ anions stabilize $\text{D4T7}^{\bullet+}$ to a greater extent. However, the effect of the counterion nature and size seems to be less pronounced in the experiments performed at high concentrations of **D4T7** ($\geq 10^{-4}$ M) than encountered at low **D4T7** concentrations (around 10^{-5} M), as previously shown in Figures 2b-c where a direct conversion of the radical cations $\text{D4T7}^{\bullet+}$ to the $[\text{D4T7}^{\bullet+}]_2$ π -dimer dications is

observed from the very beginning of the chemical oxidation (*i.e.*, without the involvement of the intermediate and transient species).

Interestingly, back reduction experiments leads to recovery of neutral parent **D4T7** (see Figure S3 in Supporting Information), with the bands of $\text{D4T7}^{\bullet+}$ and transient **T1** disappearing first, followed by $[\text{D4T7}^{\bullet+}]_2$. That is, the most stable π -dimer dication reduces less positively than the radical cation and **T1**. This conclusion from thin-layer spectroelectrochemistry has been confirmed by cyclic voltammograms recorded after chemical oxidation of **D4T7** in $\text{CH}_2\text{Cl}_2/\text{TBAH}$ with TAPF_6 at 253 K followed by slight temperature increase for solubility reasons. The irreversible cathodic wave of **T1** was observed at $E_{p,c} = -0.19$ V vs Fc/Fc^+ at 273 K and the dominant one of $[\text{D4T7}^{\bullet+}]_2$ at $E_{p,c} = -0.63$ V (see Figure S4 in Supporting Information). At 293 K only the back reduction of the ultimate oxidation product $[\text{D4T7}^{\bullet+}]_2$ was present at $E_{p,c} = -0.51$ V. The remarkably more negative reduction potentials of both **T1** and $[\text{D4T7}^{\bullet+}]_2$ compared to $E_{1/2}(\text{D4T7}^{0/+})$ testify to the large thermodynamic driving force of the π -dimerization of $\text{D4T7}^{\bullet+}$, as also confirmed by DFT calculations (*vide supra*). The dimerization is promoted by the presence of dominant counterions, in particular small and weakly coordinating PF_6^- , and becomes also facilitated by the high concentration of parent **D4T7**. The process also involves transient **T1** (a different conformation of ultimate $[\text{D4T7}^{\bullet+}]_2$) that can be stabilized at low temperature. In the next section we will demonstrate that fully oxidized **T1** is not the only transient species ascertained during the UV-Vis monitoring sequence.

2. Experimental evidence for partly oxidized $[\text{D4T7}]_2^{\bullet+}$ π -dimer radical cations

During the initial phase of the electrochemical oxidation of high-concentrated **D4T7** (see Figure 6b), two new bands appeared at 470 and 620 nm before the upsurge of the three bands assigned to the π -dimer dications **T1** and ultimate $[\text{D4T7}^{\bullet+}]_2$. These bands are attributed to additional species **T2**, whose nature is revealed from combined results of (i) cyclic voltammetry, (ii) monitoring of the chemical and electrochemical oxidation experiments where only a small portion of **D4T7** is oxidized to the radical cation, and (iii) a DFT study. As seen in Figure 7, when high-concentrated **D4T7** starts to be oxidized either chemically (Figure 7a) or electrochemically (Figure 7b), the intermediate species **T2** absorbing at 470, 620 and 950 nm appears (together with some $\text{D4T7}^{\bullet+}$ in the absence of excess PF_6^- , Figure 7a, or when $\text{B}(\text{C}_6\text{F}_5)_4^-$ is used). The electronic absorption of **T2** resembles a blend of parent **D4T7** and $\text{D4T7}^{\bullet+}$. Note that chemically produced **T2** (Figure 7a) converts slowly along with $\text{D4T7}^{\bullet+}$ directly to the ultimate π -dimer dication (upsurge of the band at 681 nm). On the other hand, electrochemically generated **T2** is stable; only the further oxidation of **D4T7** converted **T2** to the ultimate π -dimer dications (Figure 7b, left). Given the fact that **T2** can be generated at a high excess of neutral parent **D4T7**, it originates most likely from π -coupling of a neutral parent **D4T7** chain with its radical cation, leading to the formation of the $[\text{D4T7}]_2^{\bullet+}$ π -dimer radical cation in the initial phase of the oxidation. Upon further oxidation, π -dimer dications are directly formed from the $[\text{D4T7}]_2^{\bullet+}$ π -dimer radical cations, *i.e.*, on the oxidation of the neutral heptathienoacene chain in the radical cation dimers bound to a previously formed minor amount of $\text{D4T7}^{\bullet+}$. The structure of $[\text{D4T7}]_2^{\bullet+}$ ($= \text{T2}$) has been resolved by DFT calculations and the calculated TD-DFT electronic excitations have appreciably reproduced its electronic absorption spectrum (Figure 7b).

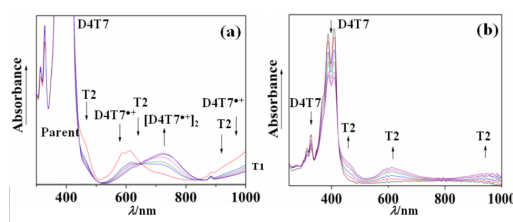


Figure 7. (a) UV-Vis-NIR spectral changes recorded after the $1e^-$ oxidation of ca 2×10^{-4} M **D4T7** with a small amount of TASbCl₆ in dichloromethane in a 1-cm air-tight cuvette. (b) UV-Vis spectral monitoring of the electrochemical oxidation of 1.84×10^{-4} M **D4T7** within an OTTE cell ($T = 293$ K, $\text{CH}_2\text{Cl}_2/3 \times 10^{-1}$ M Bu₄NPF₆).

A useful insight into the process of **T2** formation is also obtained from cyclic voltammetry. Figure 8 shows the cyclic voltammogram of high-concentrated (2×10^{-4} M) **D4T7** in $\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{N}^+\{\text{B}(\text{C}_6\text{F}_5)_4\}^-$ together with the cobaltocenium (Cc^+) internal standard. While the Nernstian Cc/Cc^+ redox couple represents a rapid and reversible electron transfer, the anodic response of **D4T7** at ca. +0.3 V vs Fc/Fc^+ consists of two close-lying, poorly resolved anodic waves and cathodic counterwaves. Based on the spectroelectrochemical monitoring, the first anodic wave is assumed to correspond to the oxidation of free **D4T7** to **D4T7^{•+}** (partly stabilized with $\{\text{B}(\text{C}_6\text{F}_5)_4\}^-$) and the slightly positively shifted wave to the oxidation of the second half of **D4T7** in the concomitantly formed **[D4T7]₂^{•+}** radical cation dimer. On the time scale of cyclic voltammetry the cathodic wave at -0.5 V due to back reduction of the resulting firmly π -bound dimer dication **[D4T7]₂²⁺** is not detectable prior to the complete chemical oxidation of **D4T7** with thianthrenium, as described above.

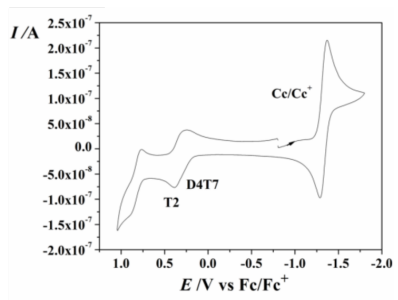


Figure 8. Cyclic voltammogram of 2×10^{-4} M **D4T7** in $\text{CH}_2\text{Cl}_2/10^{-1}$ M Bu₄N⁺{B(C₆F₅)₄}⁻ recorded at $T = 293$ K and $v = 100$ mV s⁻¹. The working electrode was a carefully polished 0.125 mm² Pt disc. Cobaltocenium (Cc^+) hexafluorophosphate was used as an internal standard ($E_{1/2} = -1.33$ V vs Fc/Fc^+).

Finally, the radical nature of **[D4T7]₂^{•+}** radical cation dimer was also probed with EPR spectroscopy. Chemical oxidation of ca 2×10^{-4} M **D4T7** with TAPF₆ was carried out directly in the EPR tube in a special way, layering the oxidant solution over the **D4T7** solution and letting blue radical cations **D4T7^{•+}** diffuse from the contact interphase into the EPR-active area containing non-oxidized **D4T7**. The presence of **[D4T7]₂^{•+}** radical cation dimer (cf. Figure 7a) was indicated by the presence of a foreign EPR signal (Figure 9) overlapping with that of dominant **D4T7^{•+}** (cf. Figure 4). The hyperfine structure of the EPR signal of **[D4T7]₂^{•+}** was not analysed in detail.

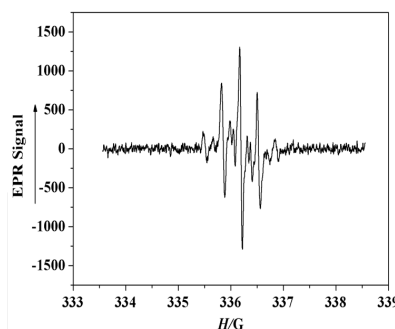


Figure 9. EPR spectrum of the solution layer where radical cations **D4T7^{•+}** (cf. Figure 4) formed by chemical oxidation of ca 2×10^{-4} **D4T7** in dichloromethane with TAPF₆ interact with an excess of non-oxidised **D4T7**, forming **[D4T7]₂^{•+}** radical cation dimer. Experimental conditions: $T = 293$ K, microwave power of 4.0 mW, modulation frequency of 9.42 GHz

DFT calculations of transitory oxidized species

In order to get further insight into the structure and stability of the intermediate (**T2**) and transient (**T1**) oxidized species, density functional theory (DFT) calculations were conducted for the **[D4T7^{•+}]₂** π -dimer dications and **[D4T7]₂^{•+}** π -dimer radical cations. The solution environment is described with two models: (i) a polarizable continuum model (PCM) and (ii) a discrete/continuum mixed model, where the **[D4T7^{•+}]₂(CH₂Cl₂)₈** or **[D4T7]₂^{•+}(CH₂Cl₂)₈** aggregates are combined with the PCM model. Three configurations (*i.e.*, parallel, antiparallel or X-shaped) for the spatial disposition of the two radical cations (or radical cation/neutral molecule in the case of the radical cation dimers) were considered. The impact of the orientations of the eight *n*-decyl side groups relative to the rings plane on the dimer stability was tested in our recent communication,^[43] with the up-down-up-down (hereinafter called u-d-u-d) orientation giving the most stable conformation.

Table 1 presents the free energy of formation at 298 K of **[D4T7^{•+}]₂** π -dimer dications in the parallel (syn), antiparallel (anti) and X-shaped configurations. Lateral and top views of their optimum structures are given in the SI (Figures S5-S7). Both the continuous and mixed solvation models predict the anti and syn configurations to be stable against dissociation, with the accurate mixed description given more stable values by about 10-12 kcal/mol. However, both anti and syn configurations are found to be nearly isoenergetic while the X-shaped configuration, in which the top radical cation, rotated by nearly 60° with respect to the main molecular axes of the bottom radical cation, is energetically unstable towards dissociation ($\Delta G_f^\circ = +4.1$ kcal/mol). This can be explained for the less efficient overlap of the SOMOs of the single chains in the X-shaped π -dimer dications in comparison with the cofacially superimposed syn and anti configurations. Additionally, the fact that the chains are not cofacially superimposed also reduces the dispersion attractive term of the interaction energy. The more accurate discrete/continuum mixed description turns the aggregate to be stable towards dissociation by -9.5 kcal/mol, although it still remains 12 kcal/mol less stable than the anti/syn π -dimers.

Table 1. Free energy of formation values at 298 K of the $[\text{D4T7}^{\bullet+}]_2$ π -dimer dication in its anti, syn and X-shaped configurations under different conditions: isolated, and in $(\text{CH}_2\text{Cl}_2)_8$ and $(\text{PF}_6^-)_2(\text{CH}_2\text{Cl}_2)_4$ aggregates. Free energy of formation (at 298 K) of the $[\text{D4T7}]_2^{\bullet+}$ π -dimer radical cation in its anti and syn orientations in $(\text{CH}_2\text{Cl}_2)_8$ aggregates are also given. All calculations are carried out in a continuous solvent environment (PCM-dichloromethane), at the M06L/6-31G(d) level.

Conformation ^a	r (Å) ^b	ΔG_f° (kcal mol ⁻¹)
$[\text{D4T7}^{\bullet+}]_2$ π -dimer dication		
anti $[\text{D4T7}^{\bullet+}]_2$	3.26	-10.4
syn $[\text{D4T7}^{\bullet+}]_2$	3.31	-9.1
X-shaped $[\text{D4T7}^{\bullet+}]_2$	3.38	+4.1
anti $[\text{D4T7}^{\bullet+}]_2(\text{CH}_2\text{Cl}_2)_8$	3.26	-21.0
syn $[\text{D4T7}^{\bullet+}]_2(\text{CH}_2\text{Cl}_2)_8$	3.30	-22.5
X-shaped $[\text{D4T7}^{\bullet+}]_2(\text{CH}_2\text{Cl}_2)_8$	3.38	-9.5
anti $[\text{D4T7}^{\bullet+}]_2(\text{PF}_6^-)_2(\text{CH}_2\text{Cl}_2)_4$	3.25	-24.1
syn $[\text{D4T7}^{\bullet+}]_2(\text{PF}_6^-)_2(\text{CH}_2\text{Cl}_2)_4$	3.25	-25.5
X-shaped $[\text{D4T7}^{\bullet+}]_2(\text{PF}_6^-)_2(\text{CH}_2\text{Cl}_2)_4$	3.38	-11.7
$[\text{D4T7}]_2^{\bullet+}$ π -dimer radical cation		
anti $[\text{D4T7}]_2^{\bullet+}(\text{CH}_2\text{Cl}_2)_8$	3.30	-28.5
syn $[\text{D4T7}]_2^{\bullet+}(\text{CH}_2\text{Cl}_2)_8$	3.35	-31.3
X-shaped $[\text{D4T7}]_2^{\bullet+}(\text{CH}_2\text{Cl}_2)_8$	3.40	-19.0

^aAn up-down-up-down (u-d-u-d) spatial disposition for the n -decyl groups was assumed for the anti and syn configurations while a down-down-down-down (d-d-d-d) conformation was imposed for the X-shaped configuration due to steric hindrance.

^bShortest C-C distance between adjacent **D4T7** molecules in the dimer.

Aimed at investigating the role played by the counterions, the free energies of formation of $[\text{D4T7}^{\bullet+}]_2(\text{PF}_6^-)_2(\text{CH}_2\text{Cl}_2)_4$ aggregates have been obtained in dichloromethane solution (PCM), see Table 1. $[\text{D4T7}^{\bullet+}]_2(\text{PF}_6^-)_2(\text{CH}_2\text{Cl}_2)_4$ aggregates are about 3 kcal mol⁻¹ more stable than $[\text{D4T7}^{\bullet+}]_2(\text{CH}_2\text{Cl}_2)_8$ aggregates which confirms the stabilizing character of the PF_6^- counterions towards the π -dimerization.

The stability of $[\text{D4T7}]_2^{\bullet+}$ π -dimer radical cations has also been explored and negative free energies of about -30 kcal/mol have been obtained for both anti and syn conformations (see Table 1). The $[\text{D4T7}]_2^{\bullet+}$ radical cation dimers are therefore ~10 kcal mol⁻¹ more stable than the $[\text{D4T7}^{\bullet+}]_2$ π -dimer dications; although the well-known self-interaction error for open-shell states on pure DFT exchange functional might introduce a spurious overestimation of its energy.^[54-55]

Time-dependent DFT (TD-DFT) calculations are now used to interpret the evolution of the electronic absorption spectra of the primary oxidation products **D4T7**^{•+} up to the $[\text{D4T7}^{\bullet+}]_2$ π -dimer dications through the formation of transient **T1** (*i.e.*, less stable conformations of $[\text{D4T7}^{\bullet+}]_2$ π -dimer dications: X-shaped configurations) and partly oxidized **T2** intermediate species (*i.e.*, $[\text{D4T7}]_2^{\bullet+}$ π -dimer radical cations). The ωB97XD long-range corrected functional is used in the TD-DFT calculations over the previous M06L optimized structures. Note that TD-DFT/M06L provides a reliable description for the electronic absorption spectra of **D4T7**^{•+} but it has failed to closely reproduce the absorption spectra of the π -dimer dication, as shown in our previous work.^[43]

As seen in Figure 10a, two intense electronic transitions are computed for **D4T7**^{•+} at 498 and 1013 nm, which greatly coincide

with the experimental absorption bands measured at 582 and 1116 nm. For the isoenergetic anti and syn $[\text{D4T7}^{\bullet+}]_2(\text{CH}_2\text{Cl}_2)_8$ aggregates, one intense band at 765 nm is predicted which is associated to the (H-1 $\rightarrow$ L) and (H-2 $\rightarrow$ L) transitions; this band nicely reproduces the experimental broad band observed at ca 700 nm for the ultimate π -dimer dication. For the less stable X-shaped $[\text{D4T7}^{\bullet+}]_2(\text{CH}_2\text{Cl}_2)_8$ aggregate, two additional transitions at 497 and 976 nm are also obtained (Figure 7-bottom and Table 2) which are in good accordance with the experimental bands observed at 490 and 876 nm associated with the formation of the transient oxidized species **T1**. Finally, for the anti $[\text{D4T7}]_2^{\bullet+}(\text{CH}_2\text{Cl}_2)_8$ π -dimer radical cation, three bands are predicted at 394, 574 and 984 nm (Figure 7b), in good agreement with the three experimental bands associated with the formation of the intermediate oxidized species **T2** (Table 2). Therefore, the TD-DFT calculations have reasonably well reproduced the experimental absorption spectra of the ultimate $[\text{D4T7}^{\bullet+}]_2$ π -dimer dication and the transitory **T1** intermediate and **T2** species formed during and after the **D4T7** oxidation.

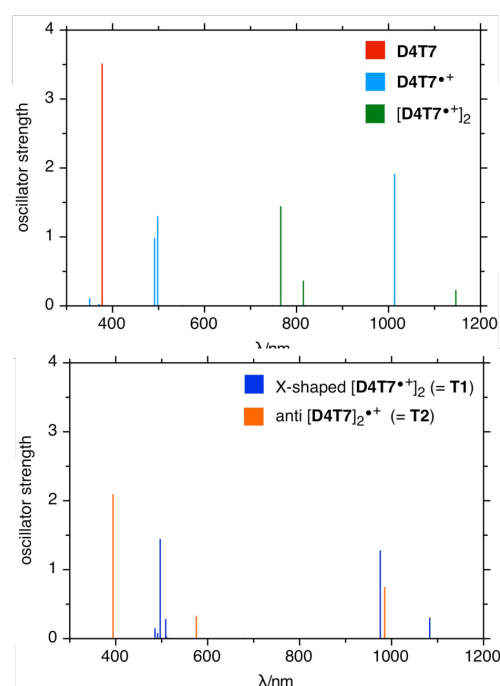


Figure 10. TD-DFT/ ωB97XD calculated vertical transition energies for neutral **D4T7**, the radical cation **D4T7**^{•+}, and the anti $[\text{D4T7}^{\bullet+}]_2$ π -dimer dication as the model for the ultimate dimer dication (a), and the X-shaped $[\text{D4T7}^{\bullet+}]_2$ π -dimer dication and the anti $[\text{D4T7}]_2^{\bullet+}$ π -dimer radical cation as the models for the transient **T1** and partly oxidized intermediate **T2** species, respectively (b).

Table 2. Observed and calculated absorption bands (λ , in nm) for neutral **D4T7**, the radical cation **D4T7^{•+}**, the π -dimer dication **[D4T7^{•+}]₂** and the π -dimer radical cation **[D4T7]₂^{•+}**.^{a,b}

Compound	$\lambda_{\text{expt}} \text{ (nm)}$	$\lambda_{\text{calcd}} \text{ (nm)}^a$
D4T7	388,409	378
D4T7^{•+}	582,1116	498,1013
[D4T7^{•+}]₂	~700 ^c	765 ^d
X-shaped [D4T7^{•+}]₂ (= T1)	490,876 ^e	497,976
Anti [D4T7]₂^{•+} (= T2)	470,620,950 ^f	394,574,984

^a Calculated at the TD-DFT/ ω B97XD/6-31G(d) level. ^b u-d-u-d conformation for the *n*-decyl groups was assumed here for the anti **[D4T7^{•+}]₂** π -dimer and anti **[D4T7]₂^{•+}** radical cation dimer and d-d-d-d conformation was considered for the X-shaped **[D4T7^{•+}]₂** π -dimer radical cation. ^c Ultimate π -dimer dication. ^d **[D4T7^{•+}]₂** π -dimer dication in its anti configuration. ^e Oxidized transient species **T1**. ^f Partly oxidized intermediate species **T2**.

Conclusion

The marked propensity towards π -dimerization showed by the radical cations of an α,β -substituted heptathienoacene **D4T7** in dichloromethane is investigated in detail by using a combined experimental and theoretical approach. The stability, nature and spectroscopic characteristics of the ultimate π -dimer dications and transitory species formed in the course of the **D4T7** oxidation are analyzed as a function of the temperature, **D4T7** concentration, and the nature and concentration of counterions. In the course of the one-electron oxidation of **D4T7** up to the formation of the final π -dimer dication that absorbs at ca 700 nm, two different transitory oxidized species are observed:

(i) Besides the band related with the ultimate π -dimer dication at ca 700 nm, either in the low temperature experiments for solutions of low concentration of **D4T7** or in the room temperature experiments for highly concentrated **D4T7** solutions, two new bands appear at 490 and 876 nm associated with less stable (EPR-silent transient **T1**) conformation of **[D4T7^{•+}]₂** π -dimer dication. The actual structure of these transient oxidized species is assumed to be very similar to the DFT-calculated X-shaped **[D4T7^{•+}]₂** configuration, that upon increasing the temperature convert into the more stable quasi-isoenergetic anti or syn aggregates which are in contrast co-facially overlapped.

(ii) Intermediate **[D4T7]₂^{•+}** π -dimer radical cations (**T2**) are found to appear prior to the fully chemically oxidized ultimate **[D4T7^{•+}]₂** π -dimer dications under a specific concentration regime where the **D4T7** concentration is high and the conversion to **D4T7^{•+}** is low. Electrochemically **[D4T7]₂^{•+}** can be obtained at higher concentrations. The electronic absorption of the intermediate species at 470, 620 and 950 nm is quite well reproduced by TD-DFT/ ω B97XD calculations that proved to be an indispensable tool for understanding its molecular structure.

In summary, this work provides fundamental knowledge of the π -dimerization process in oligothienoacene radical cations and it may help to explore new design strategies of π -dimer-based supramolecular architectures for organic electronics.

Experimental Section

Chemicals and reagents

Dichloromethane was freshly distilled from CaH₂ under a dry nitrogen atmosphere. The supporting electrolytes Bu₄NPF₆ (Aldrich) and Bu₄N{B(C₆F₅)₄} were recrystallized twice from absolute ethanol and vacuum-dried at 80 °C overnight.

The *n*-decyl substituents in the α,β terminal positions have been prepared according to the literature.^[38, 40, 56] The SbCl₆⁻ and PF₆⁻ salts of the thianthrenium radical cation (TASbCl₆, TAPF₆) were prepared by the literature methods^[57-59] and a modified literature procedure,^[60] respectively; see Supporting Information for more details.

Spectro-electrochemistry

Cyclic voltammograms were recorded at 298 K under an atmosphere of dry argon in an air-tight three-electrode cell equipped with a 0.125 mm² Pt disk working electrode, a Pt coil counter electrode and a silver wire pseudoreference electrode. Cobaltocenium hexafluorophosphate was used as internal standard for the determination of electrode potentials and signalization of possible effects of adsorption or electrode passivation. The cell in a Faraday cage was connected to a computer-controlled EG&G PAR Model 283 potentiostat or a PGSTAT 302N potentiostat (Metrohm Autolab).

UV-Vis-NIR spectroelectrochemistry was carried at 293 K, using an optically transparent thin-layer electrochemical cell^[61] positioned in the sample compartment of a Scinco S3100 diode array spectrophotometer. The working electrode (Pt minigrid, 32 wires per cm) potential was controlled with a PA4 potentiostat (Laboratory devices, Polná, Czech Republic) or an EmStat 3 USB potentiostat (PalmSens BV, The Netherlands).

Spectroscopy

Conventional UV-Vis-NIR spectra were recorded in a 10-mm quartz cuvette (Hellma) placed in a Cary 5000 UV-Vis-NIR spectrophotometer at room temperature. Aliquots of a freshly prepared TAPF₆ or TASbCl₆ solution in CH₂Cl₂ were added dropwise to the sample solution in the cuvette. After each addition and stirring, a UV-Vis-NIR spectrum was recorded.

EPR spectra were recorded with a JEOL FR30 X-band EPR spectrometer. The samples of **D4T7** in dichloromethane were oxidized with TAPF₆ directly in a narrow EPR tube under an atmosphere of dry argon. Thianthrenium radicals ($g = 2.0081$)^[62] served also as the internal *g*-value standard.

Computational Details

Density Functional Theory (DFT) calculations were carried out by means of the Gaussian 09 program^[63] running on a SGI Origin 2000 supercomputer. The M06L functional^[64] and the standard 6-31G(d) basis set were used.^[65] The M06L functional was chosen due to its ability to describe π - π interactions and estimate the energies of weak intermolecular interactions more efficiently than the B3LYP functional.^[66-67] The chemical doping and electrochemical experiments were conducted in dichloromethane solutions. Accordingly, we also evaluated the impact of the solvent interaction on the π -dimerization of **D4T7^{•+}** radical cations, using two models: (i) a polarizable continuum model (PCM) that considers the solvent (dichloromethane) as a continuous medium with a dielectric constant and represents the solute by means of a cavity built with a number of interlaced spheres^[68-69], and (ii) a discrete/continuous mixed model, where a **[D4T7^{•+}]₂** (CH₂Cl₂)₈ aggregate is combined with the PCM.

In order to get further insight into the role played by the counterions upon high PF₆⁻ concentrations, the optimum structure and stability of **[D4T7^{•+}]₂**(PF₆)₂(CH₂Cl₂)₄ aggregates have been determined in the dichloromethane solution (PCM).

Vertical electronic excitation energies were calculated by using the time-dependent DFT (TD-DFT) approach^[70-72] with the ω B97XD^[73] functional and the 6-31G(d) basis set in a PCM environment on the previously optimized M06L/6-31G(d) molecular geometries. The TD-DFT calculations of the **[D4T7]₂^{•+}**(CH₂Cl₂)₈ and **[D4T7^{•+}]₂**(CH₂Cl₂)₈ aggregates were lightened removing the eight CH₂Cl₂ molecules, since the continuous solvent produces almost identical effects. Molecular orbital contours were plotted using Molekel 4.3.^[74]

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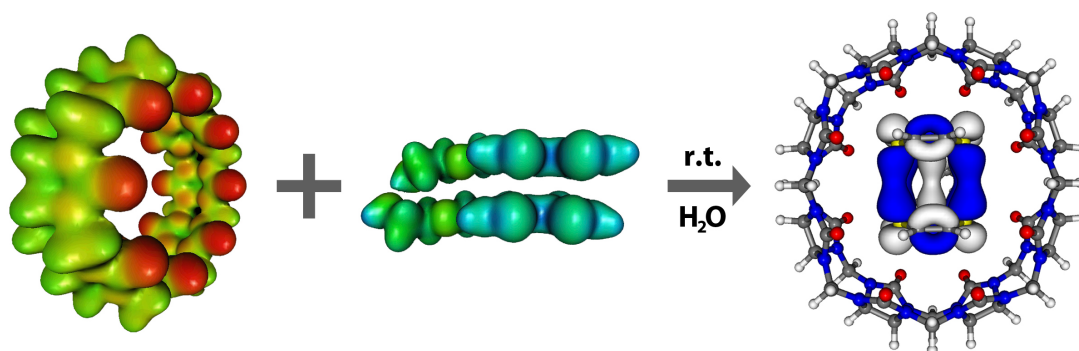
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4.4. Publication 7

The Origin of the Room Temperature Stability of $[\text{TTF}]^{\cdot+} \cdots [\text{TTF}]^{\cdot+}$ Long, Multicenter Bonds Found in Functionalized $\pi\text{-}[\text{R-TTF}]_2^{2+}$ Dimers Included in the Cucurbit[8]uril Cavity



The origin of the room temperature stability of $[\text{TTF}]^{\cdot+}\cdots[\text{TTF}]^{\cdot+}$ long, multicenter bonds found in functionalized π - $[\text{R-TTF}]_2^{2+}$ dimers included in the cucurbit[8]uril cavity

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Abstract: A computational study is carried out to identify the origin of the room temperature stability, in water solution, of functionalized π - $[\text{R-TTF}]_2^{2+}$ dimers (TTF = tetrathiafulvalene; R = $(\text{CH}_2\text{OCH}_2)_5\text{CH}_2\text{OH}$) included in the cavity of a cucurbit[8]uril (CB[8]) molecule. π - $[\text{R-TTF}]_2^{2+}$ dimers in pure water are weakly stable and are mostly dissociated at room temperature. When CB[8] is added to an aqueous π - $[\text{R-TTF}]_2^{2+}$ solution, a $(\pi$ - $[\text{R-TTF}]_2 \subset \text{CB}[8])^{2+}$ inclusion complex is formed. The same complex is obtained after the sequential inclusion of two $[\text{R-TTF}]^{\cdot+}$ monomers in the CB[8] molecule. Both processes are allowed thermodynamically and kinetically. π - $[\text{R-TTF}]_2^{2+}$ dimers dissolved in pure water present a similar $[\text{TTF}]^{\cdot+}\cdots[\text{TTF}]^{\cdot+}$ long, multicenter bond to that already identified in π - $[\text{TTF}]_2^{2+}$ dimers dissolved in organic solvents. Upon their inclusion in CB[8], the strength and other features of the $[\text{TTF}]^{\cdot+}\cdots[\text{TTF}]^{\cdot+}$ long, multicenter bond are preserved. The room temperature stability of the π - $[\text{R-TTF}]_2^{2+}$ dimers included in CB[8] is shown to originate in the π - $[\text{R-TTF}]_2^{2+}\cdots\text{CB}[8]$ interaction, whose strength is due to a strongly attractive electrostatic component and a dispersion component. Such dominant electrostatic term is due to the strongly polarized charge distribution in CB[8], the geometrical complementarity of the π - $[\text{R-TTF}]_2^{2+}$ and CB[8] geometries, and the amplifying effect of the 2+ charge in π - $[\text{R-TTF}]_2^{2+}$.

Introduction

Mono-oxidized tetrathiafulvalene, $[\text{TTF}]^{\cdot+}$, is a common component in solids having conducting,¹ superconducting,² or magnetic³ properties, among other physical properties of technological interest.⁴ However, in many solids $[\text{TTF}]^{\cdot+}$ dimerize and form diamagnetic π - $[\text{TTF}]_2^{2+}$ that results in these solids failing to present the aforementioned technological properties.⁵ The properties of these π - $[\text{TTF}]_2^{2+}$ have been associated to the formation of a $[\text{TTF}]^{\cdot+}\cdots[\text{TTF}]^{\cdot+}$ long, multicenter bond between the two radical cations that constitute the dimer. Long, multicenter bonds have an electronic structure similar to that of conventional covalent bonds, only manifested when the SOMO orbitals of two bonded radicals present a non-negligible overlap, a situation that induces the formation of a bonding and an antibonding combination of these SOMO orbitals.⁶ When the orientation of these two radicals is such that the dimer ground electronic state is dominated by a closed-shell singlet configuration (where such bonding combination is double occupied while the antibonding combination is empty), the dimer becomes diamagnetic and presents similar properties to those associated to covalent bonds.^{6,7,8} However, long, multicenter bonds differ from conventional covalent bonds in their nature, strength, equilibrium distance range and, in all the examples studied up to now, they involve more than one atomic center from each radical.⁶

Stable dimers exhibiting the properties of long, multicenter bonds have also been found in solution at low enough temperatures.^{9,10,11} However, recent experimental studies showed the

presence of stable π -[functionalized-TTF] $_2^{2+}$ dimers at room temperature in dimers involved in supramolecular complexes (vide infra),^{12, 13, 14, 15} which raised doubts about the current understanding of long, multicenter bonds. The increment of the temperature range where π -[TTF] $_2^{2+}$ dimers are stable implies an increase in their strength, a key information when rationalizing their existence in solids presenting properties of technological interest.

Radical ion dimers possessing long, multicenter bonds were first reported in salts of reduced tetracyanoethylene, [TCNE] $\cdot^-$.^{7,8} Many of them present diamagnetic π -[TCNE] $_2^{2-}$ dimers with intradimer distances of ~ 2.9 Å, therefore substantially shorter than the sum of the van der Waals radii (~ 3.4 Å), one of the signatures of the presence of [TCNE] $\cdots$ [TCNE] $\cdot^-$ long, multicenter bonds.^{7,8} Subsequently, long, multicenter bonds have also been found in pairs of other radical anions (e.g. 7,7,8,8-tetracyano-*p*-quinodimethane, TCNQ),¹⁶ dimers of neutral radicals (e.g. phenalenyl and its derivatives),¹⁷ in dimers of radical cations (e.g. the aforementioned TTF),^{5,18} and even in [radical cation] $\cdots$ [radical anion] dimers (e.g. [TTF] $\cdot^+$ $\cdots$ [TCNE] $\cdot^-$).¹⁹ However, although the potential presence of long, multicenter bonded dimers is high, a quest for these dimers is not usually performed in most studies about the nature of the magnetic interactions in radical $\cdots$ radical pairs.²⁰ Isolated dimers between radical ions bound only by long, multicenter bonds are metastable,²¹ with a small barrier with respect to dissociation (typically around 6 kcal $\cdot$ mol $^{-1}$ in π -[TCNE] $_2^{2-}$ or 2 kcal $\cdot$ mol $^{-1}$ in π -[TTF] $_2^{2+}$),²² since the stabilizing terms cannot overcome the electrostatic repulsion term.^{18,23} The key energetic factors behind the existence of long, multicenter bonds in ionic salts are illustrated with a K $_2$ [TCNE] $_2$ aggregate, Figure 1a. As shown before, the stability of this aggregate results from the sum of the cation $\cdots$ anion interactions exceeding the sum of the [radical ion] $\cdots$ [radical ion] and counterion $\cdots$ counterion repulsions.^{18,23} Although the main energetic component for radical ion dimers is the electrostatic term, the dispersive component is also relevant, increasing the stability of long, multicenter bonds.²⁴ It is also worth mentioning that dispersion component of the interaction energy is the dominant component in neutral radicals dimers.^{17c}

As already pointed out, diamagnetic dimers showing all the features of long, multicenter bonding have also been experimentally found in solution. Two well studied cases are the π -[TCNE] $_2^{2-}$,^{23,25} and π -[TTF] $_2^{2+}$ dimers.^{9,10,11} Spectroscopic (UV-vis and EPR) studies of π -[TTF] $_2^{2+}$ in several solvents allowed to determine the thermodynamic parameters of the 2 [TTF] $\cdot^+ \rightleftharpoons$ [TTF] $_2^{2+}$ equilibrium.¹¹ This equilibrium is solvent and temperature dependent. Temperature below -80 °C is required to observe such dimer in dichloromethane, the solvent where the dimer presents the weakest dimerization energy ($\Delta H_{\text{dim}} = -3.8$ kcal $\cdot$ mol $^{-1}$ and $\Delta S_{\text{dim}} = -18$ eu), whereas -40 °C is required in acetonitrile ($\Delta H_{\text{dim}} = -9.1$ kcal $\cdot$ mol $^{-1}$ and $\Delta S_{\text{dim}} = -31$ eu).¹¹ Although the structure of these diamagnetic dimers in solution is not known, their spectroscopic properties suggest that they are similar to that found in crystals. Also UV-vis spectrum remains essentially invariant with the counterion, thus suggesting that counterions are not a key factor in determining the structure of the solvated dimers.¹¹ The presence of long-lifetime long, multicenter bonds in solution is attributed to energetically stable (radical ion) $_2$ solvent $_n$ aggregates that, at their optimum geometries (Figure 1b), allow a non-negligible overlap of the radical ions SOMOs.^{18,23} The origin of the stability of (radical ion) $_2$ solvent $_n$ aggregates has been traced to the [radical ion] $\cdots$ solvent interactions, whose sum exceeds the [radical ion] $\cdots$ [radical ion] repulsion.^{18,23}

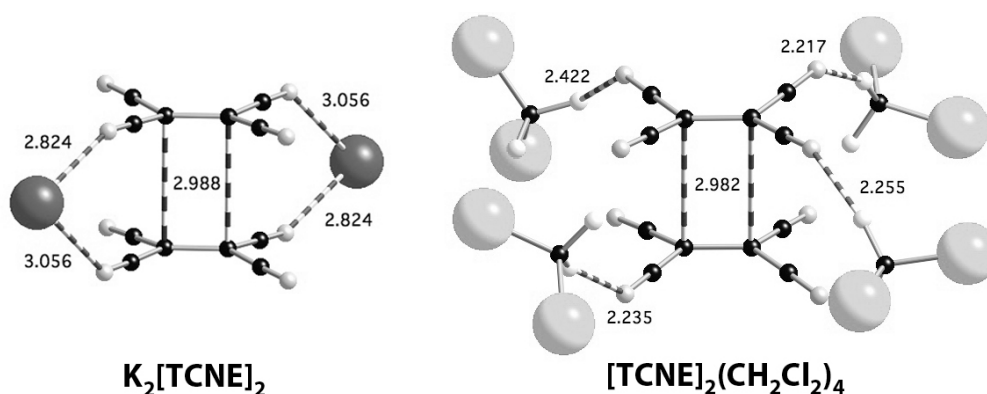


Figure 1. Geometry of the $[\text{TCNE}]_2^{2-}$ found in the $(\text{K}^+)_2[\text{TCNE}]_2^{2-}$ extracted from (left), and the optimum geometry of $[\text{TCNE}]_2^{2-}(\text{CH}_2\text{Cl}_2)_4$ aggregates computationally predicted in dichloromethane solutions (right).

As already pointed out, functionalized π -[TTF] $_2^{2+}$ dimers stable at room temperature have been reported for the following supramolecular complexes (see Figure 2): (a) [functionalized-TTF] $_2^{2+}$ dimers included in charged [3]catenane interlocked rings;¹³ (b) bis-TTF-based molecular clips;¹⁴ (c) double substituted calix[4]arenes;¹⁵ and (d) [functionalized-TTF] $_2^{2+}$ dimers included in cucurbit[8]uril macrocycles.¹² Recent computational studies^{13,26,27} have justified the origin of the room temperature stability of π -[TTF] $_2^{2+}$ dimers in [3]catenanes and in molecular clips, while a rationalization is still pending for the other two families of compounds. In this work the causes of the room temperature stability of R-functionalized π -[TTF] $_2^{2+}$ dimers (π -[R-TTF] $_2^{2+}$) included in the CB[8] macrocycle are identified. CB[*n*] molecules are ring-shaped macrocycles resulting from linking *n* glycoluril monomers, each link consisting in two bi-coordinated methylene bridges.²⁸ They are well-known capable to encapsulate neutral and positively charged compounds.²⁹ This is the case of [functionalized-TTF] $^{+}$ radical cations, which, after the addition of CB[8] to a room temperature aqueous solution, exhibit evidences of spontaneous formation of a stable host-guest complex, (π -[functionalized-TTF] $_2^{2+} \subset \text{CB}[8]$). The authors suggest that the two TTF groups are included inside the CB[8] cavity, with a geometry similar to that for stable π -[TTF] $_2^{2+}$ dissolved in other solvents, leaving the two R groups out of the cavity.¹²

The investigation of the key factors controlling the π -[R-TTF] $_2^{n+}$ and π -[TTF] $_2^{n+}$ insertion in a CB[8] molecule was carried out according to the following four steps: (1) the geometry, stability, and electronic structure of π -[R-TTF] $_2^{n+}$ dimers was determined and compared to that found in π -[TTF] $_2^{n+}$ dimers; (2) the thermodynamics and kinetics of the insertion of π -[R-TTF] $_2^{n+}$ and π -[TTF] $_2^{n+}$ dimers into a CB[8] molecule were evaluated; (3) the properties of the [TTF] $\cdots$ [TTF] $^{+}$ long, multicenter bond present in the (π -[R-TTF] $_2 \subset \text{CB}[8]$) $^{2+}$ inclusion complex were computed and compared with those for the non-included dimer; and (4) the reasons for the room temperature stability of the (π -[R-TTF] $_2 \subset \text{CB}[8]$) $^{2+}$ complex were determined. It is worth mentioning that the results of this study also allow to gain a quantitative understanding of the molecular inclusion of radical cations, which is a part of the wider field of host-guest supramolecular chemistry.³⁰ The study here presented, besides evaluating the impact on the electronic properties of the π -[TTF] $_2^{2+}$ dimers upon the inclusion, provides the first quantitative analysis of the energetics and kinetics of the inclusion in a CB[8] cavity of a single radical cation, the sequential inclusion of two radical cations, and the inclusion of a dication.³¹ It thus expands the types of host-guest complexes on which reliable quantitative information is available.^{30,32}

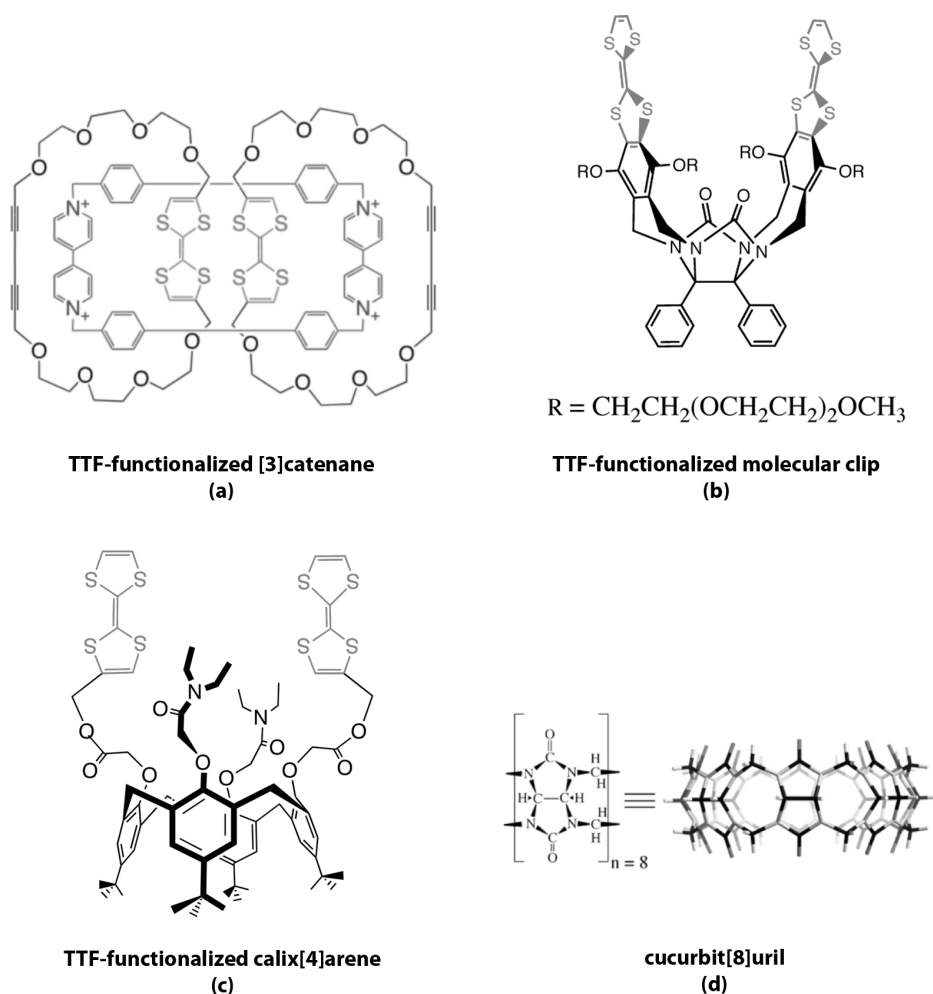


Figure 2. The four families of compounds where functionalized π -[TTF] $_2^{2+}$ dimers stable at room temperature have been reported: (a) [functionalized-TTF] $_2^{2+}$ dimers included in charged [3]catenane interlocked rings;¹³ (b) bis-TTF-based molecular clips;¹⁴ (c) double substituted calix[4]arenes;¹⁵ and (d) [functionalized-TTF] $_2^{2+}$ dimers included in cucurbit[8]uril macrocycles.¹²

Methodological details

All energy evaluations and geometry optimization have been carried out using the M06L density functional³³ and the 6-31G(d) basis set.³⁴ The impact of the lateral groups in the dimer was mimicked by a lateral $R = \text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ group in all calculations involving the π -[R-TTF] $_2^{n+}$ dimer, rather than the longer groups used in the experimental work, $(\text{CH}_2\text{OCH}_2)_5\text{CH}_2\text{OH}$.

A recent article compared the accuracy of more than 20 density functionals (GGA, meta-GGA, hybrid, RSH, and Grimme's dispersion corrections) on the description of long, multicenter bonded dimers (π -[TTF] $_2^{2+}$, π -[TCNE] $_2^{2-}$, π -[TCNB] $_2^{2-}$, and π -[TCNP] $_2^{2-}$) and the M06L functional was shown to successfully reproduce the RASPT2 reference computations based on large active spaces.²² Furthermore, M06L has also been shown to provide satisfactory results in the benchmark of large supramolecular non-bonded complexes, including two inclusion complexes of a CB[n] cavity.³⁵ The basis set was chosen based on previous dimerization studies on π -[TTF] $_2^{2+}$ dimers that showed that the addition of diffuse functions had only a minor impact on the geometric and

energetic properties of these dimers.²⁷ The same conclusion is demonstrated in Table S1 relation to the addition of polarization functions on the hydrogen atoms.

TD-DFT calculations were done using the ω B97X-D functional,³⁶ at the optimum M06L geometries in aqueous solution. The ω B97X-D functional was chosen for these calculations because literature reports indicate that properly predicts absorption spectra for similar organic compounds.³⁷

Solvent effects on the M06L total energy were estimated by means of the PCM continuous model.³⁸ Recent studies on functionalized π -[TTF]₂²⁺ dimers concluded that M06L/PCM calculations properly reproduce the optimum geometry, stability, and long, multicenter bond properties of these dimers.^{26,27}

The impact of the basis set superposition error (BSSE) on the interaction energy of the most relevant complexes studied here was estimated using the counterpoise method³⁹ (Table S2), at the optimum geometry of these complexes. It was found that its impact on their M06L/6-31+G(d) interaction energy is always less than 20%. Thus it will not be explicitly considered further on. It is worth pointing here that the small size of the BSSE computed here the DFT level, much smaller than that found in MP2 or CASPT2 calculation,⁴⁰ is consistent with that previously reported for DFT calculations on hydrogen bonded complexes.⁴¹

The properties of the [TTF]^{•+}...[TTF]^{•+} long, multicenter bond in the (π -[R-TTF]₂ $\subset$ CB[8])²⁺ inclusion complex were quantitatively compared with those for the same dimer when it is out of the CB[8] cavity. Such comparison was done by looking at the characteristic properties of the (3,-1) bond critical points (bcp) that connect the two [TTF]^{•+} groups,⁴² obtained in an Atoms-in-Molecules (AIM) analysis.⁴³

All single point energy calculations, geometry optimizations, and TD-DFT calculations were done using the Gaussian09 package,⁴⁴ while the AIM calculations were carried out using an in-house version of the PROAIM program.⁴⁵

Results and discussion

1. Structure and stability of π -[R-TTF]₂²⁺ dimers

In order to identify the most stable conformation of π -[R-TTF]₂ⁿ⁺ (n = 0, 1, 2), the optimum M06L/6-31G(d) geometry was computed for all possible conformations of each dimer (Figure 3). Table 1 summarizes their relative stability of the n = 0, 1, 2 dimers at their optimum geometry, for isolated and aqueous dimers.

Conformation **1**, where the R groups of both fragments are eclipsed, is the most stable for π -[R-TTF]₂⁺ and π -[R-TTF]₂²⁺ dimers (Table 1), while for n = 0 it is conformation **2**. However, the energy difference between both conformations is small, especially in isolated dimers.

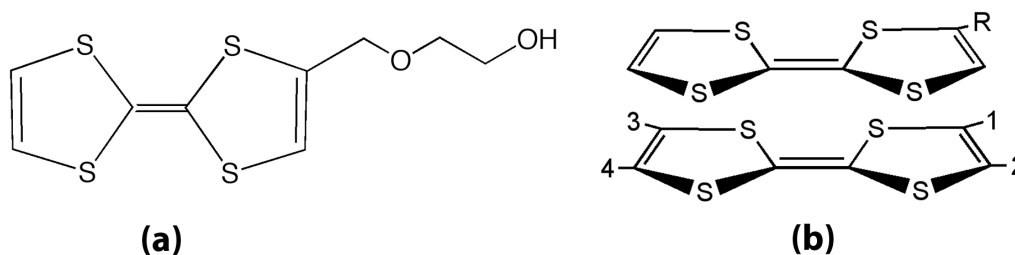


Figure 3. (a) Model of the R-TTF used in our computations. Notice the shorter length of the lateral groups $R = \text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$, compared to those used in the experimental work, $(\text{CH}_2\text{OCH}_2)_5\text{CH}_2\text{OH}$; (b) The four possible conformations concerning the two R groups in a $\pi\text{-[R-TTF]}_2^{2+}$ dimer, identified by numerals in the lower R-TTF fragment of the dimer.

Table 1. Relative stability (in $\text{kcal}\cdot\text{mol}^{-1}$) of the optimum M06L/6-31G(d) geometry of each conformation of the $\pi\text{-[R-TTF]}_2^{n+}$ ($n = 0, 1, 2$) dimers (defined in Figure 3b). The computations were performed on isolated dimers (leftmost data) and aqueous dimers (data in parenthesis). The most stable conformation of each dimer is indicated in *italics*.

Conformation ^a	$\pi\text{-[R-TTF]}_2$	$\pi\text{-[R-TTF]}_2^+$	$\pi\text{-[R-TTF]}_2^{2+}$
1	1.0 (1.4)	<i>0.0</i> (0.0)	<i>0.0</i> (0.0)
2	0.0 (0.0)	0.2 (2.7)	0.4 (3.0)
3	6.2 (6.0)	5.0 (4.4)	4.8 (4.9)
4	6.0 (5.9)	5.0 (4.4)	4.9 (5.0)

^a Position of the substituent in the lower fragment, as defined in Figure 3b

The interaction energies of the most stable conformer of the $\pi\text{-[R-TTF]}_2^{n+}$ ($n = 0, 1, 2$) dimers, at their optimum geometry, are summarized in Table 2, as are the values for $\pi\text{-[TTF]}_2^{n+}$ ($n = 0, 1, 2$) to allow comparisons. Isolated $\pi\text{-[R-TTF]}_2^{n+}$ and $\pi\text{-[TTF]}_2^{n+}$ dimers exhibit negative interaction energies on their neutral and mono-oxidized states, being the latter about twice more stable than the neutral dimers. However, the di-oxidized dimers have positive formation energies, despite being minima (i.e., they are metastable compounds).²¹ Such metastability was subject of a deeper analysis, by comparing the shape of the potential energy curve for the dissociation of the $\pi\text{-[R-TTF]}_2^{2+}$ and $\pi\text{-[TTF]}_2^{2+}$ dimers, Figure 4. Both curves of the isolated species exhibit a minimum at 3.4 – 3.5 Å with a barrier toward dissociation (a maximum is observed around 4.5 Å) of 4.1 $\text{kcal}\cdot\text{mol}^{-1}$ ($\pi\text{-[R-TTF]}_2^{2+}$) and 6.1 $\text{kcal}\cdot\text{mol}^{-1}$ ($\pi\text{-[TTF]}_2^{2+}$).

When these dimers are dissolved in water both maxima disappear and the short-distance minimum becomes more stable than their dissociated fragments. Thus, the three dimers become stable in aqueous solution (solvent effects in these dimers increase with their net charge). As seen in Table 2, $\pi\text{-[R-TTF]}_2^{n+}$ and $\pi\text{-[TTF]}_2^{n+}$ dimers follow similar changes in stability trends from isolated to aqueous media. Therefore, the interaction energy of the three $\pi\text{-[R-TTF]}_2^{n+}$ dimers is $\sim 10 \text{ kcal}\cdot\text{mol}^{-1}$ more stable. This is consistent with the formation of one $\text{O-H}\cdots\text{O}$ and two $\text{C-H}\cdots\text{O}$ hydrogen bonds between the monomer lateral chains, as evidenced on the intermolecular distances of the dimer optimum geometry (see Table S3, where they present the usual metrics expected for hydrogen bonds).⁴⁶ Table 2 also collects the free energy of formation at 298 K in aqueous solution, i.e., $\Delta G(298 \text{ K})$, the relevant property defining the room temperature stability of these dimers. These results indicate that while the neutral dimers are metastable (0.3 and 5.3 $\text{kcal}\cdot\text{mol}^{-1}$ for functionalized and non-functionalized dimers), mono-oxidized dimers are stable (-6.4 and -2.6 $\text{kcal}\cdot\text{mol}^{-1}$, respectively). Finally, the di-oxidized $\pi\text{-[R-TTF]}_2^{2+}$ dimer is weakly stable (-1.4 $\text{kcal}\cdot\text{mol}^{-1}$), while the non-functionalized $\pi\text{-[TTF]}_2^{2+}$ dimer is metastable (2.9 $\text{kcal}\cdot\text{mol}^{-1}$).

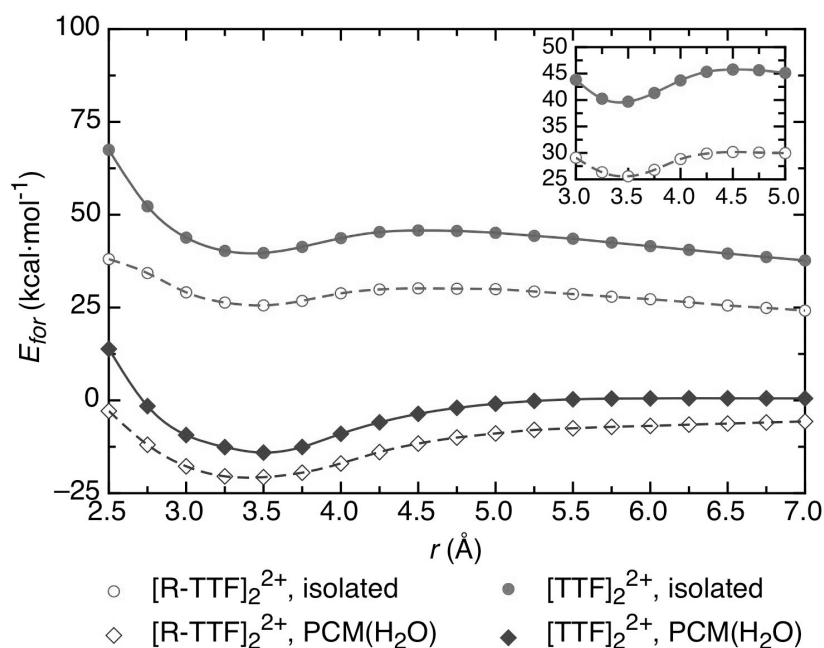


Figure 4. Potential energy curves for the dissociation of the $[R-TTF]_2^{2+}$ and $[TTF]_2^{2+}$ dimers into their $[R-TTF]^{\cdot+}$ and $[TTF]^{\cdot+}$ fragments, computed as a function of the shortest C $\cdots$ C distance (r) at the M06L/6-31G(d) level. In both cases, the curves were computed by increasing the C $\cdots$ C distance in conformation **1**, while allowing all other variables to be fully optimized.

Table 2. Shortest C $\cdots$ C and S $\cdots$ S distances (in Å) between the two radical cations and their interaction energies and free energies of formation at 298 K (both in kcal·mol $^{-1}$) of the π - $[R-TTF]_2^{n+}$ ($n = 0, 1, 2$) dimers. For comparison, the values for π - $[TTF]_2^{n+}$ ($n = 0, 1, 2$) dimers are also included in the lowest three rows. Results obtained at the M06L/6-31G(d) level.

System	C $\cdots$ C	C $\cdots$ C	S $\cdots$ S	S $\cdots$ S	E_{int}	E_{int}	$\Delta G(298\text{ K})$	$\Delta G(298\text{ K})$
	isolated	H $_2$ O	isolated	H $_2$ O	isolated	H $_2$ O	isolated	H $_2$ O
π - $[R-TTF]_2$	3.36	3.34	3.81	3.84	-21.8	-20.6	-0.4	0.3
π - $[R-TTF]_2^+$	3.32	3.34	3.65	3.64	-41.3	-30.8	-17.3	-6.4
π - $[R-TTF]_2^{2+}$	3.44	3.41	3.44	3.36	22.6	-24.8	43.2	-1.4
π - $[TTF]_2$	3.33	3.28	3.80	3.70	-10.6	-9.3	4.6	5.3
π - $[TTF]_2^+$	3.32	3.34	3.67	3.66	-28.3	-19.3	-12.0	-2.6
π - $[TTF]_2^{2+}$	3.43	3.45	3.52	3.45	39.0	-15.2	54.6	2.9

The optimum geometry of the π - $[R-TTF]_2^{n+}$ ($n = 0, 1, 2$) is shown in Figure 5 for isolated dimers and Figure S1 for aqueous dimers. Both classes of dimers present similar geometries, as manifested in the shortest interfragment C $\cdots$ C and S $\cdots$ S distance values (Table 2). Hence, although only the geometry of the isolated dimers will be analyzed in detail, the trends here found can be considered as valid for both classes. The main differences between π - $[R-TTF]_2^{n+}$ and π - $[TTF]_2^{n+}$ geometries is the lack of planarity of the fragments and their relative orientation.⁴⁷ Such differences are attributed to the presence of O-H $\cdots$ O and C-H $\cdots$ O hydrogen bonds between the lateral R chains. Their combined strength is larger than the energy difference between the coplanar and bent conformations (typical strengths of O-H $\cdots$ O and C-H $\cdots$ O hydrogen bonds are around -5 and -2 kcal·mol $^{-1}$, respectively,⁴⁸ whereas, at M06L/6-31G(d) level, the energy difference between the coplanar and bent optimum geometries is only 0.6 kcal·mol $^{-1}$).

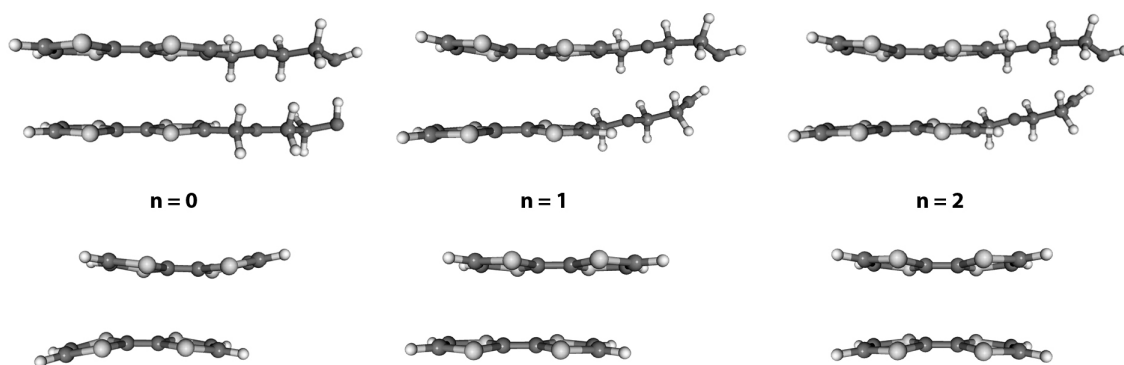


Figure 5. Optimum geometry of isolated π -[R-TTF] $_2^{n+}$ (top) and π -[TTF] $_2^{n+}$ (bottom) dimers ($n = 0, 1, 2$).

At the M06L/6-31G(d) level, the π -[R-TTF] $_2^{n+}$ and π -[TTF] $_2^{n+}$ dimers present the same ground state: a closed-shell singlet when $n = 0$, a doublet when $n = 1$, and a closed-shell singlet when $n = 2$. The ground state properties of π -[R-TTF] $_2^{2+}$ were also investigated at the CASSCF(2,2) level, concluding that π -[R-TTF] $_2^{2+}$ has a predominant closed-shell character, although with a non-negligible open-shell component (the occupation of the HOMO and LUMO orbitals is 1.65 and 0.35, respectively, being the weight of the 20 and 02 configurations⁴⁹ 0.82 and 0.18, respectively). This result manifests the formation of a long, multicenter bond between the [R-TTF] $_2^{+}$ radical cations, similar to that previously found in the π -[TTF] $_2^{2+}$ and other long-bonded dimers.^{18,22,23} This bond formation is associated to the changes in the electronic structure of the dimer, depicted for the π -[R-TTF] $_2^{2+}$ and π -[TTF] $_2^{2+}$ dimers in the MO diagrams of Figure 6. The SOMO orbitals of the radical cations, due to their non-negligible overlap, combine forming a doubly-occupied bonding and an empty antibonding orbitals in the dimer.

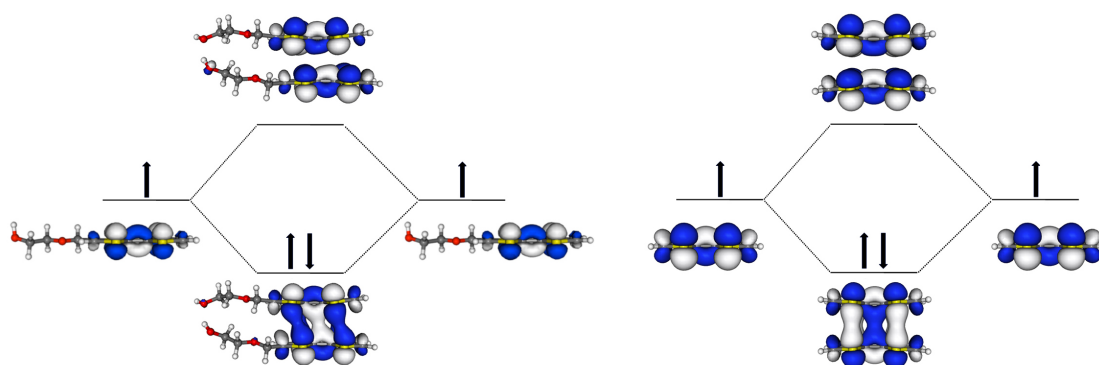


Figure 6. Highest energy region of the molecular orbital diagram of π -[R-TTF] $_2^{2+}$ (left) and π -[TTF] $_2^{2+}$ (right) associated to the interaction of the SOMO of the two radical cations.

2.- Structure and stability of π -[R-TTF] $_2^{n+}$ and π -[TTF] $_2^{n+}$ ($n = 0, 1, 2$) dimers included in the cavity of the CB[8]

The optimum structure and stability of isolated π -[R-TTF] $_2^{n+}$ ($n = 0, 1, 2$) dimers included in the cavity of CB[8], hereafter $(\pi$ -[R-TTF] $_2 \subset \text{CB}[8])^{n+}$, was computed at the M06L/6-31G(d) level (Figure 7, Table 3). In order to study the impact of the R lateral groups in the inclusion process, the optimum structure and stability of isolated π -[TTF] $_2^{n+}$ ($n = 0, 1$, and 2) dimers included in CB[8], hereafter $(\pi$ -[TTF] $_2 \subset \text{CB}[8])^{n+}$, was similarly computed. The optimum geometries of $(\pi$ -[R-TTF] $_2 \subset$

CB[8])ⁿ⁺ and (π -[TTF]₂ ⊂ CB[8])ⁿ⁺ in aqueous solution are depicted in Figures S2-S3. All these calculations were performed on the electronic ground state of each inclusion complex.⁵⁰ Previously, the CB[8] macrocycle was optimized isolated and in aqueous solution (Figure S4). Both optimized geometries are almost identical, and they also are very close to an experimental X-ray reported crystal⁵¹ (the O...O side diameter is 9.9 Å in both optimized structures and 9.7 Å in the reported crystal, and the H...H central diameter is 15.3 Å for both optimized geometries and 15.1 Å for the crystal structure).

The following trends are observed for the optimal geometries of (π -[R-TTF]₂ ⊂ CB[8])ⁿ⁺ and (π -[TTF]₂ ⊂ CB[8])ⁿ⁺, in isolated and aqueous media: (1) the relative disposition of the two TTF fragments in the dimer varies with the net charge, with the two fragments laterally displaced in the n = 0 and 1 complexes, while in the n = 2 dimer the fragments are in an eclipsed conformation; (2) the shortest C...C distance in the n = 0 or 2 complexes is similar to that found in the non-included dimers, and larger in the n = 1 dimers; (3) independent of charge, the π -[R-TTF]₂ⁿ⁺ and π -[TTF]₂ⁿ⁺ dimers have their TTF groups enclosed inside the CB[8] cavity, where their sulfur atoms present short-distance S...O contacts with two oxygen atoms of the CB[8] (each S atom exhibits two contacts of this kind and each oxygen is involved in only one of these contacts); and (4) independent of charge, the π -[R-TTF]₂ⁿ⁺ have their R groups outside the CB[8] cavity.

Interaction energies and free energies of formation at 298 K for the (π -[R-TTF]₂ ⊂ CB[8])ⁿ⁺ and (π -[TTF]₂ ⊂ CB[8])ⁿ⁺ complexes are collected in Table 3. The interaction energy for the inclusion of an isolated π -[TTF]₂ⁿ⁺ (n = 0, 1, 2) dimer into the cavity of the CB[8] is strongly stabilizing, being all E_{int} and ΔG values higher than -60 and -20 kcal·mol⁻¹, respectively (charged dimers are 40-60 kcal·mol⁻¹ more stable than neutral ones and R-functionalized dimers are also around 20 kcal·mol⁻¹ more attractive). These interaction energies, as well as their free energies of formation at room temperature, become less attractive in aqueous solution, although in such media the gain in energy in the inclusion process is still much higher than the average thermal energy at room temperature (lower than 1 kcal·mol⁻¹). Therefore, from a thermodynamic point of view, whatever the dimer net charge is, at 298 K all π -[R-TTF]₂ⁿ⁺ and π -[TTF]₂ⁿ⁺ dimers will spontaneously form (π -[R-TTF]₂ ⊂ CB[8])ⁿ⁺ and (π -[TTF]₂ ⊂ CB[8])ⁿ⁺ when CB[8] is added to the aqueous solution.

As already mentioned, once the [R-TTF] monomers are oxidized, π -[R-TTF]₂²⁺ dimers and [R-TTF]^{•+} monomers may coexist in aqueous solution. Therefore, the energetics of the inclusion of a [R-TTF]^{•+} radical cation into the cavity of a CB[8] to form ([R-TTF] ⊂ CB[8])^{•+}, and the subsequent inclusion of a second monomer, which results in the ultimate formation of (π -[TTF]₂ ⊂ CB[8])²⁺ in a two-steps monomeric pathway, has also to be investigated.

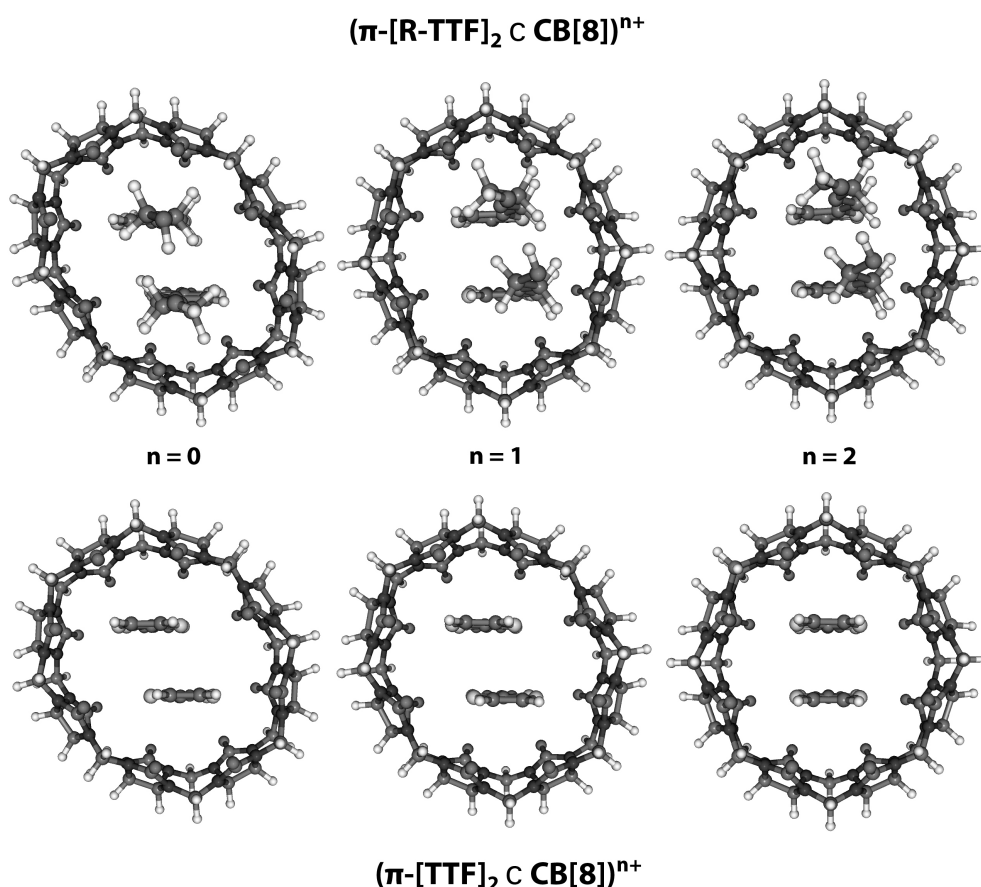


Figure 7. Front view of the optimum geometry of isolated $(\pi\text{-[R-TTF]}_2 \subset \text{CB[8]})^{n+}$ (upper row) and $(\pi\text{-[TTF]}_2 \subset \text{CB[8]})^{n+}$ (lower row) complexes ($n = 0, 1, 2$). The corresponding lateral views are shown in Figures S5-S6.

Table 3. The first two columns collect the shortest interfragment C...C distance between the central C atoms of the two TTF groups in the $(\pi\text{-[R-TTF]}_2 \subset \text{CB[8]})^{n+}$ and $(\pi\text{-[TTF]}_2 \subset \text{CB[8]})^{n+}$ ($n = 0, 1, 2$) dimers. The next two columns collect their interaction energy, whereas the last two columns collect the free energy of formation computed for the inclusion process at 298 K, for isolated and aqueous dimers, respectively. Distances are given in Å and energy values in kcal·mol⁻¹.

System	C...C	C...C	E _{int}	E _{int}	ΔG(298 K)	ΔG(298 K)
	isolated	H2O	isolated	H2O	isolated	H2O
$(\pi\text{-[R-TTF]}_2 \subset \text{CB[8]})$	3.42	3.38	-80.0	-62.9	-24.7	-11.7
$(\pi\text{-[R-TTF]}_2 \subset \text{CB[8]})^+$	3.62	3.60	-128.9	-74.9	-76.0	-29.8
$(\pi\text{-[R-TTF]}_2 \subset \text{CB[8]})^{2+}$	3.41	3.39	-120.9	-78.7	-64.2	-33.3
$(\pi\text{-[TTF]}_2 \subset \text{CB[8]})$	3.42	3.29	-60.9	-45.2	-19.7	-7.0
$(\pi\text{-[TTF]}_2 \subset \text{CB[8]})^+$	3.62	3.46	-117.4	-61.2	-71.2	-24.7
$(\pi\text{-[TTF]}_2 \subset \text{CB[8]})^{2+}$	3.39	3.43	-109.7	-64.8	-58.2	-28.3

Figure 8 plots a schematic view of free energy increments, computed at 298 K, for the two-step monomeric inclusion. In order to facilitate comparison with the previously studied one-step dimer insertion pathway, its free energies are also included in Figure 8 (in both pathways, free energy values are given for isolated and aqueous species). The formation of $(\pi\text{-[R-TTF]}_2 \subset \text{CB[8]})^{2+}$ along the two-step monomeric pathway is exothermic in both steps, both for isolated and aqueous species. On the other hand, the formation of the $\pi\text{-[R-TTF]}_2^{2+}$ from its monomers is endothermic for the isolated species, and are only -1.4 kcal·mol⁻¹ stable in aqueous solution. Thus, in aqueous solution $\pi\text{-[R-TTF]}_2^{2+}$ dimers and their monomers will be in equilibrium at room temperature, being the monomers dominating. However, the inclusion of the dimer into the CB[8] cavity is

strongly exothermic; thus, displacing the equilibrium toward the dimer formation. Consequently, although the thermodynamic properties of the two-step monomeric mechanism are more favorable, both pathways for the formation of $(\pi\text{-[R-TTF]}_2 \subset \text{CB[8]})^{2+}$ are thermodynamically allowed. The same results are obtained for the non-functionalized $(\pi\text{-[TTF]}_2 \subset \text{CB[8]})^{2+}$ inclusion complex formation.

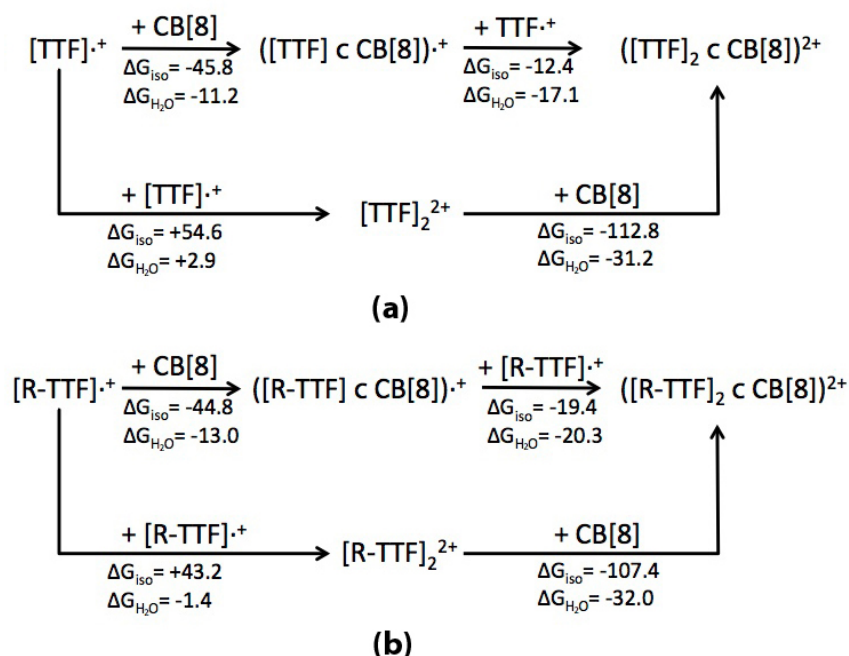


Figure 8. Free energy (at 298 K) for each of the steps for the two-step (upper pathway) and one-step (lower pathway) inclusion of $[\text{TTF}]^{\cdot+}$ radicals into CB[8] in isolated conditions and in water solution. (a) For the formation of a $(\pi\text{-[TTF]}_2 \subset \text{CB[8]})^{2+}$ complex; and (b) for the formation of a $(\pi\text{-[R-TTF]}_2 \subset \text{CB[8]})^{2+}$ complex.

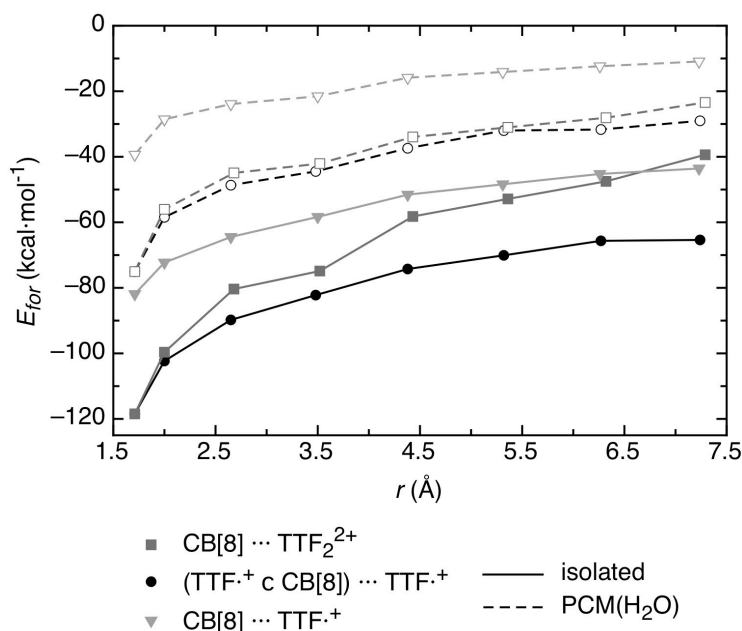


Figure 9. Potential energy curves, computed at the M06L/6-31G(d) level, for the inclusion of $\pi\text{-[TTF]}_2^{2+}$ into the CB[8] , the inclusion of a $[\text{TTF}]^{\cdot+}$ into the CB[8] , and the inclusion of a $[\text{TTF}]^{\cdot+}$ into a $([\text{TTF}] \subset \text{CB[8]})^{\cdot+}$ complex. The parameter r is defined as the distance between the midpoint of the central CC bond of one $[\text{TTF}]^{\cdot+}$ and the center of mass of the CB[8] (even in the dimer's inclusion). The curve in aqueous solution was obtained by doing single point PCM calculations on each optimum geometry of the isolated curve.

The kinetics of the inclusion of a π -[TTF] $_2^{2+}$ dimer into the cavity of the CB[8] was now explored. For such a task, the relaxed potential energy curve was computed in order to explore the possible existence of energetic barriers. These computations were done for the two inclusion pathways described above, and in both cases for isolated and aqueous species (Figure 9). Irrespective of the media, the curves show no barrier for the inclusion of one and two monomers, or the inclusion of the dimer. Therefore, both pathways are kinetically allowed.

As a final step in this section, the presence of possible π -[R-TTF] $_2^{2+} \cdots$ CB[8] exohedral complexes is studied, where the π -[R-TTF] $_2^{2+}$ is not included in the cavity of the CB[8] macrocycle, with the aim of investigating if they could compete in stability with the endohedral structures of Figure 7. π -[R-TTF] $_2^{2+}$ dimers and CB[8] macrocycles could form two types of exohedral complexes: (1) the C-H groups of the dimer could form C-H $\cdots$ X hydrogen bonds where the S and C atoms of CB[8] act as hydrogen acceptor groups; and (2) the C-H groups of CB[8] act as hydrogen bond donor groups against the S and C atoms of TTF, which serve as hydrogen bond acceptor groups. After a series of systematic tests, where various starting structures were tested, the only exohedral minimum energy structure found is shown in Figure S7, where π -[R-TTF] $_2^{2+}$ acts as an acceptor. However, the interaction energy of such exohedral minimum is about 40 kcal·mol $^{-1}$ higher than the inclusion complex (the exohedral structure has an interaction energy of -31.7 kcal·mol $^{-1}$ and a free energy of formation at 298 K of 5.6 kcal·mol $^{-1}$). These energy values render the exohedral minimum as an irrelevant competitor of the $(\pi$ -[TTF] $_2 \subset$ CB[8]) $^{2+}$ inclusion complex and therefore they will not be further considered.

3.- Properties of the long, multicenter bond in π -[R-TTF] $_2^{2+}$ dimers included in the CB[8] macrocycle, $(\pi$ -[R-TTF] $_2 \subset$ CB[8]) $^{2+}$

The definition of a bond between two interacting fragments requires the energetically stability of the dimer or aggregate resulting from the bonding interaction,⁵² a condition that is satisfied when the dimer is thermodynamically stable or also when it is metastable (i.e., thermodynamically unstable but having a barrier for dissociation higher than the available kinetic energy at the working temperature). In isolated [radical ion] $\cdots$ [radical ion] interactions, a barrier is a results of the sum of the repulsive electrostatic component (associated to the ionic part of the radical ion) and the attractive bonding component (associated to its radical character),^{7,8} explaining why isolated π -[TTF] $_2^{2+}$ and π -[R-TTF] $_2^{2+}$ dimers are metastable, while in solution both are stable at low temperatures as a result of the combined impact of the [radical ion] $\cdots$ solvent interactions.^{18,23}

When the π -[R-TTF] $_2^{2+}$ dimer is included in the CB[8] macrocycle, the resulting complex is found to be thermodynamically stable (Figure 8). Since the π -[R-TTF] $_2^{2+}$ geometry and its MO diagram are also preserved after the inclusion (Figures 6 and 10, see also Figure S8), the bonding scheme present in π -[R-TTF] $_2^{2+}$ should also be expected to be similar for the $(\pi$ -[R-TTF] $_2 \subset$ CB[8]) $^{2+}$ inclusion complex. The similarity on the MO diagrams arises from (1) the lack of CB[8] orbitals in the region of the π -[R-TTF] $_2^{2+}$ frontier orbitals; and (2) the geometry preservation of the π -[R-TTF] $_2^{2+}$ dimers, which provides a similar overlap between the orbitals of the fragments in the dimer. Therefore, these features support the presence of a [TTF] $^{\cdot+} \cdots$ [TTF] $^{\cdot+}$ long, multicenter bond between the two radical cations of the π -[R-TTF] $_2^{2+}$ dimer inside the cavity of the CB[8] macrocycle.

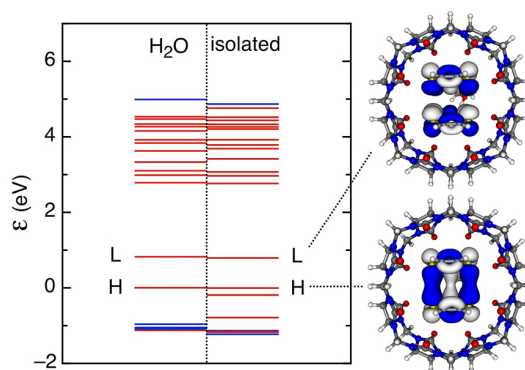


Figure 10. MO diagram of the isolated and aqueous $(\pi\text{-[R-TTF]}_2 \subset \text{CB[8]})^{2+}$ inclusion complex. Blue refer to orbitals located on CB[8], while red identify those located on the $[\text{R-TTF}]^{\cdot+}$ fragments (H and L indicate the HOMO and the LUMO, respectively).

The change in the properties of the $[\text{TTF}]^{\cdot+} \cdots [\text{TTF}]^{\cdot+}$ long, multicenter bond upon the inclusion of the $\pi\text{-[R-TTF]}_2^{2+}$ dimer in the CB[8] can be quantitatively analyzed by doing an Atoms-in-Molecules (AIM) analysis of the (3,-1) bond critical points that connect both radical cations, comparing their values when the dimer is in and out of the CB[8] macrocycle. Isolated non-functionalized $\pi\text{-[TTF]}_2^{2+}$ dimers in their ground state have eight (3,-1) bond critical points connecting the two TTF groups: four S $\cdots$ S and four C $\cdots$ C bonds (Figure 11). In contrast, $\pi\text{-[R-TTF]}_2^{2+}$ has only six bcp, due to the impact of the lateral groups. $\pi\text{-[R-TTF]}_2^{2+}$ dimers embedded in the CB[8] macrocycle also present six bcp (four S $\cdots$ S bonds and two C $\cdots$ C bonds). The characteristic properties of the six bond critical points almost do not change when the dimer is included and non-included in the CB[8] (Table S4). Therefore, the $[\text{TTF}]^{\cdot+} \cdots [\text{TTF}]^{\cdot+}$ long, multicenter bond is preserved upon the inclusion of the $\pi\text{-[R-TTF]}_2^{2+}$ dimer in the CB[8] macrocycle.

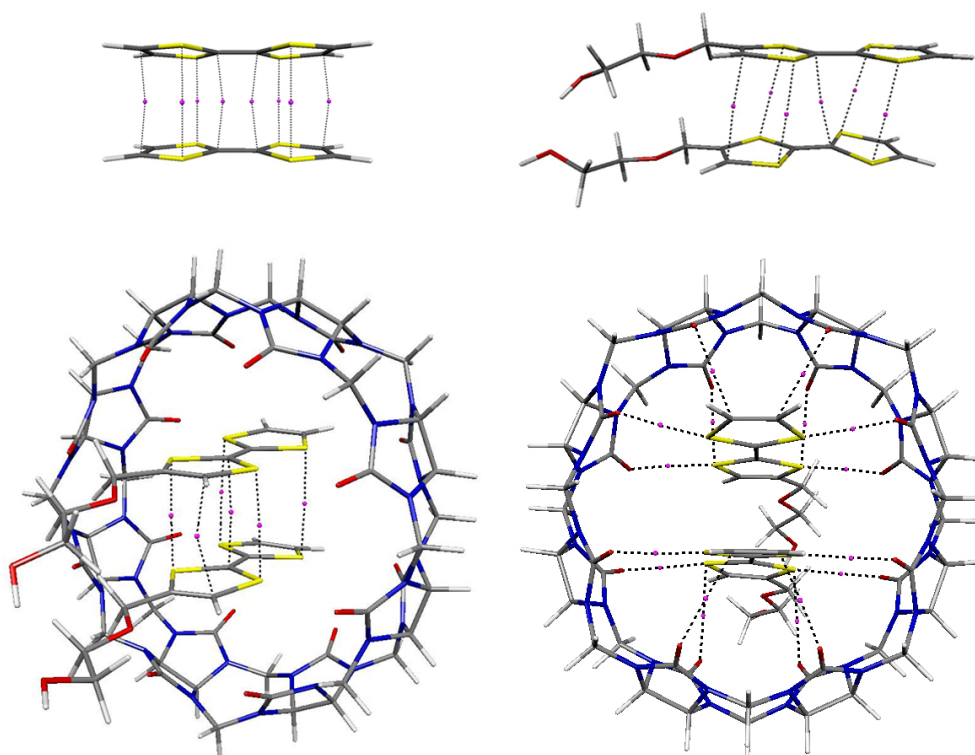


Figure 11. Intradimer (3, -1) bond critical points found in a: $\pi\text{-[TTF]}_2^{2+}$ dimer (top left), $\pi\text{-[R-TTF]}_2^{2+}$ dimer (top right), and $(\pi\text{-[R-TTF]}_2 \subset \text{CB[8]})^{2+}$ inclusion complex (bottom left). (3,-1) bcp found between the $\pi\text{-[R-TTF]}_2^{2+}$ dimers and the CB[8] in the $(\pi\text{-[R-TTF]}_2 \subset \text{CB[8]})^{2+}$ complex (bottom right).

The lowest-lying electronic transitions of the $(\pi\text{-[R-TTF]}_2 \subset \text{CB[8]})^{2+}$ inclusion complex are predicted from a computational analysis at the TD-DFT level and compared to the observed data (Table 4). A small 35-80 nm shift was found between computed and experimental transitions, although the shape of the experimental UV-vis spectrum is fully reproduced (oscillator strengths are also in good agreement with the experimental results).¹² The inclusion of the dimer in the CB[8] macrocycle only produces a ~ 10 nm shift toward lower energies to all computed bands, confirming the preservation electronic structure after its inclusion into the CB[8]. Note also that the computed electronic transitions of the $[\text{R-TTF}]^{\cdot+}$ radical cation match with the experimental UV-vis spectrum.

Table 4. TD-DFT electronic transitions (in nm) obtained at $\omega\text{B97X-D/6-31G(d)}$ level in PCM-water, on M06L/6-31G(d) optimized structures. Oscillator strengths are given in parentheses (dimensionless units). Experimental values are also given, in bold type, to allow comparison (S, M, W stand for strong, moderate, and weak bands, respectively).¹²

Three lowest energy electronic transitions			
$([\text{R-TTF}]_2 \subset \text{CB[8]})^{2+}$	812 (0.3)	483 (0.1)	319 (0.3)
	H $\rightarrow$ L	H-1 $\rightarrow$ L	H $\rightarrow$ L+2
	760 (M)	540 (W)	400 (M)
$[\text{R-TTF}]_2^{2+}$	798 (0.3)	479 (0.2)	313 (0.6)
	H $\rightarrow$ L	H-1 $\rightarrow$ L	H $\rightarrow$ L+2
$[\text{R-TTF}]^{\cdot+}$	538 (0.2)	367 (0.4)	315 (0.1)
	H $\rightarrow$ S	S $\rightarrow$ L+1	H-4 $\rightarrow$ S
	580 (M)	430 (S)	350 (M)

4. - Origin of the room temperature stability of the $\pi\text{-[R-TTF]}_2^{2+}$ dimer included in the cavity of the CB[8] macrocycle

Experimental studies show that at 298 K $\pi\text{-[TTF]}_2^{2+}$ dimers are completely dissociated in solution, independent of solvent,¹¹ whereas aqueous $\pi\text{-[R-TTF]}_2^{2+}$ dimers to which CB[8] is added do form $(\pi\text{-[R-TTF]}_2 \subset \text{CB[8]})^{2+}$ inclusion complexes, where the dimer structure is preserved even at 298 K.¹² Our M06L/6-31G(d) results reproduce these trends, indicating a possible mechanism for the inclusion. These calculations also indicate that a long, multicenter bond is present in the aqueous $\pi\text{-[R-TTF]}_2^{2+}$ dimer, in accord with the AIM analysis. The computed UV-vis spectra of these complexes are also in good agreement with experimental results. Identification of the origin of the greater stability of $\pi\text{-[R-TTF]}_2^{2+}$ after its inclusion in the CB[8] macrocycle, however, is sought. As the AIM results point out that the structure of the $\pi\text{-[R-TTF]}_2^{2+}$ and CB[8] fragments is preserved upon the formation of the $(\pi\text{-[R-TTF]}_2 \subset \text{CB[8]})^{2+}$ complex, the origin of the extra stability of the $\pi\text{-[R-TTF]}_2^{2+}$ dimers included in the cavity of the CB[8] can only be attributed to the $\pi\text{-[R-TTF]}_2^{2+} \cdots \text{CB[8]}$ intermolecular interaction. This prompted us the study of its properties.

The nature of the intermolecular interaction between two molecules, A and B, can be computationally determined by identifying the dominant energetic component in its interaction energy. Accurate perturbative methodologies, such as the IMPT method,⁵³ provide accurate expressions for such interaction energy. Assuming, as is commonly valid, that the polarization (E_{pol}) and charge-transfer (E_{ct}) components of the IMPT interaction energy are much smaller than any of the remaining components,⁵⁴ the IMPT intermolecular interaction energy between two open shell molecules can be written as:^{17c}

$$E_{int} \approx E_{er} + E_{el} + E_{disp} + E_{bond} \quad (1),$$

where: E_{er} is the exchange-repulsion energetic component (always energetically repulsive, due to the repulsion that electrons feel when they occupy the same point of the space, in accord with the Pauli Exclusion Principle);⁵⁵ E_{el} is the electrostatic energetic component of the non-polarized system;⁵⁶ E_{disp} is the dispersion energetic component;⁵⁷ and E_{bond} is the bonding energetic component, associated to the pairing of the unpaired electrons of fragments A and B. As E_{er} is always energetically repulsive, the remaining three terms (E_{el} , E_{disp} , and E_{bond}) are the only ones that can be responsible for the formation of stable AB complexes. Therefore, they require a further analysis when trying to find the dominant component of the π -[R-TTF]₂²⁺...CB[8] intermolecular interaction.

Among these three possible attractive components, E_{bond} is negligible due to the closed-shell nature of CB[8] and the predominant closed-shell nature of the diamagnetic π -[R-TTF]₂²⁺ dimer. In relation to the other two terms, the value of E_{disp} can be estimated as the difference between the MP2 and HF interaction energies (-168.6 and -105.2 kcal·mol⁻¹, respectively, i.e., E_{disp} = -63.4 kcal·mol⁻¹). The E_{el} term can be estimated by applying the usual $\sum_{i(A),j(B)} q_i(A)q_j(B)/r_{ij}$ expression, where $q_i(A)$ and $q_j(B)$ are the net atomic charge of atom i (of molecule A) and atom j (of molecule B), extracted from a Mulliken Population Analysis of these two molecules in aqueous solution, and r_{ij} is the interatomic distance. A value of -108.5 kcal·mol⁻¹ is computed when the complex is in aqueous solution (-89.6 kcal·mol⁻¹ is estimated for the isolated complex). Thus, the π -[R-TTF]₂²⁺...CB[8] intermolecular interaction in the (π -[R-TTF]₂ $\subset$ CB[8])²⁺ inclusion complex is electrostatic-dispersion, in about a 2:1 relative weight.

The dispersive character of the π -[R-TTF]₂²⁺...CB[8] intermolecular interaction is expected, in accord with the above AIM results (Figure 11), where twelve S...O and four C...O bcp connect the π -[TTF]₂²⁺ and CB[8] interacting fragments (with the expected features of van der Waals interactions, Table S4). However, the strong dominance of the π -[R-TTF]₂²⁺...CB[8] intermolecular interaction requires of a further analysis.

The unusually large magnitude of the electrostatic component can be attributed to: (1) the strong polarization of the charge distribution in both interacting fragments, Figure 12; (2) the geometrical complementarity of their charge distributions; and (3) the 2+ charge for π -[R-TTF]₂²⁺, which amplifies the previous two effects. The combined impact of these complex polarized charge distributions is reflected in the molecular electrostatic potential (MEP) maps of the two interacting fragments (Figure 12). These maps visually locate the regions where the electron localization makes the net charge negative (red colored regions) or positive (blue regions). The energetically favored conformations of the electrostatic component arise when regions of opposite sign are overlapped. As expected, these regions are in good agreement with the optimum geometries computed above and with the position of their bcp.

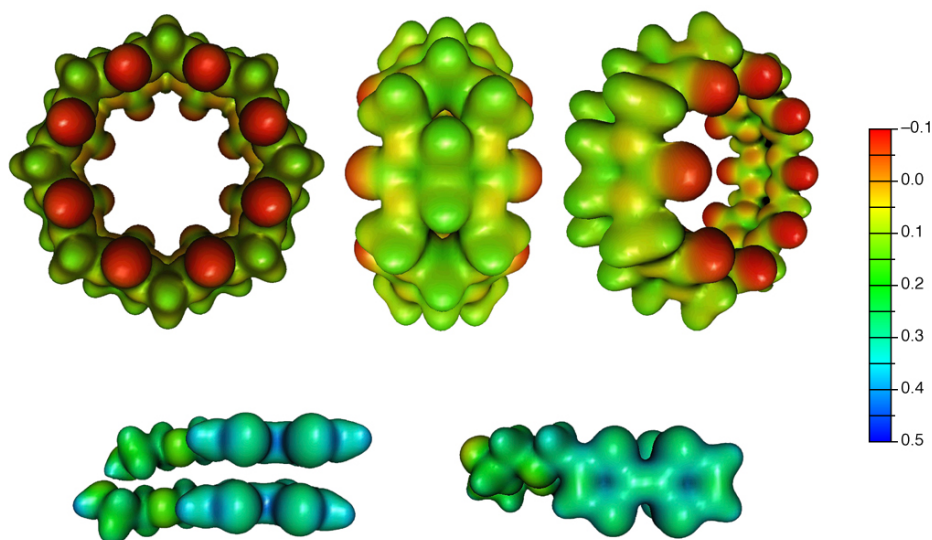


Figure 12. Molecular electrostatic potential (MEP) maps (0.02 a.u. isosurface electronic density) for the CB[8] (top three views, taken from an on-top: 0°, 90°, and 45° perspectives) and the π -[R-TTF]₂²⁺ dimer (bottom two views: top and side views). The energy scale used in all maps is that indicated in the right.

The MEP maps of π -[R-TTF]₂²⁺ indicate that the net positive charge is spread over the TTF units quite uniformly, although presenting a smaller positive charge on the S atoms. However, an analysis of the CB[8] electronic distribution suggests a strong polarization of charge, with strongly negative MEP regions on the oxygen atoms, and the presence of moderately positive MEP regions on the remaining atoms. Given the strong polarization of the electronic density in CB[8], non-negligible local dipole moments are created around the two ends of the CB[8] cavity (however, the macrocycle net dipole is negligible due to the CB[8] symmetry). Consequently, the electrostatic component of the π -[R-TTF]₂²⁺...CB[8] interaction should be more properly seen as the addition of local charge...(local dipole) interactions, rather than a charge...(neutral molecule; negligible net dipole) interaction. The geometrical complementarity of the two interacting molecules allows a maximization of these charge...(local dipole) interactions, while the 2+ charge of the dimer amplifies its net effect. All of these findings about the origin of the stability of the $(\pi$ -[R-TTF]₂ $\subset$ CB[8])²⁺ complex represent the first quantitative data on the molecular inclusion of radical ions and their dimers in CB[8] molecules. Therefore, they are also relevant for host-guest supramolecular chemistry. These results demonstrate the relevance and origin of the electrostatic energetic component of the interaction energy and the high impact of the dispersion component.

Conclusions

The reasons behind the room temperature stability of aqueous π -[R-TTF]₂²⁺ dimers included in the cavity of the CB[8] macrocycle have been investigated by means of first-principles M06L/6-31G(d) calculations. From the computed structure and stability for the most stable conformation of the π -[R-TTF]₂ⁿ⁺ (n = 0, 1, 2) dimers in aqueous solution it was concluded that the presence of R groups induces minor changes in their optimum geometry. The free energy of the inclusion process at 298 K in aqueous solution is in good agreement with their observed room temperature stability. A systematic search for minimum energy structures of exohedral π -[R-

TTF]₂²⁺...CB[8] complexes showed that their stability is remarkably lower than that for the included complex.

The overall perspective that the results of the M06L/6-31G(d) calculations provide on the stability of π -[R-TTF]₂²⁺ dimers in aqueous solutions containing CB[8] is the following: (1) π -[R-TTF]₂²⁺ dimers in pure aqueous solution should be mostly dissociated into [R-TTF]^{•+} monomers; (2) after the addition of CB[8] to the aqueous solution, [R-TTF]^{•+} monomers exhibit a strong energetic preference toward forming (π -[R-TTF]₂ $\subset$ CB[8])²⁺ following a two-step exothermic barrierless process where one [TTF]^{•+} is included in each step; (3) π -[R-TTF]₂²⁺ dimers in the presence of CB[8] also shows a strong energetic preference toward forming (π -[R-TTF]₂ $\subset$ CB[8])²⁺ in a one-step barrierless process; (4) the stability of the π -[R-TTF]₂²⁺ dimers in aqueous solution containing CB[8] at room temperature is due to the high exothermicity of the π -[R-TTF]₂²⁺...CB[8] intermolecular interaction in the (π -[R-TTF]₂ $\subset$ CB[8])²⁺ complex and not to an increase in the strength of the [TTF]^{•+}...[TTF]^{•+} long, multicenter bond found in π -[R-TTF]₂²⁺ dimers; (5) an analysis of the components of the π -[TTF]₂²⁺...CB[8] interaction energy shows that such interaction is dominated by the electrostatic component, combined by a weaker dispersion component; (6) the strong electrostatic component in the π -[TTF]₂²⁺...CB[8] interaction is mostly due to the strongly polarized charge distribution in CB[8] (better seen as a sum of strong charge...(local dipoles) terms), whose strength gets increased by the geometrical complementarity of the two interactions molecules and the amplifying effect of the 2+ charge in one of them.

The [TTF]^{•+}...[TTF]^{•+} long, multicenter bond found in the π -[TTF]₂²⁺ dimers is identified when they are in and out of the CB[8] cavity. The strength and other properties of these bonds are preserved upon the dimer inclusion into the CB[8] cavity. The ultimate cause for such preservation upon inclusion is the energetic mismatch between the π -[R-TTF]₂²⁺ and the CB[8] orbitals, which prevents their combination in the inclusion complex orbitals. Consequently, the density of the inclusion complex is a sum of the fragments densities, a fact that preserves the bond critical points in the electron density of the dimer in the inclusion complex. This also explains why the UV-vis spectrum of the π -[R-TTF]₂²⁺ dimers is also preserved upon inclusion.

Finally, the results here presented constitute the first analysis of the energetic keys that govern the molecular inclusion of single-charged radical ions and their double-charged diamagnetic dimers, specifically in a CB[8] molecule. These results are thus also of interest to gain a better understanding of this type of host-guest supramolecular processes. The mechanism of inclusion is found to be thermodynamically and kinetically allowed for the sequential inclusion of one or two radical ions, as well as for the direct inclusion of the dimer and the origin of the increased stability of the host-guest complex in solution was identified. All these results should contribute to the design of other host-guest complexes presenting similar or improved properties.

Acknowledgments

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Supporting Information

Optimized geometries of aqueous π -[R-TTF] $_2^{n+}$ dimers; Additional views of the inclusion complexes; Optimum geometry of the exohedral CB[8] $\cdots\pi$ -[R-TTF] $_2^{2+}$ complex; SOMO of the [R-TTF] $^{+}$ radical cation prior and upon inclusion; Geometry parameters and Mulliken population analysis for the π -[R-TTF] $_2^{n+}$ dimers; Impact of polarization in hydrogen atoms effects in the basis set; Impact of the BSSE in four complexes; AIM analysis details.

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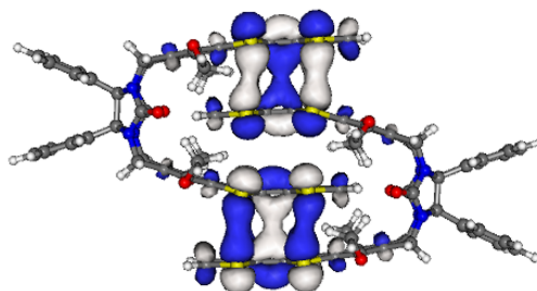
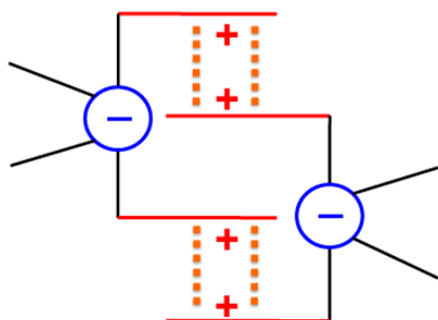
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- 57 A non-classical term that arises from the instantaneous dipole-dipole interactions resulting from the correlated motions of electrons in A and B (see references 53, 54).

4.5. Publication 8

**Keys for the Existence of Stable Dimers of Bis-TTF-Functionalized Molecular Clips
Presenting $[\text{TTF}]^{\cdot+} \cdots [\text{TTF}]^{\cdot+}$ Long, Multicenter Bonds at Room Temperature**



Keys for the Existence of Stable Dimers of Bis-tetrathiafulvalene (bis-TTF)-Functionalized Molecular Clips Presenting $[\text{TTF}]^{\bullet+} \cdots [\text{TTF}]^{\bullet+}$ Long, Multicenter Bonds at Room Temperature

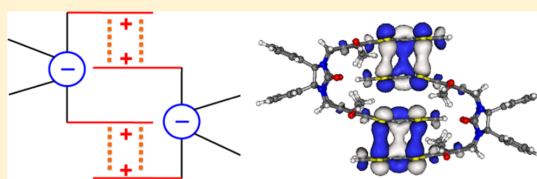
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Supporting Information

ABSTRACT: A systematic theoretical and computational investigation is performed to determine the keys governing the existence, in acetonitrile solutions, of dimers of bis-tetrathiafulvalene (bis-TTF)-functionalized diphenylglycoluril molecular clips (clip_2^{n+}) that are stable at room temperature for $n \leq 4$. Although the experimental structure of these dimers in solution is unknown, electronic absorption studies suggest that they have $[\text{TTF}]^{l+} \cdots [\text{TTF}]^{m+}$ interactions that are preserved at room temperature (note that when $l = m = 1$ these interactions become long, multicenter bonds). In good agreement with the interpretation of the experimental spectroscopic data, all clip_2^{n+} dimers whose charge is ≤ 4 present an optimum geometry that, in all cases, has three short interfragment $[\text{TTF}]^{l+} \cdots [\text{TTF}]^{m+}$ interactions. The computed $\Delta G(298 \text{ K})$ for these optimum structures matches the available experimental data on the stability of these dimers. Such optimum geometry, combined with the zwitterionic character of the electron distribution in monomers and dimers (most of the net positive charge is equally distributed among the TTF groups, while a $1 - \text{au}$ charge is located in the central fused five-membered rings) allows the formation of a maximum of two long, multicenter $[\text{TTF}]^{\bullet+} \cdots [\text{TTF}]^{\bullet+}$ bonds when all TTF groups host a $1 + \text{au}$ of charge, as in clip_2^{4+} . However, these long, multicenter bonds alone do not account for the stability of clip_2^{n+} dimers at room temperature. Instead, the studies carried out here trace the origin of their stability to (1) the zwitterionic character of their charge distribution, (2) the proper geometrical shape of the interacting monomers, which allows the intercalation of their arms, thus making possible the simultaneous formation of two short contacts, both involving the positively charged TTF group of one monomer and the negatively charged central ring of the other, (3) the simultaneous presence of three short contacts among the TTF groups in the optimum geometry of the clip_2^{n+} dimers, which become two long, multicenter bonds and one van der Waals interaction when the four TTF groups host a $1 +$ charge, and (4) the net stabilizing effect of the solvent.



1. INTRODUCTION

The electron donating capabilities of tetrathiafulvalene (TTF) make its mono- and dioxidized forms (i.e., $[\text{TTF}]^{\bullet+}$ and $[\text{TTF}]^{2+}$) useful building blocks in solids having conducting,¹ superconducting,² magnetic,³ or other physical properties.⁴ These oxidized forms are also found in supramolecular host–guest systems that act as sensors⁵ or in organic electronics devices, such as organic field-effect transistors (OFETs).⁶ However, in some cases the oxidized $[\text{TTF}]^{\bullet+}$ can form diamagnetic dimers that are unusable for the aforementioned physical properties. Consequently, a proper understanding of the dimerization processes is desirable in order to control the final physical properties of TTF-based materials.

The nature of the intermolecular interactions between radical ions has been a subject of great interest particularly since the discovery of multicenter, long bonds in their crystals^{7,8} and solutions.^{7b,9,10} In the solid state, this type of bond was first reported and characterized in salts of reduced tetracyanoethylene (TCNE),⁷ where $\pi\text{-}[\text{TCNE}]_2^{2-}$ diamagnetic dimers

showing interfragment distances substantially shorter than the sum of the van der Waals radii but larger than conventional covalent C–C bonds have been detected (the shortest interfragment distance in $\pi\text{-}[\text{TCNE}]_2^{2-}$ dimers is $\sim 2.9 \text{ \AA}$).⁷ Subsequently, an increasing number of organic radicals have been reported to have similar dimers with sub-van der Waals intradimer separations. These include, for instance, cyanil¹¹ and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ),¹² neutral radicals, such as phenalenyl and its derivatives,¹³ and radical cations, such as tetrathiafulvalene (TTF).^{14,15} Additionally, long, multicenter bonding has been reported in zwitterionic $\pi\text{-}[\text{TTF}^{\delta+} \cdots \text{TCNE}^{\delta-}]$.¹⁶ Kochi and co-workers performed an exhaustive study of the stability of various long bonded dimers in several solvents, among them the $\pi\text{-}[\text{TTF}]_2^{2+}$ dimer.¹⁷ The enthalpy and entropy of dimerization of $\pi\text{-}[\text{TTF}]_2^{2+}$ in several solvents was estimated: in dichloromethane, these two

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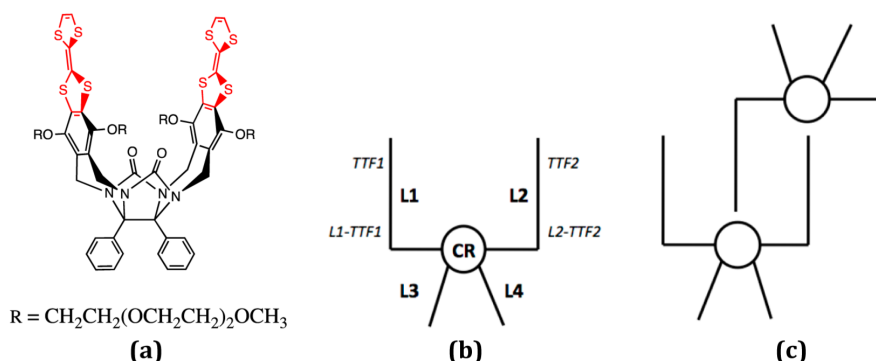


Figure 1. (a) Structure of a bis-TTF-functionalized diphenylglycoluril molecular clip, clip_1^{n+} ; (b) schematic representation of its structure, where one can observe five constituent groups, (1) central ring (CR) made out of the central fused five-membered rings, (2, 3) the two long arms, pointing upward from the central ring (L1 and L2, each having one TTF group at their end, TTF₁ and a six-membered ring, L₁-TTF₁), and (4, 5) the two short arms, pointing down (L3 and L4); (c) schematic representation of the proposed structure of clip_2^{n+} dimers.²⁵

properties become $-3.8 \text{ kcal mol}^{-1}$ and -18 eu , respectively, while in acetonitrile, their corresponding values are $-9.1 \text{ kcal mol}^{-1}$ and -31 eu , respectively. The formation of $\pi\text{-}[\text{TTF}]_2^{2+}$ dimers in dichloromethane was not observed above -80°C , while the higher polarity of acetonitrile increased this temperature up to -40°C .¹⁷

Previous studies concluded that long, multicenter bonds share all the properties of conventional covalent bonds except their nature, range of stability, and range of equilibrium distance.^{7,8,18} Thus, long, multicenter bonded dimers of charged radicals (such as $\pi\text{-}[\text{TCNE}]_2^{2-}$ or $\pi\text{-}[\text{TTF}]_2^{2+}$) are metastable. From a theoretical perspective, such metastable character arises from the repulsive Coulombic term (E_{el} , caused by their ionic character), which exceeds the sum of the attractive bonding (E_{bond} , due to their radical character) and dispersion energetic terms (E_{disp}), a nonclassical component resulting from the interactions of the instantaneous multipoles produced in both fragments by the motion of the other fragment electrons.^{10,19} However, as can already be demonstrated in small (radical ion)₂counterion₂ aggregates, long, multicenter bonds between charged radicals are formed in the solid state whenever the sum of the attractive (radical ion)⋯counterion interactions overcomes the repulsion between the radical ions participating in the long bond, plus the repulsion between the two counterions.^{10,14,19} Likewise, in solution, long bonds are stabilized because the sum of the (radical ion)⋯solvent interactions and solvent⋯solvent interactions exceeds the repulsion between the radical ions involved in the long bond.

Some oxidized [TTF-functionalized] species form stable $[\text{TTF-functionalized}]_2^{2+}$ dimers at room temperature. This behavior has been reported for four families of compounds: (a) $[\text{TTF-functionalized}]_2^{2+}$ dimers included in charged [3]-catenane interlocked rings,²⁰ whose special experimental properties have been explained on the basis of long bonds after doing an exhaustive theoretical study;^{20,21} (b) $\pi\text{-}[\text{TTF}]_2^{2+}$ included within the cavity of a cucurbit[8]uril, CB[8]²² (note, in passing, that dimers of methylviologen included in CB[8] are also stable at room temperature);²³ (c) doubly substituted calixarenes;²⁴ (d) acetonitrile solutions of bis-TTF-functionalized diphenylglycoluril molecular clips²⁵ whose dimers in solution are presumed to have sub-van der Waals $[\text{TTF}]^{\bullet+}\cdots$

$[\text{TTF}]^{\bullet+}$ interactions at room temperature, for reasons not yet fully understood.

Here, we focus our attention on the last type of case, trying to rationalize its experimental behavior. Bis-TTF-functionalized diphenylglycoluril molecular clips (clip_1^{n+}) are rigid structures that can be viewed as a central rigid core (the fused five-membered rings) to which two adjacent long arms and two adjacent short arms are attached, the two long arms pointing in opposite direction relative to the short arms (Figure 1). Each long arm has one TTF group attached at its end, which does not interact with the TTF group of the other arm, and a lateral -OR group ($R = \text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OCH}_3$) that increases the solubility of the molecular clip. Initially, bis-TTF-functionalized clips are obtained as neutral monomers, clip_1^0 . However, as in isolated TTF molecules, each TTF group clip_1^0 can be oxidized up to a maximum of 4+ per molecular clip (a maximum value of 2+ per group, that is, up to clip_1^{4+}). Voltammetric techniques allow the controlled formation of all oxidized monomers, whose positive charge is presumably delocalized over the noninteracting TTF groups. Mass spectroscopy studies²⁵ indicated the presence of clip_2^{n+} dimers stable at room temperature for $0 < n \leq 4$. Since the UV spectrum of these stable clip_2^{n+} dimers finds the characteristic features of short $[\text{TTF}]^{\bullet+}\cdots[\text{TTF}]^{\bullet+}$ long, multicenter bonds, even at room temperature, the structure in Figure 1c²⁵ was proposed. However, a full rationalization of their structure and all the other experimental results, based on sounding theoretical studies, has never been done.

The present work provides a rationalization of the experimental properties of bis-TTF-functionalized diphenylglycoluril molecular clips, based on exhaustive M06L computations on all clip_1^{m+} ($m = 0\text{--}4$) monomers and clip_2^{n+} ($n = 0, 1, 2, 3, 4, 6$, or 8) dimers. The $n = 6$ and $n = 8$ dimers were taken as representative of the behavior of $n > 4$ dimers. For each clip_2^{n+} dimer, its optimum geometry was computed and the resulting structure was analyzed focusing on the existence of short $[\text{TTF}]\cdots[\text{TTF}]$ contacts between its two monomeric fragments. Additionally, the stability of clip_2^{n+} with respect to dissociation into clip_1^{l+} and clip_1^{m+} (the sum of the monomer charge is equal to that for the dimer, that is, $n = l + m$) was also evaluated. The electronic structure and charge distribution of clip_1^{m+} and clip_2^{n+} was also computed. These studies were first performed on isolated dimers and then on dimers dissolved in

acetonitrile. Finally, the nature of the interaction energy was analyzed in order to determine the origin of the room temperature stability of the clip_2^{n+} ($n = 0-4$) dimers in acetonitrile solutions. These studies had three final aims: (a) determining the key features that govern the self-association of clip_2^{n+} dimers and how they vary with the dimer net charge; (b) finding how many, if any, sub-van der Waals $[\text{TTF}]^{4+} \cdots [\text{TTF}]^{m+}$ contacts are long, multicenter bonds; (c) comparing the bond energy of the long, multicenter $[\text{TTF}]^{4+} \cdots [\text{TTF}]^{m+}$ bond formed in clip_2^{4+} with that found in the $\pi\text{-}[\text{TTF}]_2^{2+}$ dimer and finding the reasons for the room temperature stability of clip_2^{n+} , $n \leq 4$. These findings are needed for a better understanding of the $[\text{TTF}]^{n+}$ dimerization, as well as to improve the current understanding of the properties of long, multicenter $[\text{TTF}]^{4+} \cdots [\text{TTF}]^{m+}$ bonds. They also provide an in depth quantitative knowledge of the self-association of diphenylglycoluril molecular clips, here systematically studied as a function of the monomer oxidation state. To the best of our knowledge, this is the first time that an exhaustive study of this kind is reported.

2. METHODOLOGICAL DETAILS

Previous studies on $\pi\text{-}[\text{TTF}]_2^{2+}$ dimers in solution¹⁵ concluded that the presence of $[\text{TTF}]^{4+} \cdots [\text{TTF}]^{m+}$ long, multicenter bonds in solution and all their known physical properties can be properly described by $\pi\text{-}[\text{TTF}]_2^{2+}(\text{solvent})_m$ aggregates, m being a reasonably small value that allows the inclusion of the dominant energetic components of the $\pi\text{-}[\text{TTF}]_2^{2+}$ dimer first solvation shell. Recent work on functionalized $\pi\text{-}[\text{TTF}]_2^{2+}$ dimers²¹ demonstrated that the PCM continuous solvent model²⁶ completely reproduces the stability in solution of these dimers, their optimum geometry, and the presence of long, multicenter bonds. Therefore, the PCM method was chosen in this work for the studies in solution. In none of the previous studies were counterions included in the model aggregates. Furthermore, experimental evidence²⁷ indicates that counterion-containing aggregates are not usually formed in solution at the concentration range employed in the $\pi\text{-}[\text{TTF}]_2^{2+}$ and clip_2^{n+} experimental studies.^{17,25}

The computational study of the properties of the dimers of bis-TTF-functionalized diphenylglycoluril molecular clips is carried out hereafter in four consecutive steps. First of all, the optimum geometry and the ground state electronic structure of isolated clip_1^{m+} ($m = 0-4$) monomers are computed and analyzed, in order to gain insight into the nature of the $\text{clip}_1^{4+} \cdots \text{clip}_1^{m+}$ interaction. Such information is used to guide the search for the optimum geometry of the isolated clip_2^{n+} ($n = 0, 1, 2, 3, 4, 6$, or 8) dimers, at their electronic ground state, carried out in the second step. In the third step, the optimum structure of isolated clip_1^{m+} and clip_2^{n+} computed before is reoptimized using the PCM continuous model,²⁶ thus accounting for the solvent effects. Finally, in the fourth and last step, in order to determine the origin of the room temperature stability of the clip_2^{n+} ($n = 0-4$) dimers in acetonitrile solutions, an energy partition analysis of the interaction energy of these dimers is carried out.

All energy computations were performed (on their electronic ground state) using the M06L density functional²⁸ and the 6-31G(d,p) basis set.²⁹ The use of a pure meta-GGA functional reduces significantly the computational cost compared with a hybrid functional (such as M06-2X), with only a tiny loss of accuracy in geometries and energies.³⁰ The M06L functional was chosen because (a) recent work has demonstrated its reliability on large nonbonded molecular complexes,³⁰ (b) its ability to reproduce the experimental results on supramolecular functionalized-TTF systems has been proven,^{20a,21} and (c) tests carried out in this work (see below) show that it reproduces the interaction energy of isolated $\pi\text{-}[\text{TTF}]_2^{n+}$ ($n = 0-4$) dimers obtained in extensive high-level RASPT2^{31,32} computations. These RASPT2 calculations were done using a $(28 - n, 2, 2; 11, 4, 5)$ ³³ restricted active space, n being the charge on the dimer. Such space is based on a $(28 - n, 20)$ complete active space that results from

extrapolating those employed in previous $[\text{TTF}]^0$ and $[\text{TTF}]^{n+}$ calculations.³⁴

Interaction energies have their basis set superposition error (BSSE) corrected according to the counterpoise method.^{35,36} In order to facilitate these computations, in all monomers and dimers, the two lateral OR groups ($R = \text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OCH}_3$, see Figure 1), experimentally used only to improve solubility, were substituted by methoxy groups.

The reliability of the 6-31G(d,p) basis set results against the addition of diffuse functions was tested by comparing the optimum geometry and electronic structure obtained using the 6-31G(d,p), 6-31+G(d,p), and 6-31++G(d,p) basis sets for two representative systems, clip_1^{2+} and clip_2^{4+} . The results for the basis with and without diffuse functions are almost identical (see Figure S1 and Tables S1–S3, Supporting Information), thus validating the general use of the 6-31G(d,p) basis set.

All energetic calculations were done using the appropriate options in the Gaussian09 suite of programs,³⁷ except the RASPT2 calculations, for which Molcas7.6 was used.³⁸

3. RESULTS AND DISCUSSION

3.1. Electronic Structure and Optimum Geometry of Isolated clip_1^{n+} ($n = 0-4$) Monomers.

3.1.1. The Electronic Structure and Geometry of the Neutral clip_1^0 Monomer. At the M06L/6-31G(d,p) level, the electronic ground state of the clip_1^0 monomer is a closed-shell singlet well below the energy of the lowest energy open-shell singlet and triplet states. Geometry optimization of the isolated clip_1^0 monomer in its singlet ground state leads to the V-shaped structure shown in Figure 2. In this optimum geometry each TTF has a boat-like

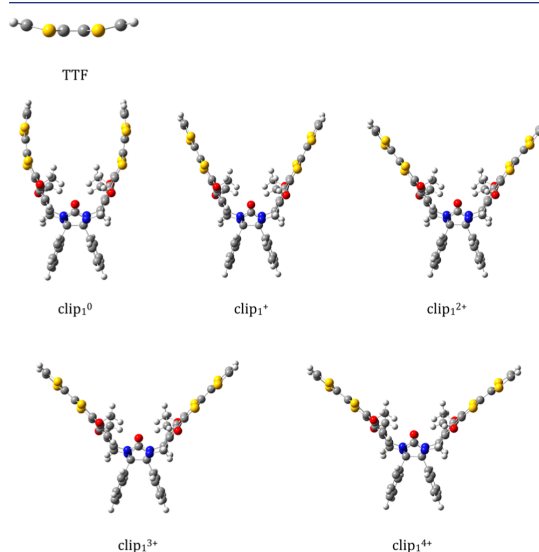


Figure 2. Optimum geometries of the neutral TTF molecule and the clip_1^{n+} ($n = 0-4$) monomers computed at the M06L/6-31G(d,p) level.

conformation, similar to that found at the optimum structure of an isolated TTF molecule (Figure 2). The shortest distance between the two TTF groups in clip_1^0 is 7.7 Å, while the angle between the two long arms is 68.4° (Table 1; see Figure S2, Supporting Information, for the geometrical parameters definition).

A first hint about the main features of the electronic structure of clip_1^0 in its singlet ground state is obtained from examining

Table 1. Values of the Shortest TTF...TTF Distance (r), Angle (α), and Dipole Moment (μ) of clip_1^{n+} ($n = 0-4$) Monomers, Both Computed Isolated and in Acetonitrile Solution, Using the PCM Model^a

	r (Å)		α (deg)		μ (D)	
	isolated	solution	isolated	solution	isolated	solution
clip_1^0	7.7	7.8	68.4	69.8	1.5	1.6
clip_1^+	8.0	7.8	75.4	72.0	10.4	14.3
clip_1^{2+}	8.6	7.9	85.3	74.4	20.5	29.3
clip_1^{3+}	9.1	8.3	93.1	80.6	24.4	42.5
clip_1^{4+}	9.5	8.3	99.6	81.0	26.2	55.1

^aBoth distance and angle are defined in Figure S2, Supporting Information. M06L/6-31G(d,p) calculations.

the net charge on the five parts in which one can naturally divide the monomer: the central ring (CR), its two long arms, L1 and L2 (each hosting a TTF group at their end), and its two short arms, L3 and L4 (Figure 1b). The net charge on each part was computed by adding the atomic charge of each of their atoms, obtained from a Mulliken population analysis of the ground state wave function (as shown in Figure S3, Supporting Information; other population analyses provide a nearly identical charge distribution). The most remarkable feature of the ground state electronic distribution is its zwitterionic character:³⁹ the CR hosts a 1− atomic unit (au) net charge, each L1 and L2 long arms has a net 0.4+ au charge, and each short arm has 0.1+ au charge (Figure 3). Such zwitterionic

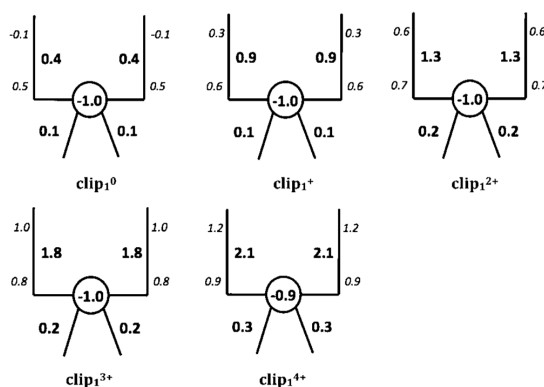


Figure 3. Representation of the net charge distribution on clip_1^{n+} ($n = 0-4$) monomers studied in this work. For each monomer, the net atomic charge in the five groups defined in Figure 1 is given, indicating in italics the charge in the TTF_i and L_i-TTF_i parts of the L_i arms. The net charge in each group is computed by adding the Mulliken atomic charges for all atoms of the group.

nature of the isolated clip_1^0 is consistent with the computed dipole moment (1.5 D), similar to that for an isolated water molecule.⁴⁰ The presence of such large charge shift from L1 and L2 to CR is only possible if the orbitals in CR are much more stable than those in L1 and L2. This results in a CR–L_i bonding orbital dominated by the CR orbitals, for both L1 and L2. Such energy mismatch also makes the through-bond L1–CR–L2 interaction very small. Since the two TTF groups are also too far away to allow any non-negligible overlap of their orbitals (and therefore any through-space interaction), the two TTF groups behave as nearly independent.

The MO structure of clip_1^0 is consistent with the aforementioned zwitterionic electronic distribution and the near independence of the two TTF groups of an isolated clip_1^0 monomer. At the M06L level, clip_1^0 has two nearly degenerate HOMOs (labeled as MO1 and MO2 in Figure 4), each one almost entirely localized on one terminal TTF group. Both orbitals have the same shape as the HOMO of an isolated [TTF] neutral molecule (Figure 4).

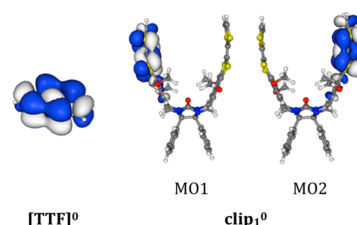


Figure 4. Shape of the highest two MOs of clip_1^0 . The orbitals have been computed for the monomer ground state (M06L/6-31G(d,p) calculations) at its optimum geometry. The HOMO of the neutral [TTF] is also plotted, for comparison.

3.1.2. The Electronic Structure and Geometry of the clip_1^+ to clip_1^{4+} Charged Monomers. Cationic clip_1^+ to clip_1^{4+} monomers are obtained by successive oxidations of clip_1^0 . Therefore, in a first approach, one can expect that the four electrons removed in these processes are those placed in the two nearly doubly degenerate HOMO orbitals of clip_1^0 , because they are the highest ones in energy. The validity of this statement along each oxidation step is checked by doing M06L/6-31G(d,p) calculations.

The ground electronic state of clip_1^+ , according to M06L/6-31G(d,p) calculations, is the doublet that results from extracting one electron from one nearly doubly degenerate HOMO orbital in clip_1^0 (Figure S4, Supporting Information). The optimum geometry optimization of clip_1^+ in its ground state also has a V-shaped structure (Figure 2), the angle between its two long arms being 7° larger than that in clip_1^0 . As a result, the shortest distance between the TTF groups increases up to 8.0 Å (Table 1). Its electronic structure has its only unpaired electron equally delocalized over both TTF units (rather than fully localized on only one of the TTF groups), consistent with its symmetric optimum geometry and charge distribution (Figure 3). Its charge distribution is also zwitterionic, with 1− au located in the CR part, 0.1+ au in each short arm, and 0.9+ au in each long arm. By comparing such charge distribution with that for the neutral monomer, one finds that the 1+ au net charge hosted by clip_1^+ is mostly stored in the long arms: each one increases their charge by 0.4+ au (each TTF group with a 0.3+ au, while 0.1+ au goes to its attached six-membered rings). Consequently, clip_1^+ has a stronger zwitterionic character than clip_1^0 , naturally reflected in a larger dipole moment (10.4 D in clip_1^+ compared with 1.5 D in clip_1^0).

Formally, when two electrons are removed from clip_1^0 to produce clip_1^{2+} , they could come from the same TTF group (therefore, formally creating a (2+,0) charge distribution on the two TTF groups) or from a different TTF group (thus ending in a (1+,1+) distribution). One expects that a (2+,0) distribution would result in a closed-shell singlet state while the (1+,1+) distribution, with one unpaired electron on each

nearly independent TTF group, would result in an open-shell singlet or a triplet ground state (keep in mind that the two TTF groups of the same monomer are too far away to allow the formation of an intramolecular long, multicenter bond, which would result in a closed-shell state). Between these two options, M06L/6-31G(d,p) calculations indicate that the open-shell singlet is the ground state, while the triplet state is just 0.1 kcal/mol higher. Thus, clip_1^{2+} is a diradical with one electron located in each TTF group (Figure S4, Supporting Information), consistent with the computed spin distribution (Figure 5). At

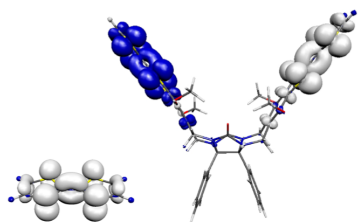


Figure 5. Spin distribution of isolated $[\text{TTF}]^{\bullet+}$ cation (left) and clip_1^{2+} dication (right) at their ground state.

room temperature, the singlet and triplet states will be equally populated and paramagnetic behavior should be observed. The clip_1^{2+} charge distribution, Figure 3, is also zwitterionic, with a net 1– au charge in the CR group, 0.2+ au in each short arm, and 1.3+ au in each long arm (0.6+ au in its TTF group and 0.7+ au in the attached six-membered ring). Therefore, the long arms host the 2+ au formal charge from the oxidation, plus some extra charge that results from the charge shift, due to the higher stability of the CR orbitals with respect to the long arms orbitals. This increase in the zwitterionic character is consistent with the increase in the dipole moment to 20.5 D. It also explains the increase in the separation between the two $[\text{TTF}]^{\bullet+}$ groups observed for the open-shell singlet ground state of clip_1^{2+} at its optimum geometry (Table 1, Figure 2).

The ground states of clip_1^{3+} and clip_1^{4+} are a doublet and a closed-shell singlet, respectively, consistent with a further decrease in the electron occupation of the nearly double-degenerate HOMOs of clip_1^0 (Figure S4, Supporting Information). The electronic structure of the two fragments are also zwitterionic, with a 1– au charge located on the central CR group and 1.7+ and 2.1+ au located in the two long arms, mostly over the TTF groups (Figure 3). As a consequence, the dipole moment becomes even larger (24.4 D in clip_1^{3+} and 26.2 D in clip_1^{4+}). The optimum geometry of isolated clip_1^{3+} and clip_1^{4+} monomers at their ground state, Figure 2, is also V-shaped, the shortest distance between the TTF groups also being larger (9.1 and 9.5 Å, respectively). Note the correlation between the increment of net charge on the TTF groups and the increase in the angle between the two long arms (and, as a result, the larger distance between the TTF groups).

3.2. Electronic Structure and Optimum Geometry of Isolated clip_2^{n+} ($n = 0, 1, 2, 3, 4, 6$, or 8) Dimers. An identification of the most stable geometry of the clip_2^{n+} dimers requires a preliminary analysis of the isolated $\text{clip}_1^{l+} \cdots \text{clip}_1^{m+}$ interaction aimed at qualitatively predicting, among all likely minimum energy structures, the most plausible orientation of the absolute minimum. Such a task was achieved in three steps. In the first one, the nature of the $\text{clip}_1^{l+} \cdots \text{clip}_1^{m+}$ intermolecular interactions was determined. Such information allowed the

identification, on qualitative grounds, of the most probable orientation of the absolute minimum as a second step. Then, in the third step, the most stable structure was optimized and analyzed for each isolated clip_2^{n+} dimer.

3.2.1. The Nature of $\text{clip}_1^{l+} \cdots \text{clip}_1^{m+}$ Intermolecular Interactions. The nature of any intermolecular interaction can be determined by finding the dominant energetic component in an IMPT⁴¹ perturbative calculation of the interaction energy. This method can also be used to obtain qualitative information about the nature of the interaction energy, by analyzing the properties of the dominant component of the interaction energy via the IMPT scheme.⁴²

Assuming, as is commonly found, that the polarization (E_{pol}) and charge-transfer (E_{ct}) components of the IMPT interaction energy are 1 order of magnitude smaller than the remaining ones,⁴² the IMPT intermolecular interaction energy between two open shell fragments, A and B, takes the following expression:^{13c}

$$E_{\text{int}} \approx E_{\text{er}} + E_{\text{el}} + E_{\text{disp}} + E_{\text{bond}} \quad (1)$$

where each term has the following physical meaning: (1) E_{er} is the exchange–repulsion energetic component that is always energetically repulsive due to the repulsion that electrons feel when they occupy the same point of the space, in accord with the Pauli exclusion principle (this term is known to be proportional to the exponential of the overlap integral between the A and B wave functions); (2) E_{el} is the electrostatic energetic component of the nonpolarized system, which can be accurately approximated as a sum of classical multipoles (i.e., the sum of the charge–charge, charge–dipole, dipole–dipole, etc. components; when the smaller polarization component, E_{pol} , is added, one obtains the true electrostatic energy); (3) E_{disp} is the dispersion energetic component, a nonclassical term that arises from the instantaneous dipole–dipole interactions resulting from the correlated motions of the electrons in A and B; (4) E_{bond} is the bonding energetic component, associated with the pairing, produced in the dimer, of the unpaired electrons of fragments A and B. Because E_{er} is always energetically repulsive, the remaining three terms (E_{el} , E_{disp} , and E_{bond}) are the only ones to be analyzed when one looks for stable geometries of an AB complex.

One can now apply these ideas to the analysis of the $\text{clip}_1^{l+} \cdots \text{clip}_1^{m+}$ interactions. Previous evidence indicates that E_{el} dominates whenever the interacting fragments are charged or have a strong dipole moment, as is the case in all clip_1^{m+} ($m = 0–4$) monomers.⁴³ The most stable orientation of two dipoles is found when they are in an antiparallel disposition. The three orientations shown in Figure 6 fulfill such a criterion and, consequently, are good initial candidates to locate the most stable orientation of clip_2^{n+} dimers. Among them, that in Figure 6c also maximizes E_{disp} , due to the presence of short-distance interactions between the lone-pair electrons of the TTF groups, whatever the dimer net charge. Finally, E_{bond} can only be present whenever the two interacting monomers have unpaired electrons and their SOMOs present non-negligible overlap. As discussed above, clip_1^{+} , clip_1^{2+} , and clip_1^{3+} have unpaired electrons, mostly located on the TTF groups (0.5, 1.0, and 1.5 electrons on each TTF, respectively). Furthermore, charged clip_2^{n+} dimers oriented as in Figure 6c allow the formation of three short-distance intermolecular TTF $\cdots$ TTF contacts that interconnect the four TTF groups. When the two TTF groups of these short-distance TTF $\cdots$ TTF contacts host one unpaired electron, as in clip_1^{2+} , these become long, multicenter bonds, a

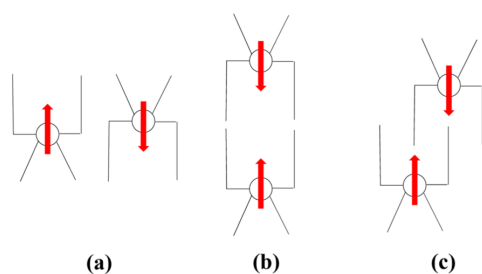


Figure 6. Three possible geometrical dispositions of the $\text{clip}_1^{n+}\cdots\text{clip}_1^{m+}$ dimers, which are reasonable candidates for their most stable orientation.

fact that affects the value of E_{bond} . A maximum of two of long, multicenter bonds can be formed in clip_2^{4+} dimers, by pairing the unpaired electrons among the four $[\text{TTF}]^{\bullet+}$ groups. This situation is experimentally detected in its UV-vis spectrum.²⁵

Using the same reasoning, the clip_2^{6+} dimer can be described as a $\text{clip}_1^{3+}\cdots\text{clip}_1^{3+}$ interaction. If one accepts that clip_1^{3+} monomers distribute their 3+ charge following a $(2+,1+)$ distribution, while the other follows a $(1+,2+)$ distribution, one long, multicenter bond could be formed in the central short $\text{TTF}\cdots\text{TTF}$ contact, where the two $[\text{TTF}]^{\bullet+}$ groups would be located. However, the bonding in clip_2^{6+} is not so simple, because there are other ways of arranging two $(2+,1+)$ distributions, besides the fact that $(1.5+,1.5+)$ distributions are also possible. A similar complex situation is faced in clip_2^{2+} , formally a $\text{clip}_1^{+}\cdots\text{clip}_1^{+}$ interaction. Now both monomers could present a $(1+,0)$ or $(0.5+,0.5+)$ charge distribution, although the presence of long multicenter bonds has not been experimentally detected in clip_2^{2+} .⁴⁴ The intermolecular bonding in clip_2^{+} , clip_2^{3+} , clip_2^{5+} , and clip_2^{7+} is also a complex matter, while clip_2^0 and clip_2^{8+} have no long, multicenter bonds because they have no unpaired electrons. Given the complex nature of the intermolecular bonding in all clips with net charge different than 4, they will be subject of a further specific study.

3.2.2. Optimum Geometry and Relative Stability of the clip_2^{n+} ($n = 0, 1, 2, 3, 4, 6$, or 8) Dimers. The most stable geometry of clip_2^0 was computed at the M06L/6-31G(d,p) level starting from a reasonable guess of Figure 6c configuration. For all other dimers, the clip_2^{n+} M06L/6-31G(d,p) geometry optimization started from the optimum geometry of $\text{clip}_1^{(n-1)+}$. The study also includes clip_2^{6+} and clip_2^{8+} , as representatives of the properties of clip_2^{n+} ($n = 5-8$) dimers, aiming at determining why they are not experimentally observed at room temperature.

The optimum geometry obtained for each isolated clip_2^{n+} ($n = 0, 1, 2, 3, 4$, or 6) dimer in their electronic ground state, along with its ground state spin multiplicity, is shown in Figure 7. The geometry of clip_2^{8+} is not shown, since it dissociates into its two clip_1^{4+} monomers. As shown in Figure 7, all minimum energy structures, besides clip_2^{6+} , preserve the starting Figure 6c configuration (a more detailed analysis of their similarities can be done by looking at Table S4, Supporting Information, where the most relevant interfragment parameters, defined in Figure S5, Supporting Information, have been collected).⁴⁵ The BSSE-uncorrected and corrected interaction energies, as well as their formation energies, of all dimers at their optimum geometry (for clip_2^{8+} , at the optimum geometry of clip_2^{6+}) are collected in Table 2. According to these formation energies, clip_2^0 , clip_2^{+} , and clip_2^{2+} are bound minima stable against their dissociation

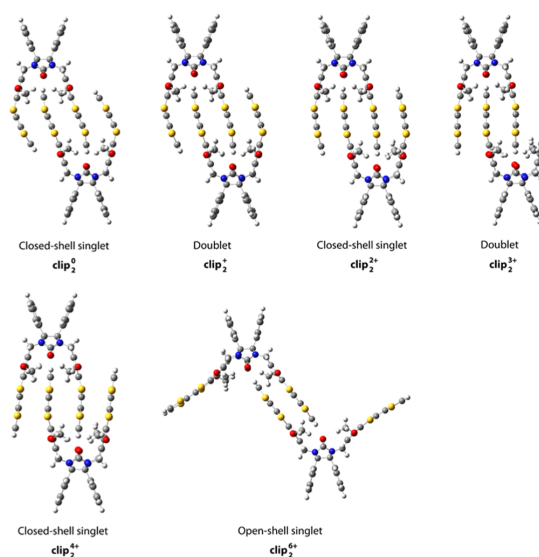


Figure 7. Optimum geometries of isolated clip_2^{n+} dimers ($n = 0, 1, 2, 3, 4$, or 6) in their ground electronic state (shown under each geometry). The optimum structure of clip_2^{8+} is not shown because it dissociates into its two monomers.

into two monomers, while clip_2^{3+} , clip_2^{4+} , and clip_2^{6+} are metastable minima.⁴⁶ A similar trend is observed when the free energies of formation at 298 K are considered (Table 2). The main difference with respect to formation energy values is that clip_2^{2+} is unstable against dissociation. These results fail to satisfy the available experimental information, thus suggesting that solvent effects could be relevant (vide infra).

In all dimers, the charge distribution in both fragments is similar to that found in their corresponding monomers. This is graphically demonstrated in Figure 8, where the charge localized in each of the five parts defined on the monomers (Figure 1b) is analyzed for the two fragments of each dimer. Therefore, each fragment of a dimer preserves its zwitterionic electronic structure, which creates an important dipole moment. Consistent with such electron distribution, the shape of the highest four occupied orbitals of clip_2^0 (Figure 9) are the bonding and antibonding combinations of the two nearly degenerate HOMOs of clip_1^0 . These four orbitals should have the eight electrons involved in the eight steps of the clip_2^0 to clip_2^{8+} oxidations. As shown in Figure 9 (left), this is only the case in the oxidations from clip_2^0 , clip_2^{+} , and clip_2^{2+} . Beyond clip_2^{3+} , the orbitals located in the L3 and L4 short arms become less stable than those located in the L1 and L2 long arms. This explains the increase of charge found in the short arms of clip_2^{8+} .

3.3. Solvent Effects: Structure and Stability of the clip_1^{m+} and clip_2^{n+} in Acetonitrile Solutions. All available experimental data on the stability of clip_2^{n+} dimers obtained in acetonitrile solution²⁵ disagree with the free energies of formation computed on isolated dimers (Table 2). Given the ionic character of these dimers, this disagreement could result from solvent effects. Hereafter, the impact of these effects on the free energy of formation of clip_2^{n+} dimers is accurately evaluated using the PCM continuous solvation model.

Table 2. Interaction and Formation Energy^a for the Optimum Geometry of Isolated clip₂ⁿ⁺ (*n* = 0, 1, 2, 3, 4, 6, or 8) Dimers (Figure 7)

	clip ₂ ⁰	clip ₂ ⁺	clip ₂ ²⁺	clip ₂ ³⁺	clip ₂ ⁴⁺	clip ₂ ⁶⁺	clip ₂ ⁸⁺
Isolated							
<i>E</i> _{int}	−61.3	−75.7	−37.0	−13.8	+70.4	+171.4	+347.7 ^b
<i>E</i> _{int} ^{CP}	−49.5	−64.2	−25.5	−2.7	+80.9	+197.1	+378.2 ^b
<i>E</i> _{for}	−50.8	−61.9	−23.0	+12.1	+98.6	+207.1	+385.9 ^b
<i>E</i> _{for} ^{CP}	−39.0	−50.3	−11.3	+23.4	+109.1	+232.9	+416.4 ^b
Δ <i>G</i> (298 K)	−19.1	−31.0	+8.2	+42.0	+123.9	+238.9	^c
In Acetonitrile Solutions							
<i>E</i> _{for}	−45.9	−52.8	−52.6	−50.7	−41.2	−16.5	+0.8
Δ <i>G</i> (298 K)	−12.2	−20.7	−20.6	−18.1	−9.5	+16.9	+29.5

^aObtained at M06L/6-31G(d,p) level, with and without counterpoise correction. Energy values in kcal/mol. ^bEstimation made at the optimum geometry of the clip₂⁶⁺ dimer. ^cIt is not a minimum in the potential energy surface of the system.

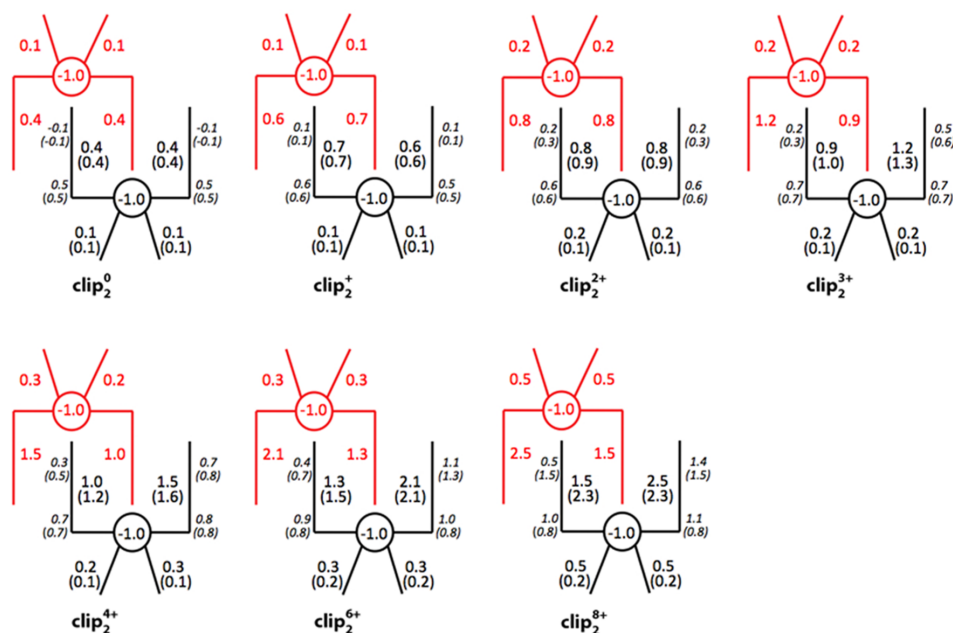


Figure 8. Representation of net charge distribution on the isolated clip₂ⁿ⁺ (*n* = 0, 1, 2, 3, 4, 6, or 8) dimers studied in this work. Charge values in acetonitrile solution are given within parentheses (since the distribution is symmetrical, they are only specified over one monomer to facilitate comprehension). The computations have been done at their optimum geometry (except in isolated *n* = 8, which was obtained at the optimum geometry of isolated clip₂⁶⁺). In each monomeric fragment of the dimers, the net atomic charge in the five groups defined in Figure 1 is given, indicating in italics the charge in the TTF_i and L_i-TTF_i parts of the L_i arms. The net charge in each group is computed by adding the Mulliken atomic charges for all atoms of the group.

3.3.1. Solvent Effects on the clip₁^{m+} Properties. With the PCM model, the optimum structures of clip₁^{m+} were first reoptimized at the M06L/6-31G(d,p) level starting from their isolated structure. The optimum geometries of clip₁⁰ to clip₁⁴⁺ monomers in acetonitrile are similar to their optimum isolated geometries, Figure S6, Supporting Information, the main difference being the smaller angle between the two long arms in acetonitrile solutions (Table 1). However, even after such decrease, the TTF groups are too far away to allow any sizable through-space overlap between their orbitals. The charge distribution of the monomers in acetonitrile solutions is also similar to that on isolated monomers (Figure 3), as in both media the two highest occupied orbitals are the same. However, due to the smaller angle between the two L_i groups, the dipole

moment of the monomers in solution is larger than when isolated (Table 1).

3.3.2. Solvent Effects on the clip₂ⁿ⁺ Properties. The optimum geometries of clip₂ⁿ⁺ (*n* < 6) dimers in acetonitrile solution (Figure S6, Supporting Information) are almost identical to their optimum isolated geometries (Figure 7). On the other hand, clip₂⁶⁺ now preserves Figure 6c configuration, while clip₂⁸⁺ presents a bound structure. Such similarity in *n* < 6 dimers is also manifested when the values of their most relevant interfragment geometrical parameters are examined (Table S4, Supporting Information). However, the charge distribution of clip₂ⁿ⁺ dimers in solution (Figure 8) has two relevant differences with respect to the isolated dimer distribution: (a) the amount of positive charge on the TTF groups in

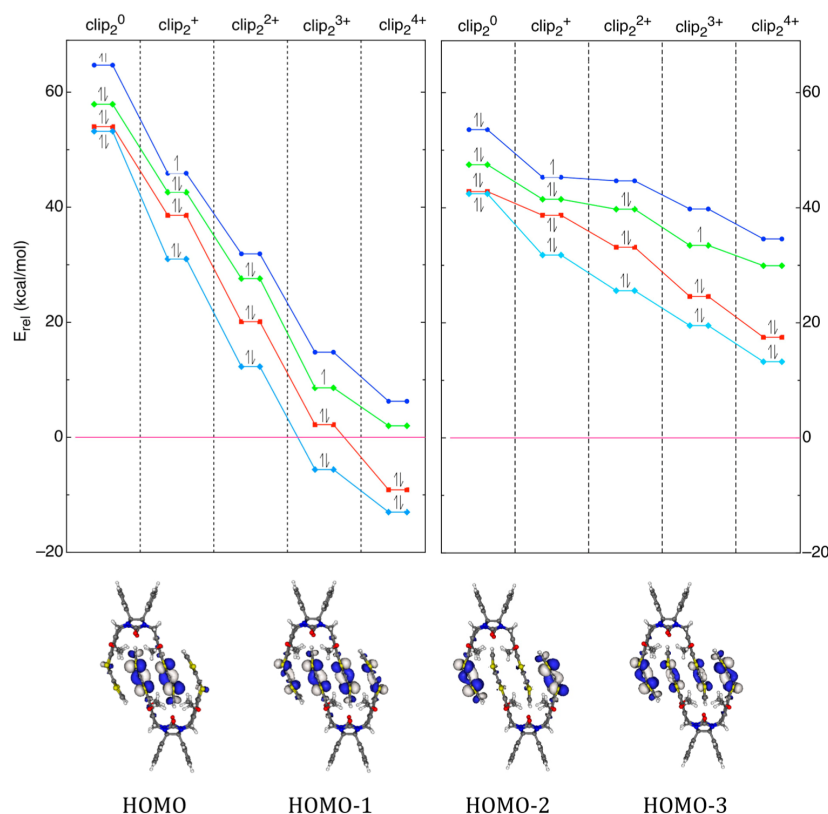


Figure 9. (top) Variation of orbital energy when clip_2^0 is oxidized to clip_2^{n+} ($n = 1-4$), both isolated (left) and in acetonitrile (right). All results come from M06L/6-31G(d,p) calculations. In each dimer, its zero energy is the energy of the highest occupied orbital localized in L3/L4 groups. (bottom) Shape of the highest four occupied orbitals of an isolated clip_2^0 dimer (in acetonitrile solutions their shape is essentially the same).

acetonitrile (Table S6, Supporting Information) is remarkably larger than that in isolated dimers (Table S5, Supporting Information), and (b) the atomic charge becomes negligible in the two short arms. Those changes are associated with the different relative stability of the long and short arm orbitals in solution (Figure 9).

The formation energy of the dimers in acetonitrile solutions is collected in Table 2, together with their associated $\Delta G(298\text{ K})$ values. The solvent destabilizes the formation of clip_2^0 and clip_2^+ dimers by 5 and 9 kcal/mol, respectively, but strongly stabilizes the formation of clip_2^{2+} , clip_2^{3+} , and clip_2^{4+} (by 30, 63, and 140 kcal/mol, respectively). Therefore, according to the formation energies in acetonitrile, all clip_2^{n+} $n \leq 6$ dimers are stable against their dissociation into monomers, and only the formation of the $n = 8$ dimer is slightly disfavored. Similar trends are found when looking at the values of $\Delta G(298\text{ K})$ in acetonitrile, the property that better describes the behavior of the clip_2^{n+} dimers under the experimental conditions. In perfect agreement with the reported experimental data, clip_2^0 , clip_2^+ , clip_2^{2+} , clip_2^{3+} , and clip_2^{4+} are found to be more stable than their dissociated monomers, while clip_2^{6+} and clip_2^{8+} are metastable.

Such metastable character of clip_2^{6+} and clip_2^{8+} in acetonitrile was further evaluated by estimating whether the barrier for their dissociation into their constituting monomers is higher than the average thermal energy at 298 K (estimated as $T\Delta S$).⁴⁷ As seen in Figure S7, Supporting Information, at 298 K such barrier is

smaller than the average thermal energy, thus allowing the dissociation of the dimer, in good agreement with the experimental data on the stability of clip_2^{n+} dimers. In other words, solvent effects are essential for a proper reproducibility of the reported experimental stability of clip_2^{n+} dimers.

The diagram in Figure 9 (right) also allows a proper rationalization of the available experimental UV-vis data on clip_2^{n+} dimers in acetonitrile solutions. In clip_2^+ and clip_2^{2+} , Chiang et al.²⁵ obtained a low-energy band ($\sim 1650\text{ nm}$). A higher energy band ($\sim 800\text{ nm}$) was also obtained in clip_2^{3+} . In contraposition, clip_2^{4+} only exhibits the higher energy band. Such behavior can be explained by considering the lowest two electronic energy transitions in these systems, which can be rationalized in terms of the MO diagram (identified in this analysis as HOMO, HOMO-1, HOMO-2, and HOMO-3), Figure 9. The lowest energy transition in clip_2^+ and clip_2^{2+} , which should be associated with the experimental $\sim 1650\text{ nm}$ band, is the HOMO-1 $\rightarrow$ HOMO. In clip_2^{3+} the HOMO-1 $\rightarrow$ HOMO transition is still the lowest one in energy, but a new transition, HOMO-2 $\rightarrow$ HOMO-1, is also possible, presumably responsible of the $\sim 800\text{ nm}$ experimental band. In clip_2^{4+} the HOMO-1 $\rightarrow$ HOMO cannot take place because the HOMO-1 orbital is empty. Consequently, the HOMO-2 $\rightarrow$ HOMO-1 transition becomes the lowest one in energy (and should be associated with the $\sim 800\text{ nm}$ experimental band).

Table 3. Values of the Four Energy Components (in kcal/mol) of eq 2 Computed for the clip₂ⁿ⁺ (*n* = 0, 1, 2, 3, 4, 6, or 8) Dimers^a

	$E(2\text{TTF}_1-2\text{TTF}_2)$	$E(\text{BR}_1-\text{BR}_2)$	$E(2\text{TTF}_1-\text{BR}_2)$	$E(\text{BR}_1-2\text{TTF}_2)$	E_{sum}	E_{int}
clip ₂ ⁰	0/0 −16.1	0/0 +0.01	0/0 −16.4	0/0 −16.4	−48.7	0/0 −49.5
clip ₂ ⁺	0/1+ −28.5 ^b	0/0 +0.01	0/0 −16.7 ^b	0/1+ −21.4 ^b	−66.5	0/1+ −64.2 ^b
clip ₂ ²⁺	1+/1+ +20.3	0/0 +0.01	1+/0 −21.5	0/1+ −21.5	−22.6	1+/1+ −25.5
clip ₂ ³⁺	1+/2+ +56.7 ^b	0/0 +0.01	1+/0 −21.0 ^b	0/2+ −36.3 ^b	−0.5	1+/2+ −2.7 ^b
clip ₂ ⁴⁺	2+/2+ +156.6	0/0 +0.01	2+/0 −36.6	0/2+ −36.6	+83.5	2+/2+ +80.9
clip ₂ ⁶⁺	3+/3+ +264.7	0/0 +0.05	3+/0 −75.3	0/3+ −73.4	+116.1	3+/3+ +189.5
clip ₂ ⁸⁺	4+/4+ +522.0	0/0 +0.05	4+/0 −100.8	0/4+ −103.8	+317.7	4+/4+ +370.5

^aThe following components were computed (see text for their definition): $2\text{TTF}_1-2\text{TTF}_2$, $2\text{TTF}_1-\text{BR}_2$, $\text{BR}_1-2\text{TTF}_2$, and BR_1-BR_2 . The sum of these components (E_{sum}) is also given. In order to allow its easy comparison with the value of the BSSE-corrected interaction energy of the isolated dimer (E_{int}), this magnitude is also given (as extracted from the second row of Table 2). The charge on both interacting fragments is indicated in each box as fragment₁/fragment₂. All energy data are BSSE-corrected. ^bThe system has two possible charge distributions, as 1+/0 or 0/1+, have been evaluated by calculating the average of both solutions.

3.4. The Origin of the Room Temperature Stability of the clip₂ⁿ⁺ Dimers. As already mentioned, nonfunctionalized $\pi\text{-}[\text{TTF}]_2^{2+}$ dimers in acetonitrile solutions are experimentally found to be stable only up to $-40\text{ }^\circ\text{C}$.¹⁷ However, clip₂⁴⁺ dimers dissolved in acetonitrile, which also have long $[\text{TTF}]^{\bullet+}\cdots[\text{TTF}]^{\bullet+}$ intradimer bonds, are experimentally detected at room temperature. Among other options, such a fact could be due to an increase in the stability of the long $[\text{TTF}]^{\bullet+}\cdots[\text{TTF}]^{\bullet+}$ intradimer bonds in clip₂⁴⁺ dimers. This was investigated by doing a quantitative energy-partition analysis of the interaction energy of clip₂ⁿ⁺, which also allowed to quantify the difference between the interaction energy of the long $[\text{TTF}]^{\bullet+}\cdots[\text{TTF}]^{\bullet+}$ intradimer bonds in $\pi\text{-}[\text{TTF}]_2^{2+}$ and clip₂⁴⁺ dimers.

Before any other analysis, the interaction energy of the $[\text{TTF}]^{\bullet+}\cdots[\text{TTF}]^{\bullet+}$ interactions present in clip₂ⁿ⁺ dimers was evaluated on isolated dimers. For such a task, in each clip₂ⁿ⁺ dimer a $\text{TTF}_4(\text{clip}_2^{\bullet+})$ aggregate was obtained by deleting all but the TTF groups,⁴⁸ and its total interaction energy, relative to two $\text{TTF}_2(\text{clip}_1^{\bullet+})$ fragments, was computed (first column of Table 3). The difference between the interaction energy of the $\text{TTF}_4(\text{clip}_2^{\bullet+})$ aggregate and the clip₂ⁿ⁺ interaction energy relative to two clip₁ⁿ⁺ fragments (last column of Table 3) manifestly suggests that the extra stability of clip₂ⁿ⁺ dimers is caused by other than the $[\text{TTF}]^{\bullet+}\cdots[\text{TTF}]^{\bullet+}$ interactions. Such difference increases gradually from 33.4 kcal/mol in clip₂⁰ to 151.5 kcal/mol in clip₂⁸⁺, thus being significant even in the neutral clip₂⁰.

The origin of the extra stability for the clip₂ⁿ⁺ dimers was further investigated by breaking each monomer *i* in two parts: (a) the two TTF groups, 2TTF_i , and (b) the rest, BR_i , which can be seen as a bridge connecting the two TTF groups of the monomer (Figure S9, Supporting Information). Within this partition scheme, the total interaction energy of a clip₂ⁿ⁺ dimer is the sum of the following four components:

$$E_{\text{int}} \approx E(2\text{TTF}_1-2\text{TTF}_2) + E(2\text{TTF}_1-\text{BR}_2) + E(\text{BR}_1-2\text{TTF}_2) + E(\text{BR}_1-\text{BR}_2) \quad (2)$$

The values of these four terms for all clip₂ⁿ⁺ dimers, computed at the optimum geometry of each dimer in acetonitrile, obtained at M06L/6-31G(d,p) level, are listed in Table 3. The validity of this partition scheme is demonstrated by noticing the similarity of the sum of these four terms (E_{sum}) and the total interaction energy (E_{int}).

It is also informative to look at the variation of the four components for the different clip₂ⁿ⁺ dimers. First of all, $E(\text{BR}_1-\text{BR}_2)$ is very small in all dimers. Notice that although the bridge groups have a zero net charge, they have a strong dipole moment, originating in their zwitterionic charge distribution (Figure S10, Supporting Information). However, the large $\text{BR}_1\cdots\text{BR}_2$ intermolecular distance renders the $E(\text{dipole-dipole})$ and E_{disp} components zero (E_{bond} is also zero because, as already described, if any unpaired electron is present in the monomers, they are located in the TTF groups).

As previously stated, the $E(2\text{TTF}_1-2\text{TTF}_2)$ component accounts for the interaction between the TTF groups of each interacting fragment. Their disposition allows the existence of three face-to-face $\text{TTF}\cdots\text{TTF}$ interactions, two external and one internal. Since nearly all the positive charge gained by the dimer on its oxidation goes to its TTF groups, the changes in the $E(2\text{TTF}_1-2\text{TTF}_2)$ energetic component of clip₂ⁿ⁺ (*n* = 0, 1, 2, 3, 4, 6, or 8) can be rationalized by looking at how the $\text{TTF}\cdots\text{TTF}$ interactions vary as the TTF groups get oxidized. Such information can be obtained from the properties of the $\pi\text{-}[\text{TTF}]_2^{n+}$ (*n* = 0–4) dimers.

M06L/6-31G(d,p) calculations were carried out on the $\pi\text{-}[\text{TTF}]_2^{n+}$ (*n* = 0–4) dimers (Figure S11, Supporting Information), checking their validity against extensive RASPT2/6-31G(d,p) calculations. The following conclusions were reached from these studies: (a) $\pi\text{-}[\text{TTF}]_2^0$ is a van der Waals dimer (where, $E_{\text{int}} \approx E_{\text{disp}}$, as $E(\text{charge-charge}) = 0$, because no net charge is present, and $E_{\text{bond}} = 0$, since there are no unpaired electrons) having a minimum 9.4 kcal/mol more stable than its dissociated fragments at an interfragment distance of about 3.45 Å; (b) $\pi\text{-}[\text{TTF}]_2^+$ has a stable dimer at an interfragment distance of 3.33 Å, whose energy is 20.4 kcal/mol more stable than that for its dissociated fragments

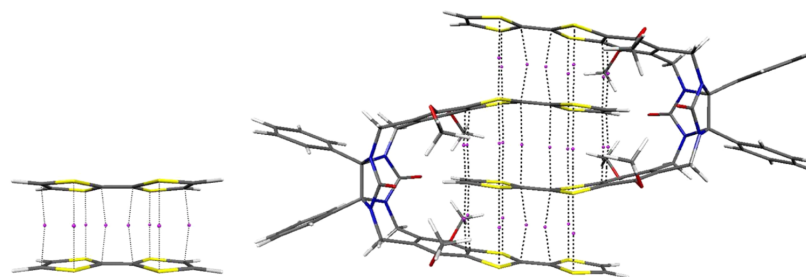


Figure 10. Position of the bond-critical points (purple) found between the $[\text{TTF}]^{\bullet+}$ groups in $\pi\text{-}[\text{TTF}]_2^{\bullet+}$ (left) and in $\text{clip}_2^{\bullet+}$ (right) at their optimum geometry in acetonitrile solution. Notice the similarity between the bond critical points in the external $[\text{TTF}]^{\bullet+}\cdots[\text{TTF}]^{\bullet+}$ interactions in $\text{clip}_2^{\bullet+}$ and in $\pi\text{-}[\text{TTF}]_2^{\bullet+}$. It is numerically demonstrated when the density in the critical points are compared, Table S7, Supporting Information.

(E_{bond} can be taken as zero, because there is only one unpaired electron and no pairing of electrons is possible, although much weaker one-electron bonds are also known; assuming that E_{disp} is dominated by the lone-pair $\cdots$ lone-pair interactions, one can expect that $E_{\text{disp}}(\pi\text{-}[\text{TTF}]_2^0) \approx E_{\text{disp}}(\pi\text{-}[\text{TTF}]_2^{\bullet+}) \approx E_{\text{disp}}(\pi\text{-}[\text{TTF}]_2^{2+})$; then, about half of the interaction energy would be due to E_{disp} , while the other half comes from the electrostatic component, thus allowing to classify this interaction as electrostatic dispersion, by looking at the dominant energetic components); (c) $\pi\text{-}[\text{TTF}]_2^{\bullet+}$ is a long bonded dimer having a metastable minimum at about 3.44 Å whose energy is 38.1 kcal/mol above that of its dissociated fragments (its interaction energy is dominated by a repulsive E_{el} contribution, being the sum of the E_{disp} plus E_{bond} weaker, as usual in all known long bonded dimers;^{7,8,10,11,13c,15} consequently, the $[\text{TTF}]^{\bullet+}\cdots[\text{TTF}]^{\bullet+}$ interaction is only produced in supramolecular aggregates due to the interaction of the $[\text{TTF}]^{\bullet+}$ groups with nearby counterions or solvent molecules),^{10,19} and (d) $\pi\text{-}[\text{TTF}]_2^{3+}$ and $\pi\text{-}[\text{TTF}]_2^{4+}$ are unstable and show no bound minima along their dissociation potential energy curve (at a interfragment distance of 3.44 Å their interaction energy is 91 and 211 kcal/mol, respectively; the dominant energetic component is the electrostatic one, $E_{\text{el}} \approx E(\text{charge-charge})$, which becomes more repulsive than that in $\pi\text{-}[\text{TTF}]_2^{2+}$).

Given the relevance of the two long, multicenter bonds in $\text{clip}_2^{\bullet+}$, its existence was subject of an in-depth analysis. Consistent with the considerations above, due to their shorter interfragment distance, in $\text{clip}_2^{\bullet+}$ the SOMO($\text{TTF}^{\bullet+}$) + SOMO($\text{TTF}^{\bullet+}$) bonding combination of the two external $[\text{TTF}]^{\bullet+}\cdots[\text{TTF}]^{\bullet+}$ interactions is more stable than that for the internal interaction. Therefore, a long, multicenter bond is formed in each external $[\text{TTF}]^{\bullet+}\cdots[\text{TTF}]^{\bullet+}$ interaction, pairing the two unpaired electrons present in both clip_1^{2+} fragments. As a consequence of their formation, no unpaired electrons remain in the dimer and the internal $[\text{TTF}]^{\bullet+}\cdots[\text{TTF}]^{\bullet+}$ interaction can only be a van der Waals interactions.⁴⁹ An atoms-in-molecules (AIM)^{50,51} analysis of the $\pi\text{-}[\text{TTF}]_2^{\bullet+}$ and $\text{clip}_2^{\bullet+}$ electronic density confirms this rationalization (both densities were computed for the singlet ground state at their optimized geometry in acetonitrile solution). The results, graphically depicted in Figure 10, show the similar connectivity of the $[\text{TTF}]^{\bullet+}\cdots[\text{TTF}]^{\bullet+}$ bond critical points in both dimers. The same similarity is found in the bond critical point parameters (all bond critical points have densities within the 0.002 to 0.011 au range, see Table S7, Supporting Information). Finally, the strength of the long, multicenter bonds in $\text{clip}_2^{\bullet+}$ and $\pi\text{-}[\text{TTF}]_2^{\bullet+}$ is also similar: 24.2 kcal/mol (12.1 kcal/mol for each

long bond)⁵² in $\text{clip}_2^{\bullet+}$ and 15.3 kcal/mol in $\pi\text{-}[\text{TTF}]_2^{\bullet+}$. Therefore, the long, multicenter bonds in $\text{clip}_2^{\bullet+}$ and $\pi\text{-}[\text{TTF}]_2^{\bullet+}$ are similar, and thus, they cannot be the origin for the room temperature stability of $\text{clip}_2^{\bullet+}$.

The last two terms in eq 2, $E(2\text{TTF}_1\text{-BR}_2)$ and $E(\text{BR}_1\text{-}2\text{TTF}_2)$, are both $[\text{TTF}]_2^{\bullet+}\cdots\text{BR}$ interactions. A detailed analysis of their geometry shows the presence of two interfragment $\text{C}(\text{sp}^2)\text{-H}\cdots\text{O}=\text{C}$ hydrogen bonds (the carbonyl located in the BR group, see Figure S9, Supporting Information) and four interfragment $\text{C}(\text{sp}^3)\text{-H}\cdots\text{S}$ hydrogen bonds (the $\text{C}(\text{sp}^3)\text{-H}$ located in the BR group). It has been shown that, when both interacting fragments have a zero net charge, $\text{C}(\text{sp}^2)\text{-H}\cdots\text{O}=\text{C}$ and $\text{C}(\text{sp}^3)\text{-H}\cdots\text{S}$ hydrogen bonds are weaker than the $\text{O-H}\cdots\text{O}$ bonds found in a water dimer.⁵³ However, in all $\text{clip}_2^{\bullet+}$ dimers a 1- au charge is located on the fused central rings (where the $\text{C}=\text{O}$ groups are placed), while the $n+$ charge is spread over the two TTF groups of each $\text{clip}_1^{\bullet+}$. Thus, both $E(2\text{TTF}_1\text{-BR}_2)$ and $E(\text{BR}_1\text{-}2\text{TTF}_2)$ terms are expected to be highly stabilizing since the two interacting fragments host charge of opposite sign (the existence of a net charge in fragments with proton donor and acceptor groups is known to enlarge the hydrogen bond strength, even beyond the 50 kcal/mol covalent limit).⁵⁴ Note that the simultaneous presence of two $E(2\text{TTF}_i\text{-BR}_j)$ interactions in each dimer is made possible by a proper design of the monomer geometry.

4. SUMMARY AND CONCLUSIONS

The reasons behind the existence of dimers of bis-TTF-functionalized diphenylglycoluril molecular clips ($\text{clip}_2^{\bullet+}$) presenting short-distance $[\text{TTF}]^{\bullet+}\cdots[\text{TTF}]^{\bullet+}$ interactions, stable at room temperature when the dimer charge is ≤ 4 , but not when $4 < n < 8$, have been investigated by computing their optimum geometry and analyzing their properties in detail. The computations were performed at the M06L/6-31G(d,p) level first on isolated dimers and then in dimers in acetonitrile solution, using the PCM model to describe the solvent effects.

All $\text{clip}_1^{\bullet+}$ monomers present a V-shaped optimum geometry, where the distance between the two TTF groups placed at the end of each long arm increases about 2.0 Å (0.5 Å) from the neutral monomer to the tetraoxidized clip_1^{4+} in isolated conditions (in solution). The optimum geometry of $\text{clip}_2^{\bullet+}$ dimers consists of their two V-shaped interacting monomers oriented in opposite directions, where their long arms are intercalated, thus allowing the simultaneous formation of two types of short-distance intermolecular contacts: (a) three face-to-face $\text{TTF}\cdots\text{TTF}$ contacts between the adjacent TTF groups and (b) two $\text{C}(\text{sp}^2)\text{-H}\cdots\text{O}=\text{C}$ and four $\text{C}(\text{sp}^3)\text{-H}\cdots\text{S}$

contacts between the TTF groups and the central fused five-membered rings. The values of $\Delta G(298\text{ K})$ computed for clip_2^{n+} dimers in acetonitrile solutions reproduce the available experimental data on the stability of these dimers. Such agreement is not found when solvent effects are not taken into account.

The electronic structure of all monomers and the two interacting fragments in all dimers is similar and has a zwitterionic character: a 1– au of net charge is hosted on the central fused five-membered rings, while the net positive charge is mostly distributed on the two TTF groups, in an even way. Due to this fact, whenever all TTF groups of a clip_2^{n+} dimer host a 1+ charge, as in clip_2^{4+} , two of the three short-distance face-to-face TTF...TTF contacts become long, multicenter $[\text{TTF}]^{\bullet+}\cdots[\text{TTF}]^{\bullet+}$ bonds, while the third one becomes a van der Waals interaction. As a result, the stability of these dimers increases.

An atoms-in-molecules analysis demonstrates that the long, multicenter bonds in clip_2^{4+} and $\pi\text{-}[\text{TTF}]_2^{2+}$ are almost identical. Furthermore, the energy partitioning analysis shows that the $[\text{TTF}]^{\bullet+}\cdots[\text{TTF}]^{\bullet+}$ interactions themselves cannot be the origin for the room temperature stability of clip_2^{n+} dimers. Instead, such energy partitioning analysis traces the four short-distance A–H...B contacts between the TTF and the fused five-membered rings to be the main force of the room temperature stability of clip_2^{n+} dimers for $n \leq 4$. This fact is a consequence of the zwitterionic character of the charge distribution of the two interacting monomers of the dimer and their proper geometrical shape. Such geometrical arrangement also allows the formation of three short-distance contacts among the TTF groups, which eventually become long, multicenter bonds in clip_2^{4+} . All these factors, combined with the net stabilizing effect of the solvent, are outlined as the origin of the room temperature stability of clip_2^{n+} dimers for $n \leq 4$.

■ ASSOCIATED CONTENT

Supporting Information

Basis set comparison, intramolecular parameters to define clip_1^{n+} monomers in Table 1, charge distribution of clip_1^{n+} monomers with several schemes, highest MOs of clip_1^{n+} monomers, intermolecular parameters to define clip_2^{n+} dimers, superimposed clip_1^{n+} structures in gas phase and solution, optimum geometries of clip_2^{n+} dimers in solution, scan of the PES in solution for the clip_2^{4+} , clip_2^{6+} , and clip_2^{8+} dimers, fragment partition used in the fragment decomposition analysis, charge distribution in the bridge fragment, RASPT2/M06L comparison for isolated $\pi\text{-}[\text{TTF}]_2^{2+}$ dimers, intermolecular parameter values of clip_2^{n+} dimers, distribution of the 1+ charge upon each subsequent oxidation, electron density at the bond critical points of clip_2^{4+} and TTF_2^{2+} , Cartesian coordinates and absolute energies of all optimized species, and complete list of authors of ref 37. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (44) Besides clip_2^{2+} and clip_2^{4+} , in an increasing order of net charge in the clip_2^{n+} dimer, (1) clip_2^{2+} is a $\text{clip}_1^{+} \cdots \text{clip}_1^{+}$ interaction presenting one three-electron $[\text{TTF}]^{+} \cdots [\text{TTF}]^{+}$ interaction and one $[\text{TTF}] \cdots [\text{TTF}]$ closed-shell interaction, (2) clip_2^{3+} is a $\text{clip}_1^{2+} \cdots \text{clip}_1^{+}$ interaction presenting one $[\text{TTF}]^{+} \cdots [\text{TTF}]^{+}$ long bond interaction and one three-electron $[\text{TTF}]^{+} \cdots [\text{TTF}]^{+}$ interaction; (3) clip_2^{5+} is a $\text{clip}_1^{3+} \cdots \text{clip}_1^{2+}$ interaction presenting one one-electron $[\text{TTF}]^{2+} \cdots [\text{TTF}]^{+}$ interaction and one $[\text{TTF}]^{+} \cdots [\text{TTF}]^{+}$ long bond interaction; (4) clip_2^{6+} is a $\text{clip}_1^{3+} \cdots \text{clip}_1^{3+}$ interaction presenting two one-electron interactions, $[\text{TTF}]^{2+} \cdots [\text{TTF}]^{+}$ and $[\text{TTF}]^{+} \cdots [\text{TTF}]^{2+}$; and (5) clip_2^{8+} is a $\text{clip}_1^{4+} \cdots \text{clip}_1^{4+}$ interaction presenting two closed-shell $[\text{TTF}]^{2+} \cdots [\text{TTF}]^{2+}$ interactions, so no long bonds can be formed in this case.
- (45) A detailed quantitative analysis of the optimum geometry of all dimers was done, comparing the values of the intermolecular parameters defined in Figure S4, Supporting Information. The results (Table S1, Supporting Information) confirmed the similar geometrical disposition of the fragment in all dimers. The two TTF groups from one monomer are interlocked with those of the other, forming a four-membered π -stack. Depending on the net charge of the TTF groups, their relative disposition varies from a fully oblique conformation (similar to that found in isolated $[\text{TTF}]_2^0$ and $[\text{TTF}]_2^{+}$ dimers, see Figure S2, Supporting Information) into an on-top disposition (as in the optimum structure of isolated $[\text{TTF}]_2^{2+}$, Figure S2, Supporting Information). Also relevant is the presence of short C–H $\cdots$ O intermolecular contact ($d_2(\text{O–H})$) between the terminal TTF of one fragment and the C=O bond of the central ring of the other. When the clip hosting the C–H group is oxidized, the TTF group get the extra positive charge, while the CR group where the C=O is located hosts a 1– net charge. These are the conditions for a very strong ion–ion hydrogen bond, see: D’Oria, E.; Novoa, J. J. *J. Phys. Chem. A* **2011**, *115*, 13114.
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that for their dissociation fragments, but where the existence of a barrier towards dissociation prevents such a dissociation process.

(47) The barriers were estimated as follows: (1) the potential energy curve for the separation of the dimer into their monomers in solution was computed, after freezing the monomer geometries at their value in the dimer structure; (2) the geometry of the highest energy point was fully optimized, fixing only the monomer separation.

(48) The two C–C bonds that connect them to the rest of the clip were substituted by C–H bonds, the H atoms oriented along the same direction than the C–C bonds, but placed at a C–H distance of 1.07 Å.

(49) Consistent with this view, the external $[\text{TTF}]^{\bullet+} \cdots [\text{TTF}]^{\bullet+}$ interactions present a geometry close to the usual one in π - $[\text{TTF}]_2^{2+}$ dimers, which present long, multicenter bonds, while the internal $[\text{TTF}]^{\bullet+} \cdots [\text{TTF}]^{\bullet+}$ interaction present a distance similar to that found in π - $[\text{TTF}]_2^0$ dimers, a van der Waals dimer.

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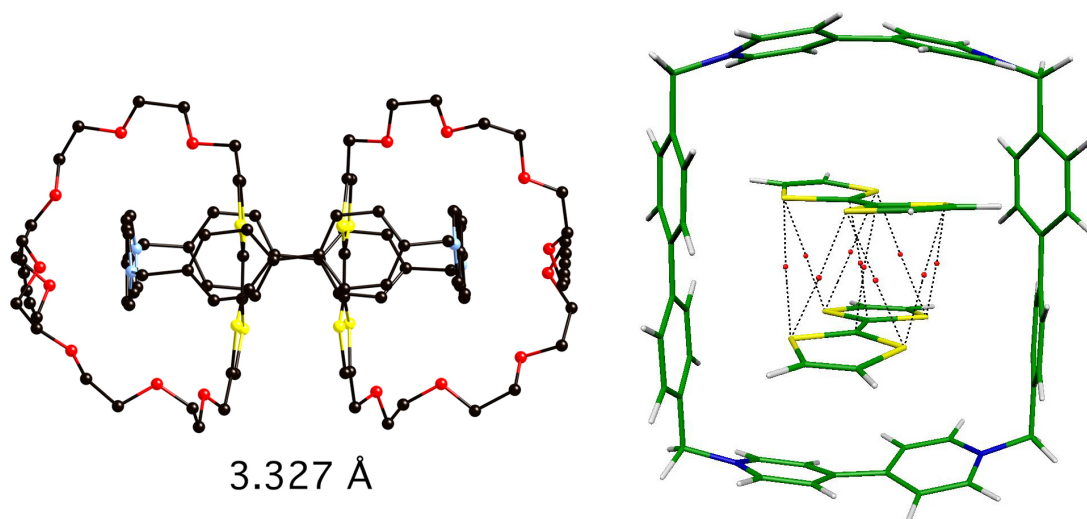
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4.6. Publication 9

The Nature of the $[\text{TTF}]^{\cdot+} \cdots [\text{TTF}]^{\cdot+}$ Interactions in the $[\text{TTF}]_2^{2+}$ Dimers Embedded in Charged [3]Catenanes: Room-Temperature Multicenter Long Bonds



FULL PAPER

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The Nature of the $[\text{TTF}]^{\cdot+} \cdots [\text{TTF}]^{\cdot+}$ Interactions in the $[\text{TTF}]_2^{2+}$ Dimers Embedded in Charged [3]Catenanes: Room-Temperature Multicenter Long Bonds**

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Abstract: The properties of tetrathiafulvalene dimers ($[\text{TTF}]_2^{2+}$) and the functionalized ring-shaped bispropargyl (BPP)-functionalized TTF dimers, $[\text{BPP-TTF}]_2^{2+}$, found at room temperature in charged [3]catenanes, were evaluated by M06L calculations. The results showed that their isolated $[\text{TTF}]_2^{2+}$ and $[\text{BPP-TTF}]_2^{2+}$ dimers are energetically unstable towards dissociation. When enclosed in the 4⁺-charged central cyclophane ring of charged [3]catenanes (CBPQT⁴⁺), $[\text{TTF}]_2^{2+}$ and $[\text{BPP-TTF}]_2^{2+}$ dimers are also energetically unstable with respect to leaving the CBPQT⁴⁺ ring; since the barrier

for the exiting process is only about 3 kcal mol⁻¹, that is, within the reach of thermal energies at room temperature (neutral $[\text{TTF}]_2^0$ dimers are stable within the CBPQT⁴⁺ ring). However, the $[\text{BPP-TTF}]_2^{2+}$ dimers in charged [3]catenanes cannot exit, because this would imply breaking the covalent bonds of the BPP-TTF⁺ macrocycle. Finally, it was shown that the $[\text{TTF}]_2^{2+}$,

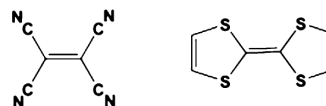
$[\text{BPP-TTF}]_2^{2+}$ dimers, and charged [3]catenanes are energetically stable in solution and in crystals of their salts, in the first case due to the interactions with the solvent, and in the second case mostly due to cation–anion interactions. In these environmental conditions at room temperature the TTF units of the $[\text{BPP-TTF}]_2^{2+}$ dimers make short contacts, thus allowing their SOMO orbitals to overlap: a room-temperature multicenter long bond is formed, similar to those previously found in other $[\text{TTF}]_2^{2+}$ salts and their solutions.

Keywords: aggregation • bond theory • catenanes • density functional calculations • noncovalent interactions

Introduction

The presence of long multicenter bond between charged radicals was first observed and theoretically analyzed for salts of reduced tetracyanoethylene (TCNE), in which π - $[\text{TCNE}]_2^{2-}$ dimers were found.^[1–10] Isolated π - $[\text{TCNE}]_2^{2-}$ dimers are energetically unstable and should thus dissociate, as was observed in solution at room temperature.^[4] However, dimers do form in solids and in low-temperature solutions. In solids, π - $[\text{TCNE}]_2^{2-}$ dimers are formed due to the attractive electrostatic cation $\cdots$ (radical anion) interactions dominating the repulsive electrostatic $[\text{TCNE}]^{\cdot-}$ interactions present in the π - $[\text{TCNE}]_2^{2-}$ dimer (note that there is also a small attractive energetic contribution originating from the dispersion component present in the (anion radical) $\cdots$ (anion radical) interaction).^[11] This has been observed for cation₂TCNE₂ aggregates, in which the sum of the four attractive cation $\cdots$ $[\text{TCNE}]^{\cdot-}$ interactions exceeds the sum of the (anion radical) $\cdots$ (anion radical) $\cdots$ and cation $\cdots$ cation $\cdots$ repulsive interactions. In solution, π - $[\text{TCNE}]_2^{2-}$ dimers are

formed due to the $[\text{TCNE}]^{\cdot-} \cdots$ solvent interactions exceeding the $[\text{TCNE}]^{\cdot-} \cdots [\text{TCNE}]^{\cdot-}$ repulsion, which is in agreement with the computational results for $[\text{solvent}]_n[\text{TCNE}]_2^{2-}$ aggregates. The energetic stability of the cation₂TCNE₂ and $[\text{solvent}]_n[\text{TCNE}]_2^{2-}$ aggregates allows its two $[\text{TCNE}]^{\cdot-}$ units to be close enough (≈ 2.9 Å) to overlap the b_{2g} SOMO of each radical anion. This enables formation of a b_{2u} bonding and a b_{1g} antibonding orbitals in the $[\text{TCNE}]_2^{2-}$ dimer that are doubly occupied and empty in the singlet ground state, respectively. Hence, despite their intrinsic energetic repulsive nature, $[\text{TCNE}]_2^{2-}$ has the same MO diagram as that observed for conventional covalent bonds. Thus, one can talk about the presence of long multicenter bonds between the $[\text{TCNE}]^{\cdot-}$ radical anions in $[\text{TCNE}]_2^{2-}$. The preference for a closed-shell singlet ground state that emerges from this diagram explains the diamagnetic character of these dimers.^[2]



An increasing number of organic compounds are observed to exhibit, in their crystalline form, similar properties to those previously reported for $[\text{TCNE}]_2^{2-}$ dimers; behavior that can also be explained by the presence of long-distance bonding. In addition to other anions (e.g., cyanil^[12] and

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[**] TTF = tetrathiafulvalene

7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ)),^[4,13–18] examples include neutral radicals, such as phenalenyl,^[19] and radical-cation dimers: more specifically, the (tetrathiafulvalene)₂²⁺, π -[TTF]₂²⁺ dimer.^[20–33] The formation of diamagnetic π -[TTF]₂²⁺ dimers has also been reported in water^[34] and ethanol^[35] solutions at very low temperature. UV/Vis and EPR spectroscopic studies have established the thermodynamic parameters for this cation-radical dimerization in ethanol, acetone, DMF, MeCN, THF, and dichloromethane.^[36] The 2[TTF]^{•+} ⇌ [TTF]₂²⁺ equilibrium is solvent and temperature dependent, and < –70 °C is required to observe the dimer in dichloromethane, the solvent with the weakest dimerization energy, in which $\Delta H_{\text{dim}} = -3.8 \text{ kcal mol}^{-1}$ and $\Delta S_{\text{dim}} = -18 \text{ eu}$. It is important to note that the absorption spectrum of the [TTF]₂²⁺ dimer in solution at –90 °C is similar to that in [TTF]₂²⁺ salts,^[20–22] and remains essentially invariant, when the solvent or counterions are changed. This suggests that the structure of the [TTF]₂²⁺ dimers in solution and in the crystal is similar and is also largely unaffected by the environment.^[37]

Recently, the existence of solution-stable [TTF]₂²⁺ dimers at room temperature has been reported in inclusion complexes of [TTF]^{•+},^[38,39] in molecular clips and calixarenes,^[40–42] and in interlocked [3]catenanes.^[43] The formation of solution-stable dimers at room temperature is not unique for [TTF]₂²⁺ dimers, because they have also been recently reported for [TCNQ]₂^{2–} dimers included in the cavity of a porphyrin-containing macrocycle.^[44] Herein, we focus on the last class of compounds, the structures of which are depicted in Figure 1. They present two external macrocycles

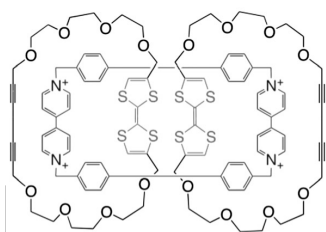


Figure 1. Structure of the [3]catenane^{*n*+} complexes studied in this work.^[43] Gray indicates the CBPQT⁴⁺ cyclophane, black indicates the bispropargyl-functionalized TTF ring, BPP–TTF, which can also be charged. The TTF group of BPP–TTF is represented in dark gray.

threaded to a central cyclophane ring with a 4+ net charge: cyclobis(paraquat-4,4'-biphenylene), termed CBPQT⁴⁺. This central ring is interlocked by two external macrocycles, each being a bispropargyl-functionalized TTF derivative (hereafter BPP–TTF). If the BPP–TTF ring has zero charge, the [3]catenane complex has a 4+ net charge. Upon electrochemical oxidation of [3]catenane, the TTF part of each BPP–TTF macrocycle can be independently oxidized, increasing its TTF net charge to 1+ or 2+. In other words, the net charge of [3]catenane can be 4+, 5+, 6+, 7+, or 8+ (4+ when the two BPP–TTF chains present a neutral non-oxidized [TTF]₂ dimer, and 8+ when the two chains

have a 2+ charge). Hence, it is necessary to indicate the total charge (*n*+) on these systems as follows: [3]catenane^{*n*+}.

Among the possible [3]catenane^{*n*+} compounds, [3]catenane⁶⁺ (which has a [BPP–TTF]₂²⁺ dimer) is of special interest, since its [BPP–TTF]₂²⁺ dimer has a geometry that allows the presence of short-distance [BPP–TTF]₂²⁺ contacts and thus a multicenter long bond of the type observed in [TTF]₂²⁺ salts or solutions at low enough temperature.^[37] However, the [BPP–TTF]₂²⁺ dimers found in [3]catenanes⁶⁺ exhibit two striking properties, which were not previously seen in the [TTF]₂²⁺ dimers found in salts and solutions: first, [BPP–TTF]₂²⁺ are stable at room temperature (rather than below –70 °C^[36]), and second, the nature of the [BPP–TTF]^{•+}...[BPP–TTF]^{•+} interaction in these dimers was reported to be different from that previously reported in other [TTF]₂²⁺ dimers, such as [BPP–TTF]₂²⁺ dimers, which were reported to be intrinsically stable.^[45] These two facts prompted us to perform a detailed theoretical investigation on the nature of the [BPP–TTF]^{•+}...[BPP–TTF]^{•+} interactions in [3]catenanes^{*n*+} (*n* = 4, 5, 6, and 8), a study that was also extended to the nature of the associated [(TTF)₂^{*n*+} ⊂ CBPQT⁴⁺]^{4–*n*} inclusion complex, which can be obtained from [3]catenanes^{*n*+} by substituting the BPP–TTF molecules by TTFs.

Computational Methods

The nature of the [TTF]^{•+}...[TTF]^{•+} interactions in [3]catenanes^{*n*+} (*n* = 4+, 5+, ...8+) and particularly [3]catenane⁶⁺ shown in Figure 1, was theoretically investigated by DFT calculations with the M06L functional. The study was done in five consecutive steps, outlined below.

In the first step, the stabilizing or destabilizing energetic character^[46] of isolated [TTF]^{*n*+}...[TTF]^{*n*+} interactions was determined for two [BPP–TTF]^{*n*+} rings present in the [3]catenane⁴⁺, [3]catenane⁵⁺, and [3]catenane⁶⁺ crystals. The same study was also done for isolated [TTF]₂^{0,1+,2+} dimers. Note that [TTF]₂ was found in the crystals of the [(TTF)₂ ⊂ CBPQT⁴⁺] inclusion complex, which has the same central CBPQT⁴⁺ cyclophane ring found in [3]catenane. These studies were performed by using the M06L density functional,^[47] chosen due to its ability to describe π – π interactions, for reproducing the structure and energy of interlocked molecules well,^[48] and for compatibility with the functional used in [43]. The geometry of the [TTF]₂⁰ and [BPP–TTF]₂^{0,1+,2+} dimers was extracted from the crystals, in which they are present. To date, crystal structures for the 1+ and 2+ salts of the [TTF]₂^{*n*+} ⊂ CBPQT⁴⁺]^{4–*n*} inclusion complex have not been determined, and their optimum [TTF]₂^{1+,2+} geometry was obtained by M06L/6-31G geometry optimization.

In the second step of our study, the energetic character of embedding [TTF]₂^{0,1+,2+} and [BPP–TTF]₂^{0,1+,2+} dimers in [(TTF)₂^{*n*+} ⊂ CBPQT⁴⁺]^{4–*n*} and [3]catenane^{*n*+} complexes, respectively, was evaluated. Special attention was paid to the [3]catenane⁶⁺ and associated [TTF]₂²⁺ ⊂ CBPQT⁴⁺ complexes. The crystal structures of [3]catenane^{*n*+} (*n* = 4, 5, and 6) and [(TTF)₂ ⊂ CBPQT⁴⁺] [PF₆]₄ are known.^[43] However, as already mentioned, no crystallographic structures have yet been reported for [TTF]₂^{•+} ⊂ CBPQT⁴⁺]⁵⁺ and [TTF]₂²⁺ ⊂ CBPQT⁴⁺]⁶⁺. Consequently, the evaluation of the interaction energy computations for the last two complexes has to be done by using their optimum M06L geometries. It could be shown that neither the [3]catenane⁶⁺ nor the [(TTF)₂²⁺ ⊂ CBPQT⁴⁺]⁶⁺ complexes are energetically stable against the loss of their [TTF]₂²⁺ and [BPP–TTF]₂²⁺ dimers, thus explaining why the [(TTF)₂²⁺ ⊂ CBPQT⁴⁺] complex has still not been isolated (as shown

below, mechanical restrictions explain why $[3]\text{catenane}^{6+}$ exists, despite being energetically unstable against losing its two $[\text{BPP-TTF}]^{n+}$ rings).

In step three, we showed that only after adding the anions that neutralize the $[3]\text{catenane}^{6+}$ and $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ complexes, one can obtain energetically stable aggregates, in which species of this type are found, thus explaining the presence of $[\text{BPP-TTF}]_2^{2+}$ dimers in crystals of their salts.

The synthesis and many experimental studies on the properties of $[3]\text{catenane}^{6+}$ and $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ are done in solution. Consequently, we also evaluated the impact of the solvent interaction on the stability of the $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ and $[3]\text{catenane}^{6+}$ complexes, and on that for the $[\text{TTF}]_2^{2+}$ and $[\text{BPP-TTF}]_2^{2+}$ dimers, which represents the fourth step of our study. The study of the solvent effects was achieved by doing polarizable continuum model (PCM) calculations,^[49] with acetonitrile as the solvent used in the experimental studies.^[43]

Finally, in the fifth step of this work, the reasons for the existence of $[\text{TTF}]_2^{2+}$ and $[\text{BPP-TTF}]_2^{2+}$ dimers embedded in a CBPQT^{4+} ring at room temperature were determined, combining all results obtained in previous sections. All calculations were carried out by using the Gaussian 09 suite of programs^[50] and the 6-31G and 6-31G(d,p) Gaussian basis sets (the first was used for the geometry optimizations, and the second for single point calculations).^[51]

Results and Discussion

The energetic character of isolated $[\text{TTF}]^{n+} \cdots [\text{TTF}]^{m+}$ and $[\text{BPP-TTF}]^{n+} \cdots [\text{BPP-TTF}]^{m+}$ interactions:

The first three rows in Table 1 (first column) collect the M06L-computed interaction energy between the TTF units of a $[\text{TTF}]_2^0$ dimer (extracted from the $[(\text{TTF})_2 \subset \text{CBPQT}^{4+}] [\text{PF}_6]_4$ crystal^[43]), of a $[\text{TTF}]_2^{1+}$ dimer (extracted by doing a M06L/6-31G geometry optimization^[52] of $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]$, Figure 2), and of a $[\text{TTF}]_2^{2+}$ dimer (extracted from the optimum M06L/6-31G geometry of $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$, Figure 2). The next three rows in Table 1 collect the interaction energy between the two BPP-TTFⁿ⁺ rings found in $[3]\text{catenane}^{4+}$, mono-oxidized $[3]\text{catenane}^{5+}$, and dioxidized $[3]\text{catenane}^{6+}$. Finally, the last two rows in Table 1 collect the interaction energy between the two $[\text{BPP-TTF}]^{n+}$ rings from a rotated $[3]\text{catenane}^{6+}$ and a $[3]\text{catenane}^{8+}$ complexes, the geometries of which are shown in Figure 3 (it has been reported that the BPP-TTF rings in $[3]\text{catenane}^{8+}$ rotate,^[43] thus making impossible the existence of overlap between the orbitals sitting in the two TTF groups).

The results in Table 1 indicate that $[\text{TTF}]_2^0$ and $[\text{BPP-TTF}]_2^0$ are weakly stable dimers, their interaction energy being within the range expected for π - π van der Waals dimers. The similar stability of these two dimers indicates that the BPP part of the BPP-TTF rings interact weakly. However, the $[\text{TTF}]_2^{2+}$ and $[\text{BPP-TTF}]_2^{2+}$ dimers are about four times more stable than their nonoxidized counterparts (once again, the BPP groups make a negligible impact on the interaction energy). Finally, the $[\text{TTF}]_2^{2+}$ and $[\text{BPP-TTF}]_2^{2+}$ dimers both have destabilizing interaction energies (the second being less destabilizing than the first, probably due to charge delocalization). The destabilizing character of the interaction energy in the $[\text{TTF}]_2^{2+}$ and $[\text{BPP-TTF}]_2^{2+}$ dimers is in good agreement with the results from previous studies of other $[\text{TTF}]_2^{2+}$ dimers.^[37] It also indicates that the existence of short-distance contacts between the two fragments of the $[\text{BPP-TTF}]_2^{2+}$ rings in $[3]\text{catenane}^{6+}$ does not imply a stabilizing interaction energy between the two fragments, as was erroneously concluded in a previous work.^[43a]

We focus now on rotated $[3]\text{catenane}^{6+}$, which results from the rotation of two BPP-TTF rings of $[3]\text{catenane}^{6+}$ 180° around the central CBPQT^{4+} ring (see Figure 3 for the M06L/6-31G optimum geometry). In Table 1, rotated $[3]\text{catenane}^{6+}$ is more stable (i.e., less repulsive) than its nonrotated counterpart, $[3]\text{catenane}^{6+}$, and thus, in an isolated $[3]\text{catenane}^{6+}$, the two $[\text{BPP-TTF}]^{n+}$ rings should rotate. Also note that rotated and nonrotated $[3]\text{catenane}^{6+}$ are

Table 1. Interaction energy (in kcal mol⁻¹) between the fragments of the $[(\text{TTF})_2^{n+} \subset \text{CBPQT}^{4+}]^{m+}$ ($n=0, 1+, 2+$ and $m=n+4$) inclusion complexes and the rings of the $[3]\text{catenanes}^{n+}$ ($n=0, 1+,$ and $2+$), shown in Figure 1 and 2. $[\text{TTF}]_2^{n+} \cdots [\text{TTF}]_2^{m+}$ collects the interaction energy between the two unsubstituted (first three rows) or substituted (next three rows) TTF units and $[\text{TTF}]_2^{n+} \cdots \text{CBPQT}^{4+}$ the interaction energy between the (unsubstituted or substituted) TTF unit 1 or 2 and the cyclophane CBPQT^{4+} ring. The sum of the first three columns is collected under E_{tot} , an approximation to the interaction energy in a pairwise approximation, whereas E_{int} is the exact interaction energy (computed as the difference between the total energy of the complex minus the sum of the energies of the isolated fragments). When available, the second row value refers to the same property within a continuous solvent model (see text). All energies were computed at the M06L/6-31G(d,p) level.

System	$[\text{TTF}]_2^{n+} \cdots [\text{TTF}]_2^{m+}$	$[\text{TTF}]_2^{n+} \cdots \text{CBPQT}^{4+}$	$[\text{TTF}]_2^{n+} \cdots \text{CBPQT}^{4+}$	E_{tot}	E_{int} $E_{\text{int, MeCN}}$
$[(\text{TTF})_2 \subset \text{CBPQT}^{4+}]^{4+}$	-7.0 -7.1	-37.9	-36.3	-81.2	-82.3 -61.6
$[(\text{TTF})_2^{1+} \subset \text{CBPQT}^{4+}]^{5+}$	-28.8 -18.9	154.3	-29.8	95.7	100.6 -47.5
$[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$	38.2 -11.3	149.5	152.6	340.3	336.8 -31.2
System	$(\text{BPP-TTF})_2^{n+} \cdots (\text{BPP-TTF})_2^{m+}$	$(\text{BPP-TTF})_2^{n+} \cdots \text{CBPQT}^{4+}$	$(\text{BPP-TTF})_2^{n+} \cdots \text{CBPQT}^{4+}$	E_{tot}	E_{int} $E_{\text{int, MeCN}}$
$[3]\text{catenane}^{4+}$	-8.4 -7.7	-111.3	-114.5	-234.2	-228.3 -113.3
$[3]\text{catenane}^{5+}$	-27.9 -17.6	73.2	-115.0	-69.7	-48.7 -109.3
$[3]\text{catenane}^{6+}$	23.9 -14.6	65.2	60.8	149.9	147.8 -95.5
rotated $[3]\text{catenane}^{6+}$	16.7 4.8	27.7	20.8	65.2	54.1 -32.8
$[3]\text{catenane}^{8+}$	nam ^[a]	nam ^[a]	nam ^[a]	nam ^[a]	nam ^[a]
rotated $[3]\text{catenane}^{8+}$	59.0 1.4	140.0	142.7	341.7	324.2 -50.2

[a] Not a minimum in the potential energy surface because it converts into the rotated conformer (see Figure 3 for structure).

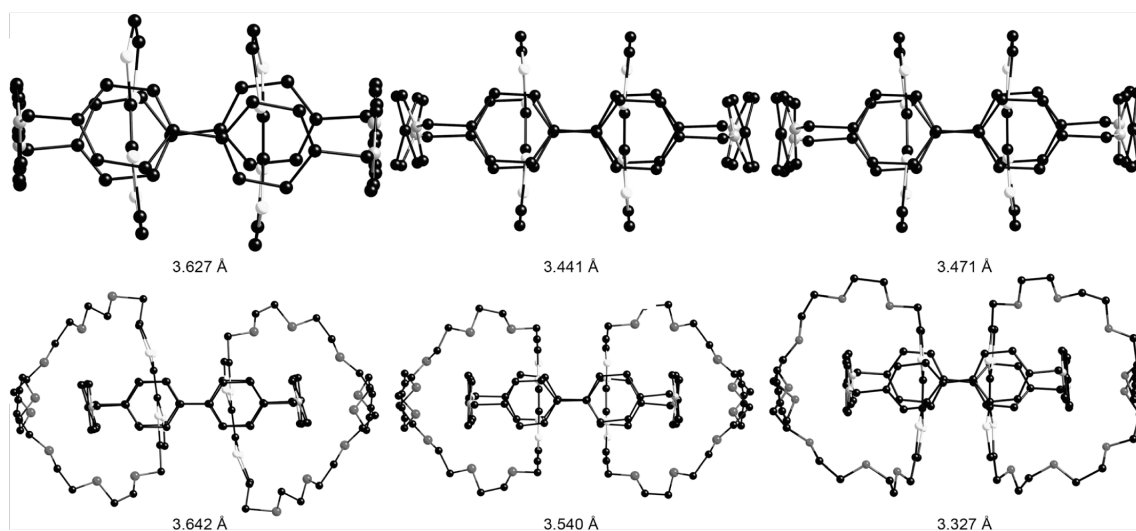


Figure 2. Upper row: geometry of the $[(\text{TTF})_2\text{C}(\text{CBPQT})^{4+}]^{4+n}$ ($n=0, 1+$, and $2+$) inclusion complexes used in Table 1 computations. Those for $n=0$ is taken from the $[(\text{TTF})_2\text{C}(\text{CBPQT})^{4+}][\text{PF}_6]_4$ crystal structure,^[43] whereas the remaining two are M06L/6-31G optimum geometries. Bottom row: geometry of the [3]catenane $^{4+}$, [3]catenane $^{5+}$, and [3]catenane $^{6+}$ aggregates studied in Table 1 (all were extracted from their crystals^[43]). The shortest distance between the TTF groups is given in all complexes. Hydrogen atoms are omitted for clarity.

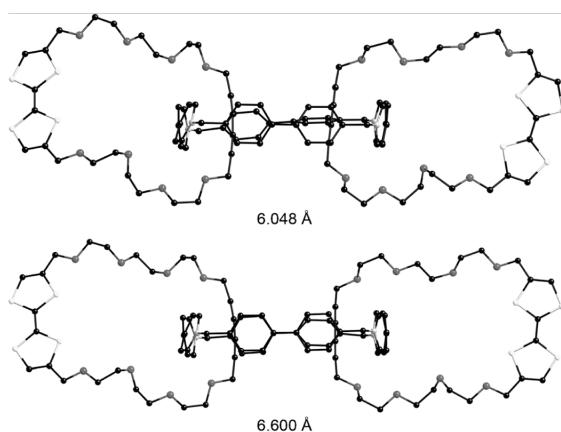


Figure 3. Optimum geometry of the rotated [3]catenane $^{6+}$ and [3]catenane $^{8+}$ complexes computed at the M06L/6-31G level. The shortest distance between the bispropargyl-functionalized TTF is also indicated. Hydrogen atoms are omitted for clarity.

both minimum-energy structures on the potential energy surface of these complexes, a fact that implies that there is a barrier for the rotation of the two [BPP-TTF] $^+$ rings, which was not estimated here. However, one can infer that such barrier has to be higher than the available thermal energy at room temperature, because the rotation of [3]catenane $^{6+}$ is not observed experimentally.^[43] Note that when solvent effects are also included, thus better mimicking the

solution environment, the nonrotated [3]catenane $^{6+}$ becomes the more stable conformation (Table 1).

The last row of Table 1 collects the interaction energy for the rotated and nonrotated conformations of [3]catenane $^{8+}$, the optimum structure of which is shown in Figure 3. The interaction energy between two [BPP-TTF] $^{2+}$ rings is more repulsive than that between two [BPP-TTF] $^+$ rings, and is in good agreement with the larger repulsive Coulombic term originating in the larger charge placed in [BPP-TTF] $^{2+}$ (the bonding contribution also disappeared after each BPP-TTF ring lost one second electron, thus becoming a closed-shell singlet). As shown in Table 1, the rotated conformation is much more stable than the nonrotated conformation, and is in good agreement with the experimental findings.^[43] Our computations also show that nonrotated [3]catenane $^{8+}$ is not a minimum-energy structure and spontaneously converts into rotated [3]catenane $^{8+}$, when both isolated or in solution.

At this point, it is also worth evaluating and comparing the distribution of net charges on the $[(\text{TTF})_2\text{C}(\text{CBPQT})^{4+}]^{4+}$ and $[(\text{TTF})_2\text{C}(\text{CBPQT})^{4+}]^{6+}$ complexes (Table 2). The calculated Mulliken atomic charges indicate that, although before the double oxidation each TTF fragment had a net charge of $+0.23 e^-$, after this double oxidation they have a charge of $+0.71 e^-$, with a net gain of $+0.48 e^-$ (according to an electrostatic potential (ESP) analysis, the gain is $+0.35 e^-$). Therefore, part of the $2+$ formal charge that the $[\text{TTF}]_2^{2+}$ dimer should have after the double oxidation becomes transferred to the CBPQT^{4+} ring ($+0.58 e^-$ in the Mulliken analysis, and $+1.02 e^-$ in the ESP analysis).

Table 2. Computed Mulliken and ESP net-atomic charges on the eight fused rings that form the CBPQT⁴⁺ cyclophane ring (four phenyls and four pyridyls, Figure 1) and the two TTF molecules computed for the $[(\text{TTF})_2 \subset \text{CBPQT}^{4+}]^{4+}$ and $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ complexes at the M06L/6-31G level.

	$[(\text{TTF})_2 \subset \text{CBPQT}^{4+}]^{4+}$		$[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$	
	Mulliken	ESP	Mulliken	ESP
TTF 1	0.23	0.13	0.71	0.48
TTF 2	0.23	0.13	0.71	0.50
pyridyl 1	0.65	0.64	0.83	0.84
pyridyl 2	0.65	0.65	0.83	0.84
phenyl 1	0.24	0.30	0.32	0.43
phenyl 2	0.24	0.26	0.32	0.41
pyridyl 3	0.65	0.66	0.83	0.83
pyridyl 4	0.65	0.65	0.83	0.83
phenyl 3	0.24	0.27	0.32	0.41
phenyl 4	0.24	0.31	0.32	0.43

The energetic character of embedding $[\text{TTF}]_2^{0,1,2+}$ and $[\text{BPP-TTF}]_2^{0,1,2+}$ dimers in $[(\text{TTF})_2^{n+} \subset \text{CBPQT}^{4+}]^{(4+n)+}$ and $[\text{3]catenane}^{n+}$ aggregates: As shown in Table 1, embedding one $[\text{TTF}]_2^{2+}$ dimer inside a CBPQT⁴⁺ ring to form $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ is energetically destabilizing by 340 kcal mol⁻¹ (Figure 2). Similar values are obtained when using the pair approach ($E_{\text{int}} = E[(\text{TTF})_1^{n+} \cdots (\text{TTF})_2^{m+}] + E[(\text{TTF})_1^{n+} \cdots \text{CBPQT}^{4+}] + E[(\text{TTF})_2^{m+} \cdots \text{CBPQT}^{4+}]$) or the exact expression ($E_{\text{int}} = E[(\text{TTF})_1^{n+} \cdots (\text{TTF})_2^{m+} \cdots \text{CBPQT}^{4+}] - E[(\text{TTF})_1^{n+}] - E[(\text{TTF})_2^{m+}] - E[\text{CBPQT}^{4+}]$). Similarly, embedding a $[\text{BPP-TTF}]_2^{2+}$ dimer inside a CBPQT⁴⁺ ring to form $[\text{3]catenane}^{6+}$ (Figure 2) is energetically destabilizing by 150 kcal mol⁻¹. Given the fact that these are vibrationally tested minimum energy structures, necessarily $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ and $[\text{3]catenane}^{6+}$ are metastable minima, and thus should present a barrier for the loss of a $[\text{TTF}]_2^{2+}$ or a $[\text{BPP-TTF}]_2^{2+}$ dimer (see below). Such destabilizing energetic character originates mostly in the $[\text{TTF}]^{2+} \cdots \text{CBPQT}^{4+}$ and $[\text{BPP-TTF}]^{2+} \cdots \text{CBPQT}^{4+}$ pair interactions (both expected to be repulsive, due to the cationic nature of the two interacting fragments).

The inclusion of a $[\text{TTF}]_2^{2+}$ dimer in CBPQT⁴⁺ to form the $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ complex is also repulsive. Only when the complex charge is decreased to 4+, that is $[(\text{TTF})_2 \subset \text{CBPQT}^{4+}]^{4+}$, is the inclusion of $[\text{TTF}]_2$ energetically stable. Such an energetic trend is in agreement with the existence of crystals of $[(\text{TTF})_2 \subset \text{CBPQT}^{4+}]^{4+}$, but not of its doubly oxidized form. Similarly, although $[\text{3]catenane}^{6+}$ is energetically unstable towards the exit of their two BPP-TTF rings, $[\text{3]catenane}^{5+}$ and $[\text{3]catenane}^{4+}$ are stable towards this loss (Table 1). Besides, for the same net charge $[\text{BPP-TTF}]^{n+} \cdots [\text{BPP-TTF}]^{n+}$ interactions are more stable than $[\text{TTF}]^{n+} \cdots [\text{TTF}]^{n+}$, the reason being the delocalization of net charge over the whole supramolecular ring in the first case.

The kinetics for the loss of one $[\text{TTF}]^{2+}$ and one $[\text{TTF}]_2^{2+}$ dimer was investigated in the $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ complex at the M06L/6-31G level (Figure 4). Both exiting processes showed a small barrier of about 3 kcal mol⁻¹, placed at $[\text{TTF}]^{2+} \cdots [\text{TTF}]^{2+}$ separations slightly larger than that for

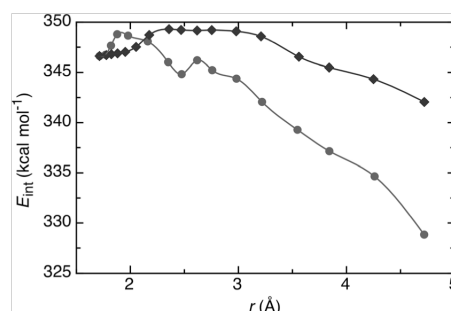


Figure 4. Potential energy curve for the exiting of one $[\text{TTF}]^{2+}$ fragment and for the simultaneous loss of the two fragments from $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ (computed at the M06L/6-31G level). The parameter r is defined as the distance between the centers of the C=C bond in the $[\text{TTF}]^{2+}$ radical cations and the center of the CBPQT⁴⁺ ring. ● = $[\text{CBPQT}^{4+} \cdots \text{TTF}_2^{2+}]$; ◆ = $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+} \cdots [\text{TTF}]^{2+}$.

the fully optimized minima. Such a small barrier is within the range of available thermal energies at room temperature and, consequently, at room temperature $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ should spontaneously lose either one $[\text{TTF}]^{2+}$ radical or the entire $[\text{TTF}]_2^{2+}$ dimer. The loss of one or two $[\text{BPP-TTF}]^{2+}$ rings in $[\text{3]catenane}^{6+}$ was not investigated, because it implies the rupture of at least one of the covalent bonds that link the groups of the $[\text{BPP-TTF}]^{2+}$ rings, which is a highly endothermic process. However, the kinetics of the loss of one $[\text{TTF}]_2^{2+}$ dimer from the $[(\text{TTF})_2^{4+} \subset \text{CBPQT}^{4+}]^{8+}$ complex was investigated (Figure 5). Such a process is barrierless, that is, at any temperature any isolated $[(\text{TTF})_2^{4+} \subset \text{CBPQT}^{4+}]^{8+}$ complex should spontaneously lose its $[\text{TTF}]_2^{4+}$ group.

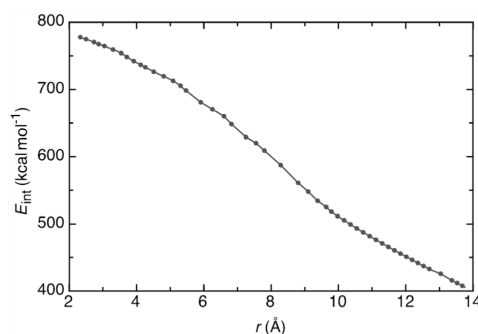


Figure 5. Variation of the total interaction energy of the $[(\text{TTF})_2^{4+} \subset \text{CBPQT}^{4+}]^{8+}$ complex with the interfragment distance r for the exiting of the $[\text{TTF}]_2^{4+}$ dimer from $[(\text{TTF})_2^{4+} \subset \text{CBPQT}^{4+}]^{8+}$. The curve computed at the M06L/6-31G level was obtained by allowing the geometry of the $[(\text{TTF})_2^{4+} \subset \text{CBPQT}^{4+}]^{8+}$ system to optimize. The parameter r is the distance between the center of the C=C bond in the $[\text{TTF}]^{2+}$ cations and the center of the CBPQT⁴⁺ ring. As they leave the cavity, the two fragments of the $[\text{TTF}]_2^{4+}$ dimer progressively split.

Adding anions: the energetics of $[(\text{TTF})_2]^{2+}\text{CBPQT}^{4+}]^{6+}[\text{PF}_6]^-_6$ and $[3]\text{catenane}^{6+}[\text{PF}_6]^-_2[\text{ClO}_4]^-_4$ aggregates: Due to our primary interest in the intrinsic stability of isolated $[\text{TTF}]_2^{2+}$ and $[\text{BPP-TTF}]_2^{2+}$ dimers, and then on the stability of these dimers when they are embedded in a CBPQT^{4+} ring, the anions (required to preserve the charge balance in salts and their solutions) were left out of all previous energetic analyses. However, as shown in this section, these anions are key to the existence of $[\text{TTF}]_2^{2+}$ and $[\text{BPP-TTF}]_2^{2+}$ dimers in $[(\text{TTF})_2]^{2+}\text{CBPQT}^{4+}]^{6+}$ and $[3]\text{catenane}^{6+}$ complexes in crystals, although the solvent plays the same key role in solutions.

To demonstrate the key role played by the anions on the stability of the $[\text{TTF}]_2^{2+}$ and $[\text{BPP-TTF}]_2^{2+}$ dimers in $[(\text{TTF})_2]^{2+}\text{CBPQT}^{4+}]^{6+}$ and $[3]\text{catenane}^{6+}$ complexes, six PF_6^- anions were added to the energetically unstable $[(\text{TTF})_2]^{2+}\text{CBPQT}^{4+}]^{6+}$ complex, to counterbalance the excess positive charge, which resulted in the neutral $[(\text{TTF})_2]^{2+}\text{CBPQT}^{4+}]^{6+}[\text{PF}_6]^-_6$ complex. The energetic stability of the resulting neutral complexes towards its dissociation into their constituent fragments was investigated for the fully optimized structure (Figure 6, M06L/6-31G optimization).^[52] At its optimum energy geometry, the neutral $[(\text{TTF})_2]^{2+}\text{CBPQT}^{4+}]^{6+}[\text{PF}_6]^-_6$ complex is $-822.9 \text{ kcal mol}^{-1}$ more stable than its constituent fragments. Therefore, the reason for the stability of $[\text{TTF}]_2^{2+}$ dimers in $[(\text{TTF})_2]^{2+}\text{CBPQT}^{4+}]^{6+}[\text{PF}_6]^-_6$ results from the combined effect of the cation $\cdots$ anion interactions, which overcome the repulsive character of the $[\text{TTF}]_2^{2+}\cdots\text{CBPQT}^{4+}$ interaction (helped by a smaller dispersion component acting between the two $[\text{TTF}]^{+\cdot}$ radicals^[10]).

The energetic stability of the neutral $[(\text{TTF})_2]\text{CBPQT}^{4+}]^{4+}[\text{PF}_6]^-_4$ complex (Figure 6), which is obtained after adding four PF_6^- anions to the energetically stable $[(\text{TTF})_2]\text{CBPQT}^{4+}]^{4+}$ complex (by $-81.2 \text{ kcal mol}^{-1}$) was also evaluated and found to be $-568.2 \text{ kcal mol}^{-1}$. In both neutral complexes, the anions are placed above and below the plane of the CBPQT^{4+} ring without distorting the geometry of the $[(\text{TTF})_2]\text{CBPQT}^{4+}]^{4+}$ and $[(\text{TTF})_2]^{2+}\text{CBPQT}^{4+}]^{6+}$ cations.

Finally, the energetic stability of a $[3]\text{catenane}^{6+}[\text{PF}_6]^-_2[\text{ClO}_4]^-_4$ cluster (Figure 6) was investigated. This neutral cluster was extracted from a crystal, without further optimization. Its interaction energy was found to be $-848.8 \text{ kcal mol}^{-1}$, at the M06L/6-31G(d,p) level. Once again, when this value is compared with the interaction energy of an isolated $[3]\text{catenane}^{6+}$ complex, $149.9 \text{ kcal mol}^{-1}$, an estimate of the combined energetic impact of the cation $\cdots$ anion interactions can be obtained.

The results from this and the previous sections lead to the following conclusion concerning the existence of $[\text{TTF}]_2^{2+}$ and $[\text{BPP-TTF}]_2^{2+}$ dimers in $[(\text{TTF})_2]^{2+}\text{CBPQT}^{4+}]^{6+}[\text{PF}_6]^-_6$ and $[3]\text{catenane}^{6+}[\text{PF}_6]^-_2$ complexes and in their crystals: although $[\text{TTF}]_2^{2+}$ and $[\text{BPP-TTF}]_2^{2+}$ dimers are not stable when isolated or embedded in a CBPQT^{4+} ring, they become stable in $[(\text{TTF})_2]^{2+}\text{CBPQT}^{4+}]^{6+}[\text{PF}_6]^-_6$ aggregates and crystals due to the combined impact of the cat-

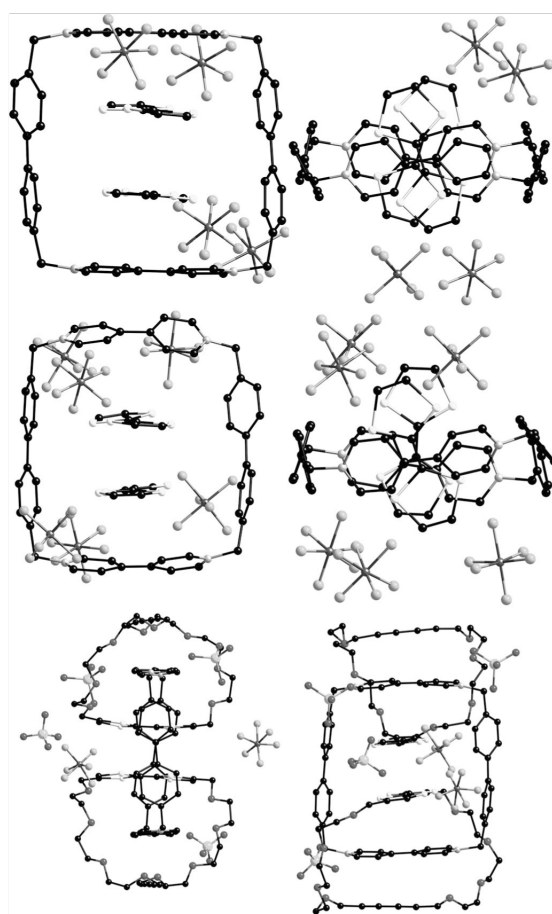


Figure 6. Top and middle: optimized geometries of $[(\text{TTF})_2]\text{CBPQT}^{4+}]^{4+}[\text{PF}_6]^-_4$ and $[(\text{TTF})_2]^{2+}\text{CBPQT}^{4+}]^{6+}[\text{PF}_6]^-_6$ aggregates obtained at the M06L/6-31G level. Bottom: geometries of the $[3]\text{catenane}^{6+}[\text{PF}_6]^-_2[\text{ClO}_4]^-_4$ cluster taken from its crystal. Hydrogen atoms are omitted for clarity.

ion $\cdots$ anion interactions, which exceed the repulsive interactions. As a result of the presence of adjacent anions, $[\text{TTF}]_2^{2+}$ and $[\text{BPP-TTF}]_2^{2+}$ dimers are driven to geometries, in which their SOMOs overlap, forming a bonding and an antibonding combination (Figure 7). In other words, the molecular orbital diagram has all the signatures associated with the existence of a multicenter long bond between the two $[\text{TTF}]^{+\cdot}$ radical cations,^[37] which this study shows can also be extended to $[\text{BPP-TTF}]^{+\cdot}$ cation radicals. Consistent with the existence of long bonds, the ground state for $[(\text{TTF})_2]^{2+}\text{CBPQT}^{4+}]^{6+}$ and $[3]\text{catenane}^{6+}$ is a closed-shell singlet (i.e., diamagnetic), as was found experimentally.^[43] Note that the molecular orbital diagram in Figure 7 has been computed at the optimum geometry of the $[(\text{TTF})_2]^{2+}\text{CBPQT}^{4+}]^{6+}$ complex, in which the rotation between the two radical cations (defined by the C $\cdots$ C-C dihedral

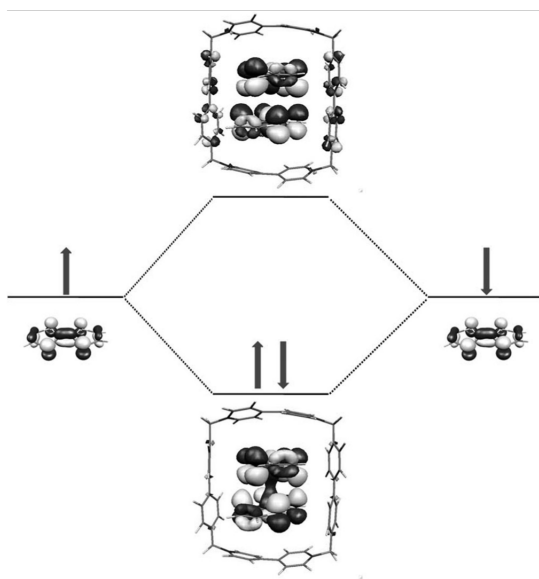


Figure 7. MO diagram associated with the overlap of the SOMO orbitals of the $[\text{TTF}]^{+\bullet}$ cation radicals embedded into a CBPQT^{4+} ring, as in the $[(\text{TTF})_2]^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ complex (M06L/6-31G(d,p) computations).

angle between the central C–C bond of each fragment) is 45.6° (no crystal of this complex has yet been obtained for comparison). This dihedral angle implies that the bonding component (also called the E_{bond} component^[53]) is not the dominant component in the interaction energy between the two radical-cation fragments, because in this case the SOMO of each fragment would try to maximize their overlap (the maximum in such overlap would be when C–C $\cdots$ C–C is zero^[52,54]). Further studies are in progress to evaluate the relative importance of the E_{bond} component in various dimers of radical anions by using correlated ab initio methods.

It is possible to analyze in detail the properties of the multicenter long bond in $[(\text{TTF})_2]^{2+} \subset \text{CBPQT}^{4+}]^{6+}$, taken as a prototype of that which is also present in the [3]catenane⁶⁺ complex. Thus, an atoms-in-molecules (AIM) analysis^[55] of the $[(\text{TTF})_2]^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ electron density was performed (previous studies on $[\text{TTF}]_2^{2+}$ dimers embedded in smaller clusters^[37] have shown that the addition of the counterions does not significantly affect the results of the AIM analysis, so they will be left out of this analysis).

There are ten bond critical points (bcp) connecting the two $[\text{TTF}]^{+\bullet}$ radical cations (Figure 8).^[56] Therefore, according to the AIM analysis, the multicenter long bond in the $[\text{TTF}]_2^{2+}$ dimer here is a 2-electron 20-center bond. The characteristic properties of each of the ten bcps (Table 3) are similar to those found in other multicenter long bonds, particularly the $[\text{TTF}]_2[\text{ClO}_4]_2$ salt^[37], and will not be analyzed further. Based on the later salt results, note that the different geometrical disposition of the radical cations and

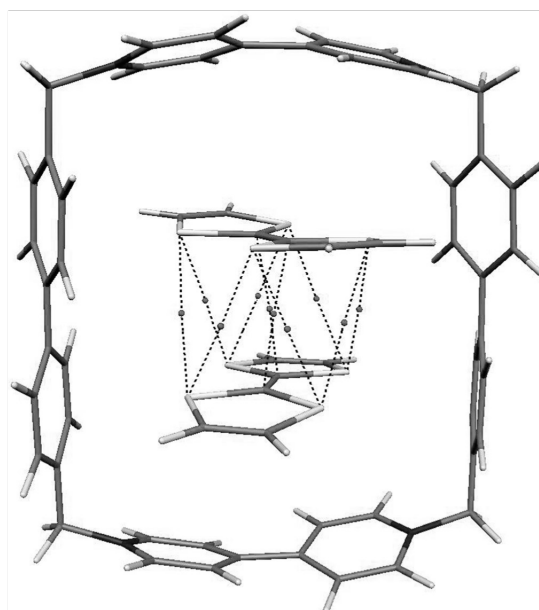


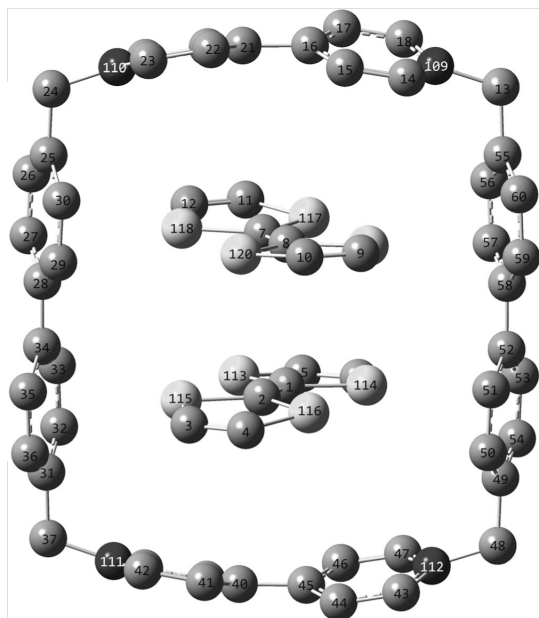
Figure 8. Position of the $[\text{TTF}]^{+\bullet} \cdots [\text{TTF}]^{+\bullet}$ intermolecular bond critical points found in the $[(\text{TTF})_2]^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ complex when performing an AIM analysis of the M06L/6-31G(d,p) total density.

the surrounding anions induces a change in the number of $[\text{TTF}]^{+\bullet} \cdots [\text{TTF}]^{+\bullet}$ bcps from the six previously found in the $[\text{TTF}]_2[\text{ClO}_4]_2$ salt.^[37] Also note that although the bond critical point properties are still a subject of study,^[57] their use in this work is as a tool to allow a proper quantitative classification of the long bond properties (it has been argued that their existence is a necessary, but sometimes not sufficient condition for the existence of a bond^[57]).

$[\text{TTF}]_2^{2+}$ and $[\text{BPP-TTF}]_2^{2+}$ dimers in solution: The [3]catenane⁶⁺ complex and its associated $[(\text{TTF})_2]^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ complex are obtained in a two-step reaction in solution: first, the nonoxidized forms are assembled, and then in a second step a double oxidation of the nonoxidized form takes place, also in solution. It is important here to evaluate the impact of the solvent on the stability of the $[\text{TTF}]_2^{2+}$ and $[\text{BPP-TTF}]_2^{2+}$ dimers, and on the $[(\text{TTF})_2]^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ and [3]catenane⁶⁺ complexes, and to compare it with the results obtained in the previous sections and by other groups.^[43]

The values of the $[\text{TTF}]^{+\bullet} \cdots [\text{TTF}]^{+\bullet}$ interaction when the two cation radicals are solvated is also presented in Table 1. It is well known that the solvent screens the Coulombic field and thus, decreases the repulsion between charges of the same sign.^[58] This screening explains that when both cations are solvated, the $[\text{TTF}]^{+\bullet} \cdots [\text{TTF}]^{+\bullet}$ interaction is energetically stabilizing (this result is consistent with those previously obtained for $[(\text{TTF})_2]^{2+}(\text{CH}_2\text{Cl}_2)_n$ clusters for $n \leq 8$ ^[37]). Similarly, the solvated $[\text{BPP-TTF}]^{+\bullet} \cdots [\text{BPP-TTF}]^{+\bullet}$ interac-

Table 3. Characteristic values of the intermolecular bond-critical points (bcps) found between the fragments of the $[(\text{TTF})_2^2+\text{CBPQT}^{4+}]^{6+}$ complex when performing an AIM analysis (on the density computed at the M06L/6-31G(d,p) level), in which r is the distance between the atoms bonded by the bcp. The atom numbering is indicated in the figure. The geometry of the complex is the optimum obtained at the M06L/6-31G level.



Atoms involved	Pair of molecules	r [Å]	Density [a.u.]	Laplacian [a.u.]
C2–C8	$[\text{TTF}]^{2+} \cdots [\text{TTF}]^{2+}$	3.471	6.127×10^{-3}	1.571×10^{-2}
C1–C7	$[\text{TTF}]^{2+} \cdots [\text{TTF}]^{2+}$	3.471	6.128×10^{-3}	1.572×10^{-2}
S114–S119	$[\text{TTF}]^{2+} \cdots [\text{TTF}]^{2+}$	3.965	4.128×10^{-3}	1.119×10^{-2}
S116–S119	$[\text{TTF}]^{2+} \cdots [\text{TTF}]^{2+}$	3.924	4.479×10^{-3}	1.348×10^{-2}
S116–S120	$[\text{TTF}]^{2+} \cdots [\text{TTF}]^{2+}$	3.855	5.066×10^{-3}	1.590×10^{-2}
S115–S120	$[\text{TTF}]^{2+} \cdots [\text{TTF}]^{2+}$	3.924	4.478×10^{-3}	1.347×10^{-2}
S115–S118	$[\text{TTF}]^{2+} \cdots [\text{TTF}]^{2+}$	3.965	4.127×10^{-3}	1.119×10^{-2}
S113–S118	$[\text{TTF}]^{2+} \cdots [\text{TTF}]^{2+}$	3.924	4.484×10^{-3}	1.349×10^{-2}
S113–S117	$[\text{TTF}]^{2+} \cdots [\text{TTF}]^{2+}$	3.854	5.070×10^{-3}	1.591×10^{-2}
S114–S117	$[\text{TTF}]^{2+} \cdots [\text{TTF}]^{2+}$	3.924	4.482×10^{-3}	1.348×10^{-2}
S118–C19	$[\text{TTF}]^{2+} \cdots \text{CBPQT}^{4+}$	3.880	3.295×10^{-3}	9.363×10^{-3}
S117–C17	$[\text{TTF}]^{2+} \cdots \text{CBPQT}^{4+}$	4.543	9.855×10^{-4}	3.198×10^{-3}
S119–C14	$[\text{TTF}]^{2+} \cdots \text{CBPQT}^{4+}$	3.879	3.298×10^{-3}	9.372×10^{-3}
S120–C22	$[\text{TTF}]^{2+} \cdots \text{CBPQT}^{4+}$	4.544	9.844×10^{-4}	3.195×10^{-3}
S114–C47	$[\text{TTF}]^{2+} \cdots \text{CBPQT}^{4+}$	3.879	3.300×10^{-3}	9.376×10^{-3}
S116–C44	$[\text{TTF}]^{2+} \cdots \text{CBPQT}^{4+}$	4.544	9.849×10^{-4}	3.196×10^{-3}
S115–C42	$[\text{TTF}]^{2+} \cdots \text{CBPQT}^{4+}$	3.878	3.303×10^{-3}	9.386×10^{-3}
S113–C39	$[\text{TTF}]^{2+} \cdots \text{CBPQT}^{4+}$	4.543	9.865×10^{-4}	3.200×10^{-3}
S118–C28	$[\text{TTF}]^{2+} \cdots \text{CBPQT}^{4+}$	3.368	7.975×10^{-3}	2.665×10^{-3}
S119–C58	$[\text{TTF}]^{2+} \cdots \text{CBPQT}^{4+}$	3.368	7.970×10^{-3}	2.663×10^{-3}
S114–C52	$[\text{TTF}]^{2+} \cdots \text{CBPQT}^{4+}$	3.368	7.973×10^{-3}	2.664×10^{-3}
S115–C34	$[\text{TTF}]^{2+} \cdots \text{CBPQT}^{4+}$	3.369	7.970×10^{-3}	2.663×10^{-3}

tion becomes energetically stabilizing by $-14.6 \text{ kcal mol}^{-1}$. Finally, contrary to what was found in isolated $[\text{3}] \text{catenane}^{6+}$, in solution, the nonrotated conformation of $[\text{3}] \text{catenane}^{6+}$ is more stable than the rotated one.

The interaction energy for the formation of $[(\text{TTF})_2\text{CBPQT}^{4+}]^{6+}$ and $[\text{3}] \text{catenane}^{4+}$ and their double-oxidized $[(\text{TTF})_2^2+\text{CBPQT}^{4+}]^{6+}$ and $[\text{3}] \text{catenane}^{6+}$ complexes from its components was also evaluated in solution (last column in Table 1). These values indicate that the formation of the nonoxidized complexes is stable in the gas phase and in solution, although weaker in the latter. Both oxidized forms that were unstable in the gas phase become stable in solution. The same trend is valid for rotated $[\text{3}] \text{catenane}^{6+}$ and $[\text{3}] \text{catenane}^{8+}$ (the latter aggregate is $324 \text{ kcal mol}^{-1}$ repulsive in the gas phase, but becomes stable by $-50.2 \text{ kcal mol}^{-1}$ when in solution). In summary, solvent effects are also able to stabilize the inclusion of the $[\text{TTF}]_2^2+$ and $[\text{BPP-TTF}]_2^2+$ dimers in a CBPQT^{4+} ring, a fact that explains the experimental detection of these supramolecular complexes observed in solution and corresponds well to previously reported computational studies.^[43]

Why $[\text{TTF}]_2^2+$ and $[\text{BPP-TTF}]_2^2+$ dimers are still stable at room temperature: As already noted, most $[\text{TTF}]_2^2+$ dimers in solution are only stable at low temperature (i.e., below -70°C in dichloromethane solutions),^[20–22,36] whereas $[\text{3}] \text{catenane}^{6+}$ in solution at room temperature shows the presence of $[\text{BPP-TTF}]_2^2+$ dimers with short contacts between their two TTF groups. Such a striking difference can be explained by considering the experimental conditions in which the $[\text{3}] \text{catenane}^{6+}$ complexes were synthesized (see below).

Both, $[(\text{TTF})_2^2+\text{CBPQT}^{4+}]^{6+}$ and $[\text{3}] \text{catenane}^{6+}$, were obtained in solution by oxidation of their previously assembled nonoxidized forms, $[(\text{TTF})_2\text{CBPQT}^{4+}]^{4+}$ and $[\text{3}] \text{catenane}^{4+}$. As was previously shown, in solution all of these forms are stable (by -31.2 and $-95.5 \text{ kcal mol}^{-1}$, respectively, which is larger than that found in other dissolved $[\text{TTF}]_2^2+$ dimers in the $-10 \text{ kcal mol}^{-1}$ range^[20–22,36]). This extra stability in solution is probably the reason for the existence of $[(\text{TTF})_2^2+\text{CBPQT}^{4+}]^{6+}$ complexes at room temperature. On the other hand, $[\text{3}] \text{catenane}^{6+}$, generated by oxidation of $[\text{3}] \text{catenane}^{4+}$, is energetically stable in solution against the loss of any of its $[\text{BPP-TTF}]^{2+}$ rings. Furthermore, such a loss requires the rupture of covalent bonds in the rings, which is a very endothermic process. Due to the fact that in solution the nonrotated conformation of $[\text{3}] \text{catenane}^{6+}$ is the most stable one, $[\text{3}] \text{catenane}^{6+}$ preserves in solution, even at room temperature, the short-distance contacts between its two TTF groups. This explains why in $[\text{3}] \text{catenane}^{6+}$ the multicenter long bond is preserved at room temperature in a way that corresponds not only to the previously reported properties for $[\text{TTF}]_2^2+$ dimers in solution or in crystals,^[36,37] but also to the experimental data known to date for $[(\text{TTF})_2^2+\text{CBPQT}^{4+}]^{6+}$ and $[\text{3}] \text{catenane}^{6+}$ complexes.^[43]

Conclusion

The presence of $[\text{TTF}]_2^2+$ dimers in $[(\text{TTF})_2^2+\text{CBPQT}^{4+}]^{6+}$ complexes and of bispropargyl-functionalized

TTF dimers $[\text{BPP-TTF}]_2^{2+}$ in $[3]\text{catenane}^{6+}$ complexes was investigated. It was shown that the presence, even at room temperature, of short-distance $[\text{TTF}] \cdots [\text{TTF}]$ contacts between the TTF groups of $[\text{BPP-TTF}]^{2+}$ rings in $[3]\text{catenanes}^{6+}$ is not due to the intrinsic attractive energetic nature of the $[\text{TTF}]^{2+} \cdots [\text{TTF}]^{2+}$ interaction in these complexes, as sometimes was thought.^[43a] When isolated, the $[\text{TTF}]_2^{2+}$ and $[\text{BPP-TTF}]_2^{2+}$ dimers are energetically unstable. Isolated $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ and $[3]\text{catenane}^{6+}$ complexes are also unstable with respect to losing their $[\text{TTF}]_2^{2+}$ or $[\text{BPP-TTF}]_2^{2+}$ dimer. Losing a $[\text{TTF}]_2^{2+}$ dimer in an isolated $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ complex, an energetically favored process, only requires overcoming a small barrier of approximately 3 kcal mol^{-1} ; in other words, it is within the reach of thermal energy at room temperature (this may explain why this complex has never been isolated). However, the $[\text{BPP-TTF}]^{2+}$ rings are kept in $[3]\text{catenane}^{6+}$ because its dissociation implies the rupture of the covalent bonds in these rings. Finally, the exiting of a $[\text{TTF}]_2^{2+}$ dimer in the $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ complex is also an energetically favored process that shows no barrier towards dissociation.

Interactions with the solvent make the $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ and $[3]\text{catenane}^{6+}$ complexes stable in solution (a fact that does not change the intrinsic destabilizing nature of the $[\text{TTF}]_2^{2+} \cdots \text{CBPQT}^{4+}$ interaction in $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ or the $[\text{BPP-TTF}]_2^{2+} \cdots \text{CBPQT}^{4+}$ interactions in $[3]\text{catenanes}^{6+}$). In the most stable conformation in solution of $[3]\text{catenane}^{6+}$ the two TTF groups make short contacts.

Interactions with the anions make the $[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$ and $[3]\text{catenane}^{6+}$ complexes stable in crystals. That such energetic stability originates in crystals in the cation...anion interaction is in good agreement with previous studies on long-bonded complexes. All of the observed crystals structures revealed short-distance contacts between the TTF groups.^[43] The optimum structures of all studied complexes present short-distance contacts between the TTF groups.

Overall, the previous results fit well with all reported properties of $[\text{TTF}]_2^{2+}$ dimers in crystals or in solution,^[36,37] and particularly with the presence of a multicenter long bond between the fragments of the $[\text{TTF}]_2^{2+}$ dimers, which now is extended to $[\text{BPP-TTF}]_2^{2+}$ dimers. Its stability at room temperature is due to the high energy required to break the covalent bonds in the $[\text{BPP-TTF}]_2^{2+}$ dimers. An AIM analysis indicated that this long-distance bond is of the 2-electron and 20-center type, that is, a $2e^-/20c$ bond.

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4.7. Summary

The features concerning the room-temperature stability of long, multicenter bonded dimers have been studied in this chapter. The work has provided insight in both of the two categories of compounds so far reported to preserve long, multicenter bonding at room temperature, i.e. oligomeric donors or acceptors and supramolecular aggregates. The first two publications were focused on the α,β -substituted heptathienoacene (D4T7). The side alkyl chains induce a high stabilization, being even able to almost double the interaction energy between the $[D4T7]^{+\cdot}$. A high excess of counterions in the solution also provides a higher stabilization. Moreover, the π -dimerization of $[D4T7]^{+\cdot}$ in solution involves the formation of two intermediate species: the $[D4T7]_2^{+\cdot}$ mixed-valence dimer is formed during the oxidation process, and a less stable conformation of the $[D4T7]_2^{2+}$ appears prior the final stabilization in the *anti* or *syn* ultimate π -dimer. The questions raised by the experimental sights were successfully elucidated using TD-DFT calculations.

Three representative examples of supramolecular aggregates preserving room-temperature long, multicenter bonding center the work of the last three publications. The inclusion of a functionalized $[R-TTF]_2^{2+}$ dimer into the cavity of a cucurbit[8]uril, the dimerization of molecular clips containing TTF units as building blocks, and a [3]catenane that includes a TTF unit in each external macrocycle were carefully studied, pointing out the reasons behind their room temperature stability. The CB[8] macrocycle stabilizes the dimer formation mainly through electrostatic interactions, complemented by dispersion interactions. The formation of the $(\pi-[R-TTF]_2 \subset CB[8])^{2+}$ inclusion complex is a spontaneous process that exhibits no barriers. Electrostatic interactions are also the key factor behind the dimerization of the TTF-functionalized glycoluril-based molecular clips. This molecular clip presents a zwitterionic charge distribution (i.e., there is a -1 a.u. charge localized in the clip's central ring regardless the oxidation state), which stabilizes the positive charge on the TTF units. Finally, the $[TTF]_2^{2+}$ in the [3]catenane is found to be highly repulsive in isolated conditions, which would induce a rotation of the external macrocycles. However, the effects driven by solvation can attenuate the high electrostatic repulsion in such a manner that they are even preserved at room temperature. All the long, multicenter bonding features (AIM analysis, MO diagram, etc) are preserved upon the formation of the aforementioned supramolecular aggregates.

CHAPTER FIVE

Conclusions

The evaluation of long, multicenter bonding between organic radicals has been addressed in this thesis from a computational chemistry perspective. DFT and multiconfigurational second-order perturbation theory calculations provided insights into, on the one hand, their fundamental description and, on the other hand, their eventual room-temperature stability. The following conclusions are reached after the sequential analysis of the results issued throughout the thesis:

Fundamental description of long, multicenter bonding

- A minimal (2,2) active space provides a qualitative description of long, multicenter bonded dimers' wavefunction, but quantitative energies require the direct π -space parallel to the bonding axis. The full π -space parallel to the bonding axis is needed to quantitatively describe the dissociation process.
- Dispersion corrections have to be considered for a proper (qualitative) description of long, multicenter bonding. Range-separated hybrid functionals fail in their description, even when dispersion corrections are included.
- The nature of long, multicenter bonding is dominantly electrostatic. Dispersion is the main stabilizing term, although the bonding term is more influent in determining the relative orientation of the fragments.
- The true orientational preference in the solid state is ultimately determined by the counterions (and thus the crystal packing) in long, multicenter bonded radical ions.
- The previous assignment of parallel displaced L_c π -[TCNE] $_2^{2-}$ dimers was a misinterpretation. Instead, π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] long, multicenter heterodimers are formed.
- The long, multicenter bond in π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] is preserved (instead of forming a σ -bond) due to the high exchange-repulsion interactions, albeit the attractive nature between the fragments.
- Cations do not play not a crucial role in the stabilization of π -[TCNE] $_2^{2-}$ in dichloromethane solution.
- π -[TCNE] $_2^{2-}$ first solvation shell is comprised of 20 CH $_2$ Cl $_2$ solvent molecules, although the 8 molecules located in the surrounding region equidistant from both monomers provide a greater stabilization. CH $_2$ Cl $_2$ molecules stabilize the π -[TCNE] $_2^{2-}$ through H...N contacts.
- π -[TCNE] $_2^{2-}$ geometry is preserved in solution, exhibiting only small fluctuations from the solid state well-reported structure. The free energy profile at 175 K presents a stable dimer by -5.5 kcal·mol $^{-1}$, with an energetic barrier toward dissociation of 9.6 kcal·mol $^{-1}$.

Room-temperature long, multicenter bonding

- Side alkylic chains and a high excess of counterions in the solution are factors that enhance long, multicenter bonding stability.
- The formation of long, multicenter bonded dimers of oligothienoacene radical cations, $[D4T7]^{\cdot+}$, presents a mechanism where two intermediates are identified: a mixed-valence $[D4T7]_2^{\cdot+}$ radical cation dimer formed during the oxidation process, and a less stable conformation of the $[D4T7]_2^{2+}$ dication dimer that ultimately converts to the *anti* or *syn* more stable π -dimer.
- All the features of long, multicenter bonds are preserved upon the formation of supramolecular aggregates.
- Electrostatic effects are crucial in order to stabilize the formation of long, multicenter bonded dimers between radical ions.
- The polarized charge distribution of the cucurbit[8]uril, CB[8], is the responsible for the great stabilization of the $(\pi-[R-TTF]_2 \subset CB[8])^{2+}$ inclusion complex, complemented by a dispersion stabilization. The formation of the inclusion complex is a spontaneous process that exhibits no barriers.
- The TTF-functionalized glycoluril-based molecular clip presents a zwitterionic charge distribution (there is a -1 a.u. charge localized in the clip's central ring regardless the oxidation state), which stabilizes the positive charge on the TTF units when the supramolecular aggregate is formed.
- The formation of a π - $[TTF]_2^{2+}$ dimer in the [3]catenane that contains TTF in each of its external macrocycles is found to be highly repulsive in isolated conditions and it would induce a rotation of such external macrocycles. The effects driven by solvation drastically attenuate the high electrostatic repulsion and permit the dimer formation.
- The M06L density functional has been thoroughly assessed as a reliable method to successfully predict properties and trends concerning long, multicenter bonded dimers and large supramolecular complexes.

CHAPTER SIX

Contribution to publications

The results of this thesis are presented as a compendium of publications, which are coauthored by more than just the author of this thesis. This chapter describes the contribution of the author of this thesis to each publication.

*"Unusually Long, Multicenter Cation^{δ+}...Anion^{δ-} Bonding Observed for Several Polymorphs of [TTF][TCNE]". M. Capdevila-Cortada, J. J. Novoa, J. D. Bell, C. E. Moore, A. L. Rheingold, J. S. Miller. *Chem. – Eur. J.* (2011) 17, 9326-9341.*

Contribution: performance of all calculations and analysis of the obtained data.

*"Substituent and counterion effects on the formation of π -bound dimers from one-electron oxidized end-capped heptathienoacenes". C. Capel Ferrón, M. C. Ruiz Delgado, V. Hernández, J. T. López Navarrete, B. Vercelli, G. Zotti, M. Capdevila Cortada, J. J. Novoa, W. Niu, M. He, F. Hartl. *Chem. Commun.* (2011) 47, 12622-12624.*

Contribution: performance of all calculations, analysis of the obtained data, and writing the manuscript.

*"The Nature of the [TTF]⁺...[TTF]⁺ Interactions in the [TTF]₂²⁺ Dimers Embedded in Charged [3]Catenanes: Room-Temperature Multicenter, Long Bonds". M. Capdevila-Cortada, J. J. Novoa. *Chem. – Eur. J.* (2012) 18, 5335-5344.*

Contribution: performance of all calculations, analysis of the obtained data, and writing the manuscript.

*"Keys for the Existence of Stable Dimers of Bis-tetrathiafulvalene (bis-TTF)-Functionalized Molecular Clips Presenting [TTF]⁺...[TTF]⁺ Long, Multicenter Bonds at Room Temperature". M. Fumanal, M. Capdevila-Cortada, J. S. Miller, J. J. Novoa. *J. Amer. Chem. Soc.* (2013) 135, 13814-13826.*

Contribution: analysis of the obtained data and writing the manuscript.

*"Assessing the Performance of CASPT2 and DFT Methods for the Description of Long, Multicenter Bonding in Dimers between Radical Ions". M. Capdevila-Cortada, J. Ribas-Arino, J. J. Novoa. *J. Chem. Theory Comput.* (2014) 10, 650-658.*

Contribution: performance of all calculations, analysis of the obtained data, and writing the manuscript.

*"The Origin of the Room Temperature Stability of $[TTF]^+\cdots[TTF]^+$ Long, Multicenter Bonds Found in Functionalized π - $[R-TTF]_2^{2+}$ Dimers Included in the Cucurbit[8]uril Cavity". M. Capdevila-Cortada, J. S. Miller, J. J. Novoa. *Chem. – Eur. J.* (2014) DOI: 10.1002/chem.201402256.*

Contribution: performance of all calculations, analysis of the obtained data, and writing the manuscript.

*"Multistep π -dimerization of heptathienoacene radical cations: a spectro-electrochemical and DFT study". C. Capel Ferrón, M. Capdevila-Cortada, R. Balster, F. Hartl, W. Niu, M. He, J. J. Novoa, J. T. López Navarrete, V. Hernández, M. C. Ruiz Delgado. *Submitted*.*

Contribution: performance of all calculations, analysis of the obtained data, and writing the manuscript.

*"The Importance of the Cation-Anion Interactions for the Orientational Preference of Long, Multicenter Bonds: A Study-Case Based on $[TCNB]_2^{2-}$ and $[TCNP]_2^{2-}$ Dimers". M. Capdevila-Cortada, J. S. Miller, J. J. Novoa. *Submitted*.*

Contribution: performance of all calculations, analysis of the obtained data, and writing the manuscript.

*"Study on the Solvation and Stability of $[TCNE]_2^{2-}$ Dimers in Dichloromethane through Molecular Dynamics Simulations". M. Capdevila-Cortada, J. Ribas-Arino, A. Chaumont, G. Wipff, J. J. Novoa. *Submitted*.*

Contribution: performance of all calculations, analysis of the obtained data, and writing the manuscript.

In addition to the publications that constitute the present thesis, the following articles are also coauthored by the Ph.D. candidate.

*"The Nature of the $Cl\cdots Cl$ Intermolecular Interactions Found in Molecular Crystals. A General Theoretical-Database Study in the 2.75 – 4.0 Å Range". M. Capdevila-Cortada, J. Castelló, J. J. Novoa. *CrystEngComm* (2014) Accepted.*

*"Structure and Properties of Nitrogen-Rich 1,4-Dicyanotetrazine, C_4N_6 . A Comparative Study with Related Tetracyano Electron Acceptors". H.-L. Vo, J. L. Arthur, M. Capdevila-Cortada, S. H. Lapidus, P. W. Stephens, J. J. Novoa, A. M. Arif, J. S. Miller. *Submitted*.*

CHAPTER SEVEN

Resum en català

En la següent memòria es recull un resum de la tesi doctoral que duu per títol “Enllaços Multicentre a Larga Distància Presents en Interaccions Radical···Radical: Un estudi Computacional”.

7.1. Introducció

Els enllaços presents en química orgànica són comunament ben representats per la descripció 2-electrons 2-centres ($2e^-/2c$). La posterior troballa dels borans (e.g. el diborà, B_2H_6), espècies deficitàries d'electrons, va suposar la invocació dels enllaços 2-electrons 3-centres ($2e^-/3c$).¹ Tot i així, certs ions orgànics radicalaris exhibeixen un tipus d'enllaç no convencional que requereix una descripció més avançada. Amb la síntesi i caracterització dels primers ions radicals orgànics varen trobar-se interaccions entre radicals diamagnètics en dissolució a baixa temperatura, quan aquestes haurien de ser paramagnètiques.^{2,3} Posteriors experiments mostraren que aquestes interaccions diamagnètiques eren degudes a π -dimeritzacions i van ser caracteritzades anys després en estat sòlid a través de difracció de raigs X. Així van trobar-se π -dímers de $[TMPD]^{+\cdot}$ (tetrametil-*p*-fenildiamina),³⁻⁵ $[TCNQ]^{-\cdot}$ (tetraciano-*p*-quinodimetà),^{6,7} $[TCNE]^{-\cdot}$ (tetracianoetilè)^{8,9} i $[TTF]^{+\cdot}$ (tetratiafulvalè),¹⁰ els quals posseïen distàncies intermoleculars en el rang 2.8 – 3.5 Å (Figura 7.1.1). Aquest rang de distàncies comporta que cap enllaç covalent és creat entre els monòmers. Conseqüentment, aquestes interaccions no poden ser descrites mitjançant enllaços $2e^-/2c$, sinó que requereixen un nou tipus de formalisme: enllaços 2-electrons multicentre ($2e^-/mc$) o, també, enllaços multicentre a llarga distància.¹¹

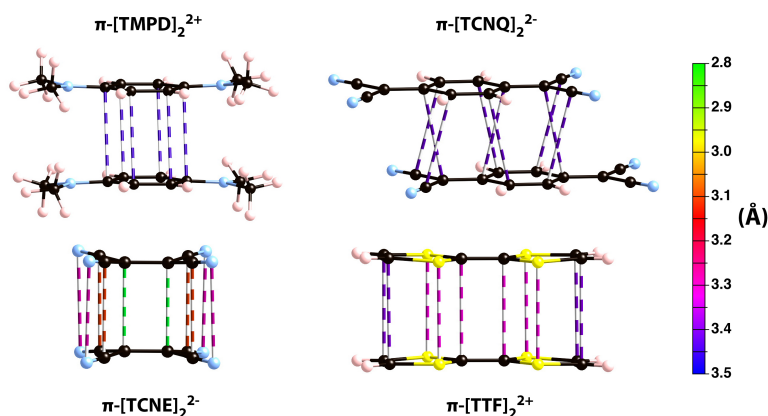
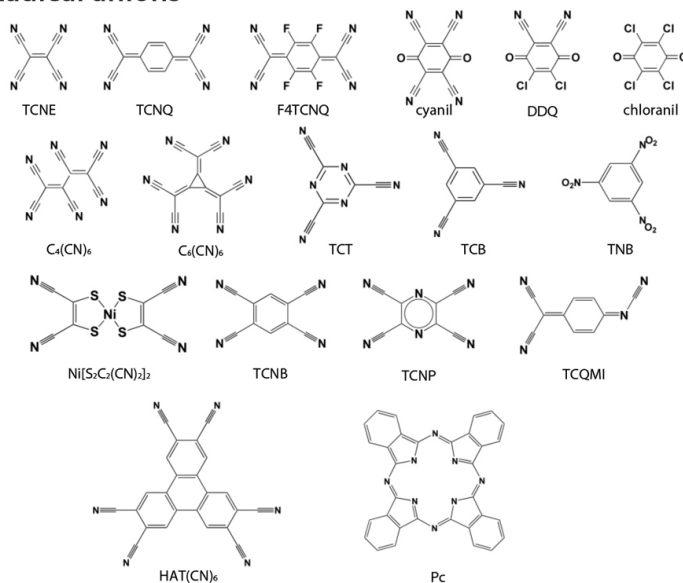


Figura 7.1.1. Estructura cristal·lina dels quatre π -dímers mencionats. Les distàncies intermoleculars es mostren en línies discontinuïques, on el color indica el valor de la distància (veure llegenda). Llegenda àtoms: negre (C), blau (N), groc (S), blanc (H).

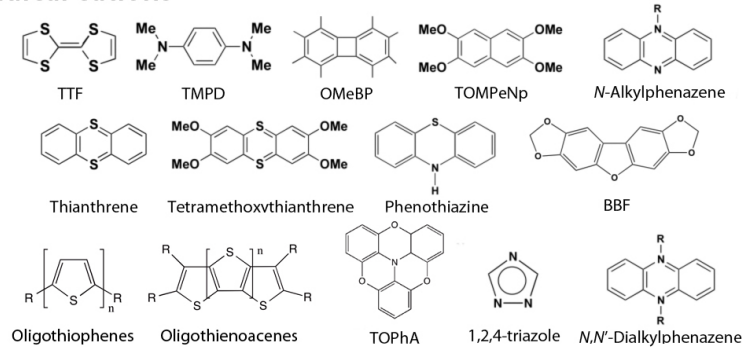
L'any 2001, el dímer π -[TCNE]₂²⁻ va ser objecte d'un extens estudi teòric-experimental,¹²⁻¹⁴ el qual va comportar tot un seguit d'estudis posteriors. En ells, es va demostrar com els orbitals SOMO dels anions radicals se solapen i combinen donant lloc a un HOMO i un LUMO doblement ocupats i desocupat, respectivament. Aquesta doble-ocupació d'un orbital deslocalitzat en tot el dímer és l'origen del diferent espectre UV-vis del dímer respecte el de l'anió radical. Tot i així, els dímers de ions radicals que presenten enllaços multicentre a llarga distància tenen una energia d'interacció repulsiva, degut al seu caràcter iònic, amb una barrera de dissociació entorn les 5 kcal·mol⁻¹. Així doncs, els dímers multicentre de llarga distància

entre radicals iònics són metastables. Com tenen lloc, doncs, aquests enllaços? Estudis computacionals revelaren que les interaccions [ió radical]...contraió són suficients per a estabilitzar l'agregat [ió radical]₂(contraió)₂, i així formar un dímer multicentre a llarga distància entre els ions radicals.¹⁵⁻¹⁷ De la mateixa manera, interaccions [ió radical]...dissolvent estabilitzen l'agregat [ió radical]₂(contraió)_n, tot i que de manera molt més dèbil.¹⁶⁻¹⁸ Això provoca que π -dímers només han estat observats en dissolució a baixes temperatures.^{19,20} El conjunt de radicals orgànics fins ara caracteritzats per a presentar dimerització a llarga distància es mostra a la Figura 7.1.2.

Radical anions



Radical cations



Neutral radicals

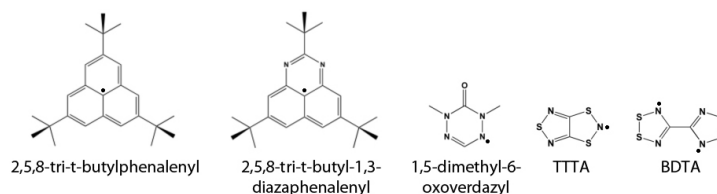


Figura 7.1.2. Radicals orgànics els quals es coneix que formen π -dímers.

Salts de transferència electrònica involucrant radicals orgànics de la Figura 7.1.2 són ben coneguts per a presentar importants propietats tecnològiques. Per exemple, el TCNE o TCNQ

formen materials ferromagnètics.²¹ Ara bé, la formació de π -dímers entre els radicals orgànics comporta la pèrdua d'ordre magnètic, resultant-ne materials diamagnètics.²² De la mateixa manera, salts de TCNQ o TTF presentaren molt alta conductivitat elèctrica,^{23,24} la qual també es veu minvada degut a la formació de dímer multicentre a llarga distància.²⁵ Finalment, durant els últims anys la síntesi d'agregats supramoleculars involucrant TTF o BIPY (bipiridina) ha augmentat,^{26–28} els quals formen π -dímers quan són oxidats, obtenint-se així diverses conformacions en funció del grau d'oxidació.^{29,30} Degut a això aquests agregats supramoleculars han estat proposats com a *interruptors* moleculars.³¹

Aquesta tesi es basa en l'estudi computacional dels enllaços multicentre a llarga distància en diversos estat (fase gas, dissolució i estat sòlid), així com en l'estudi de l'origen de la seva estabilitat a temperatura ambient en dues famílies de π -dímers.

7.2. Metodologia

Els resultats obtinguts en aquesta tesi es basen en càlculs computacionals a través de diverses metodologies. En funció del problema a tractar s'ha escollit la metodologia més adient per a resoldre'l. Per al càlcul d'energies d'interacció de l'estat fonamental s'ha emprat teoria de pertorbacions sobre una funció multireferent a través del mètode RASPT2 (també, en menys freqüència, CASPT2 o MCQDPT).^{32,33} D'aquesta manera han pogut calibrar-se diversos funcionals de la densitat (DFT), el qual ha estat el mètode més usat en aquesta tesi.^{34,35} A través de DFT també s'han obtingut optimitzacions de geometria. El funcional sobre el qual es basa majoritàriament aquesta tesi és el M06L,³⁶ el qual és un funcional meta-GGA parametritzat per a donar resultats satisfactoris en interaccions no-covalents. Energies d'excitació per a transicions verticals electròniques han estat calculades amb DFT depenent del temps (TD-DFT),³⁷ el qual es basa en aplicar la dependència temporal com una pertorbació dins el marc DFT.

Per tal d'aprofundir més en la naturalesa de les interaccions intermoleculars, s'ha realitzat una descomposició de l'energia d'interacció en les seves components. Metodologies com l'IMPT o el SAPT proporcionen una eina fonamental per a la descripció de la naturalesa de l'energia d'interacció,^{38,39} però no poden tractar interaccions entre radicals. Aleshores, basant-se amb el mateix principi, s'introdueix una component addicional per a descriure l'estabilització deguda a l'aparellament dels electrons radicalaris, el terme d'enllaç (E_{bond}).⁴⁰ L'energia d'interacció queda descrita doncs per l'equació (7.1). A més a més, una anàlisi de la densitat electrònica a través de la teoria d'àtoms en molècules (AIM) permet caracteritzar més a fons les interaccions intermoleculars.⁴¹

$$E_{int} = E_{exch} + E_{el} + E_{disp} + E_{bond} \quad (7.1)$$

Finalment, s'han realitzat simulacions de dinàmiques clàssiques (MD) per tal de descriure el comportament dels dímers multicentre a llarga distància en fase condensada. Per a dur a terme tal tasca, s'ha emprat tant MD de camps de força com MD *ab initio*.

La Taula 7.2.1 recull els programes utilitzats per a dur a terme cada metodologia, així com el capítol de la tesi (dins el resum) on es mostren els corresponents resultats.

Taula 7.2.1. Resum del programari emprat durant el transcurs de la tesi.

Mètode	Programa	Capítol
DFT	Gaussian ⁴²	7.3, 7.4
TD-DFT	Gaussian ⁴²	7.4
CASSCF/CASPT2	Molcas ⁴³	7.3
RASSCF/RASPT2	Molcas ⁴³	7.3
CASSCF/MCQDPT	GameSS ⁴⁴	7.3
FFMD	Amber ⁴⁵	7.3
AIMD	CPMD ⁴⁶	7.3
AIM	ProAIMs ⁴⁷	7.3, 7.4

7.3. Descripció fonamental dels enllaços multicentre a llarga distància

Els enllaços multicentre a llarga distància havien estat descrits habitualment a través de càlculs CASPT2 basats en espais actius petits, o de càlculs DFT, bàsicament B3LYP. Degut a la manca de càlculs de referència per aquest tipus d'enllaç, es van realitzar corbes d'energia d'interacció per als dímers π -[TCNE] $_2^{2-}$, π -[TCNB] $_2^{2-}$, π -[TCNP] $_2^{2-}$ i π -[TTF] $_2^{2+}$ en funció de la distància intermolecular. Aquestes corbes varen ser realitzades amb 23 funcionals DFT: els funcionals purs PBE, BP86, M06L i B97, els funcionals híbrids B3LYP, BH&HLYP, BMK, M06, M062X, els funcionals de separació de rang CAM-B3LYP, HSE06, ω B97X i M11, i el funcional doble híbrid B2PLYP. A més, correccions de dispersió de Grimme D2, D3 i D3(BJ) van ser introduïdes per als funcionals PBE, B97, B3LYP i ω B97X. Les corbes d'energia d'interacció van ser comparades amb les de càlculs extensius RASPT2 basats en un espai actiu que inclou tot el sistema π paral·lel a l'enllaç (i.e., (22,20) per al TCNE, (30,28) per als TCNB i TCNP, i (26,20) per al TTF). La Figura 7.3.1 recull els errors mitjans absoluts (MAE) dels set funcionals que són capaços de reproduir les quatre corbes RASPT2. Com es veu, és necessari introduir correccions de dispersió d'alguna manera per tal d'obtenir una bona descripció d'aquest tipus d'enllaç. El funcional B97-D3(BJ) és el que millor reproduceix els resultats RASPT2, seguit del funcional PBE-D3(BJ), mentre que els funcionals B3LYP-D3(BJ) i M06L també donen resultats satisfactoris.

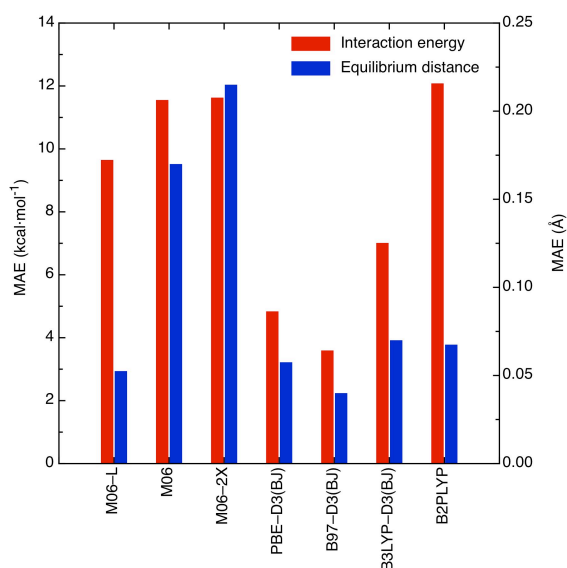


Figura 7.3.1. MAEs corresponents a les energies d'interacció (vermell, eix esquerra) i les distàncies d'equilibri (blau, eix dret) dels set funcionals que reproduïxen les corbes RASPT2. Càlculs realitzats amb la base 6-31+G(d), amb l'error de superposició de base corregit.

Fins aquest moment, tot càlcul d'enllaços multicentre a llarga distància en dissolució havia estat realitzat emprant un model de solvatació continu. A través de simulacions de dinàmica molecular de camps de força i de dinàmica molecular Car-Parrinello (CPMD), s'ha estudiat aquí el comportament del dímer π -[TNCE] $_2^{2-}$ en una caixa de diclorometà explícit. La Figura 7.3.2 (a) mostra els perfils energètics per a la dissociació de l'esmentat dímer a dues temperatures, 175 i 300 K. Es veu com a 175 K el dímer presenta un mínim a la distància d'equilibri, mentre que a 300 K es mostra el contrari. Aquests resultats concorden amb les observacions experimentals.

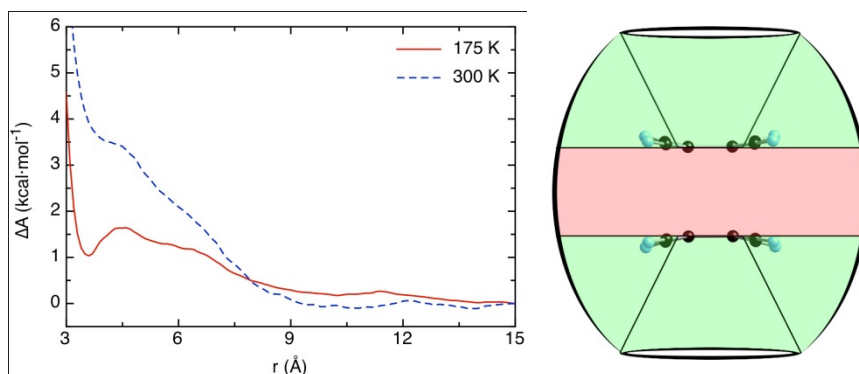


Figura 7.3.2. (a) Perfil d'energia lliure per a la dissociació de π -[TCNE] $_2^{2-}$ en diclorometà a través de dinàmica molecular de camps de força. (b) Esquema de la primera esfera de solvatació de l'esmentat dímer, obtinguda a través de dinàmica molecular Car-Parrinello (veure text).

L'estudi de dinàmica CPMD permet estudiar la solvatació del dímer de π -[TNCE] $_2^{2-}$. L'anàlisi detallada de les trajectòries mostra com a la zona vermella de la Figura 7.3.2 (b) les molècules de CH_2Cl_2 romanen fixes, i així són les que juguen un paper fonamental en l'estabilització del dímer. Per altra banda, les molècules de la zona verda són més làbils i mòbils, algunes d'elles inclús sortint de l'esfera de solvatació. L'esfera de solvatació del dímer de π -[TNCE] $_2^{2-}$ s'ha trobat de ser de 20 molècules de diclorometà.

Un cas important a estudiar és la diferent orientació relativa dels monòmers que conformen els dímers en estat sòlid. Per exemple, el π -[TCNP] $_2^{2-}$ es troba en dos cristalls moleculars, en conformació eclipsada D_{2h} i rotat 30° un monòmer respecte l'altre. Per altra banda, l'únic cristall que conté π -[TCNB] $_2^{2-}$ presenta dímers rotats 60° . Alguns estudis han tractat de racionalitzar l'orientació relativa dels dímers, però tractant el dímer de manera aïllada. Aquestes evidències van ser de base per a realitzar una anàlisi de les components de l'energia d'interacció en funció de l'angle diedre (Figura 7.3.3).

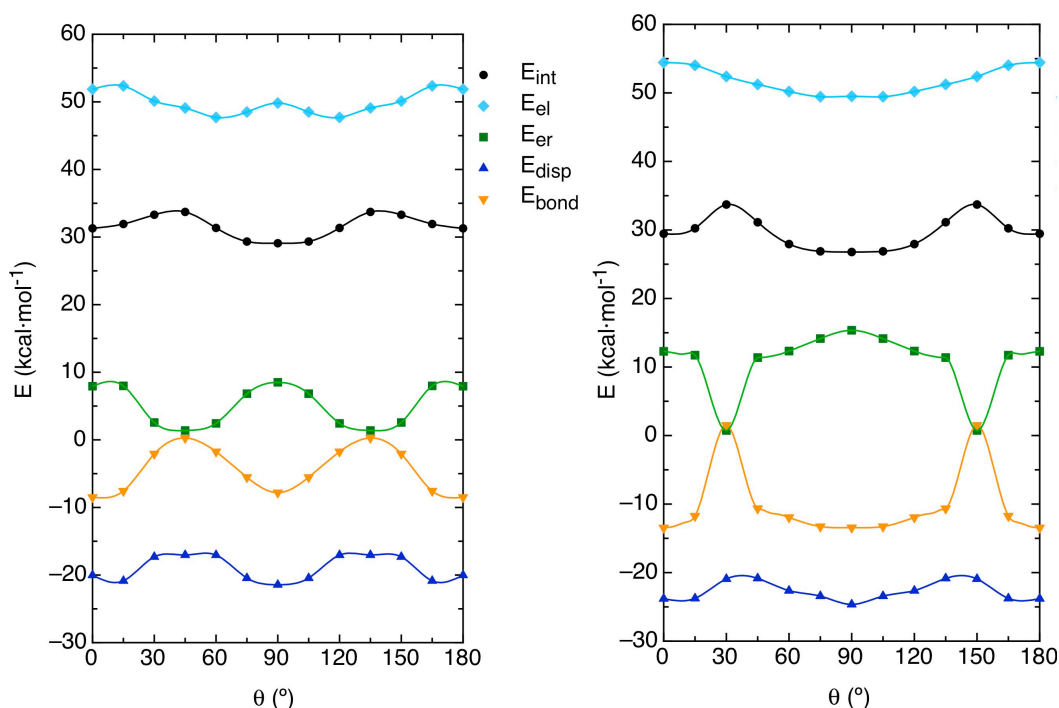


Figura 7.3.3. Descomposició de l'energia d'interacció en les seves components en funció de l'angle diedre d'orientació relativa d'un monòmer respecte l'altre, per al π -[TCNB] $_2^{2-}$ (esquerra) i π -[TCNP] $_2^{2-}$.

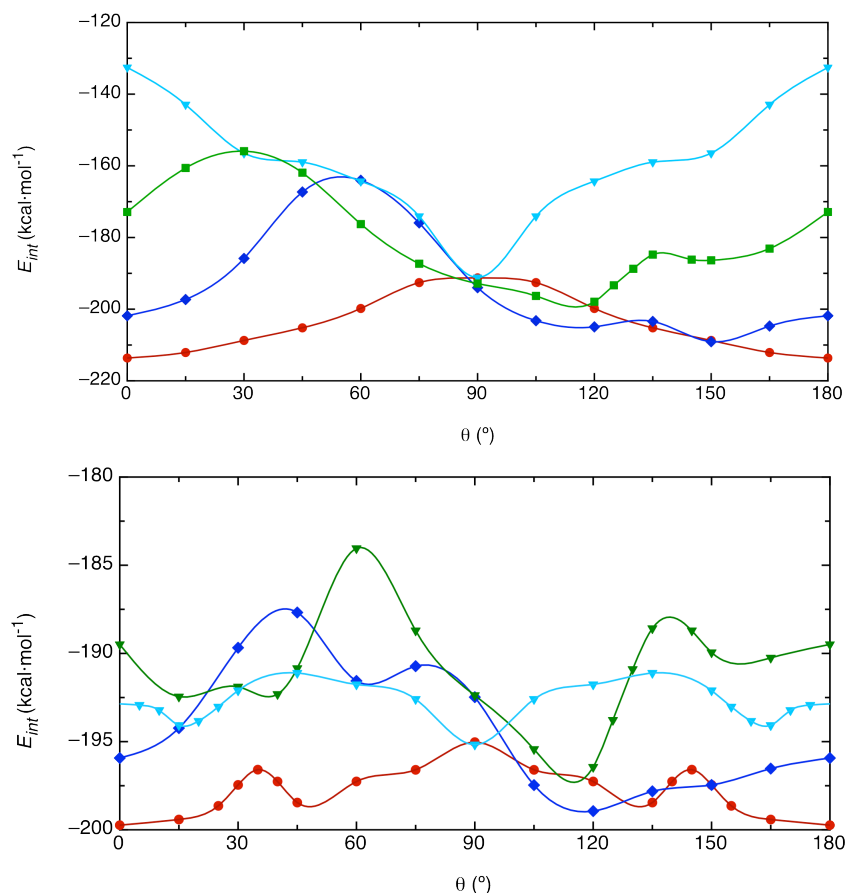


Figura 7.3.4. Energia d'interacció en funció de l'angle diedre per als agregats $K_2[TCNB]_2$ (gràfica superior) i $K_2[TCNP]_2$ (gràfica inferior), per a quatre disposicions diferents dels cations K^+ respecte al dímer.

L'anàlisi de la descomposició de l'energia d'interacció permet concloure que el terme estabilitzant que més varia en funció del diedre és el terme d'enllaç (E_{bond}). La dependència angular dels dímers aïllats no dona informació respecte als diversos dímers presents en els diferents cristalls moleculars. És per això que es va realitzar un estudi de l'energia d'interacció en funció de l'angle diedre dels agregats $K_2[TCNB]_2$ i $K_2[TCNP]_2$, per a quatre disposicions dels cations K^+ diferents (Figura 7.3.4). Així, amb un model simple, es reproduïxen els mínims experimentals.

Fins al moment, dos tipus de $\pi\text{-}[TCNE]_2^{2-}$ eren coneguts, el dímer eclipsat (D_{2h}) i dímer amb distorsió lateral (Figura 7.3.5). Aquest últim només s'havia observat en dímers presents en dues formes polimòrfiques del cristall de $[TTF][TCNE]$ (en les fases α i β). Les fases α - i β - $[TTF][TCNE]$ estan constituïdes per cadenes de la següent forma $\cdots D \cdots A \cdots A \cdots D \cdots D \cdots A \cdots$, i són diamagnètiques. Aquest diamagnetisme, juntament amb la transferència de càrrega entorn $0.6e^-$, s'associava a la formació d'enllaços $\pi\text{-}[TCNE]_2^{2-}$ i $\pi\text{-}[TTF]_2^{2+}$.

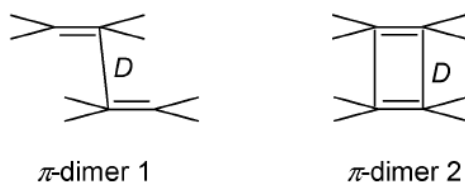


Figura 7.3.5. Esquema del dímers amb distorsió lateral (1) i eclipsat D_{2h} (2) del $\pi\text{-}[TCNE]_2^{2-}$.

En un article en col·laboració amb un grup experimental de Utah, mostrem dues fases noves de [TTF][TCNE], les fases δ i γ . La primera presenta cadenes $\cdots D \cdots A \cdots D \cdots A \cdots$, mentre que la segona són cadenes segregades $\cdots A \cdots A \cdots A \cdots$ i $\cdots D \cdots D \cdots D \cdots$. Ambdues fases són també diamagnètiques. La fase γ és degut a dimeritzacions $\pi\text{-[TCNE]}_2^{2-}$ i $\pi\text{-[TTF]}_2^{2+}$. En canvi la fase δ mostra la formació d'enllaç multicentre $\pi\text{-[TTF} \cdots \text{TCNE]}$ (Figura 7.3.6). Càlculs MCQDPT indiquen que és una interacció estable amb un mínim sobre 3.1 Å i una energia d'interacció entorn $-13 \text{ kcal}\cdot\text{mol}^{-1}$.

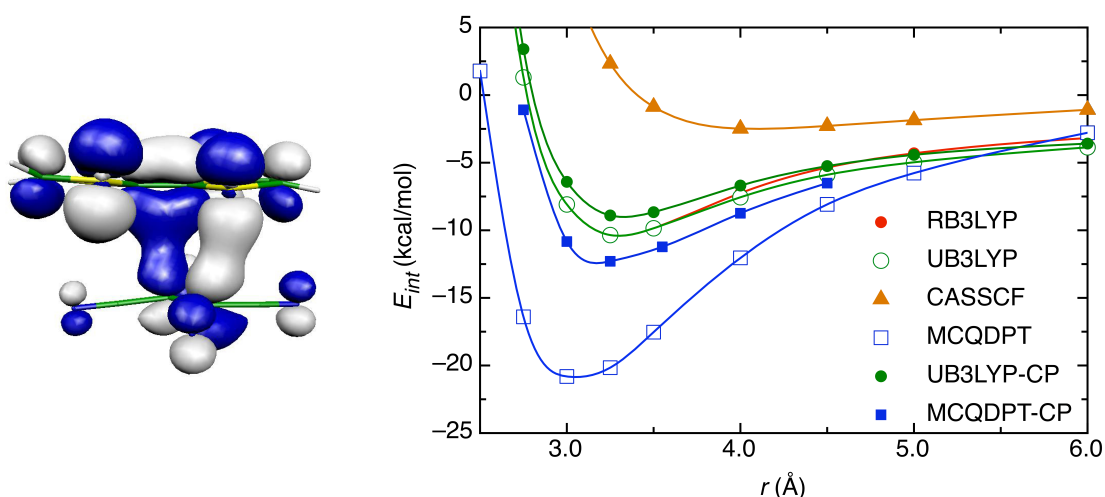


Figura 7.3.6. Esquerra: HOMO del complex $\pi\text{-[TTF} \cdots \text{TCNE]}$. Dreta: corbes d'energia d'interacció de l'esmentat complex obtingudes amb diversos mètodes, amb la base 6-31+G(d). L'error de superposició de base ha estat corregit mitjançant el mètode Counterpoise, quan així s'indica (CP).

A més a més, una anàlisi de les fases α i β mostra que el causant del seu comportament diamagnètic és la formació d'enllaços $\pi\text{-[TTF} \cdots \text{TCNE]}$, i no pas dels dímers amb distorsió lateral que es creia originalment (Figura 7.3.7).

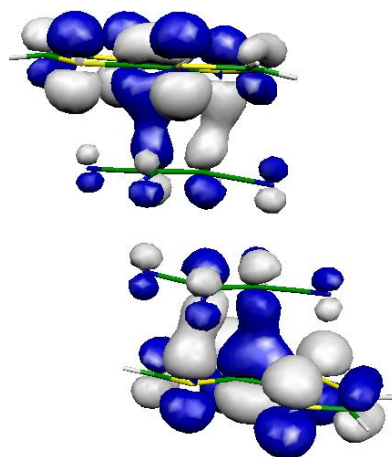


Figura 7.3.7. HOMO del fragment d'una cadena de quatre membres DAAD del cristall $\beta\text{-[TTF]TCNE}$, obtingut a nivell B3LYP/6-31+G(d).

7.4. Enllaços multicentre a llarga distància a temperatura ambient

Tal i com s'ha demostrat en el capítol anterior, els dímers multicentre a llarga distància només es mantenen en dissolució a temperatures prou baixes. Tot i així, existeixen certs casos on π -dímers entre ions radicals són observats a temperatura ambient. Aquests casos es poden agrupar en dues famílies: a) els dímers de radicals d'oligomers, i b) dímers que formen part d'agregats supramoleculars. Dins la primera categoria, bàsicament s'hi inclouen oligotiofens, oligotienoacens i oligopirrols, mentre que en la segona categoria les espècies radicalàries són TTF o derivats de BIPY.

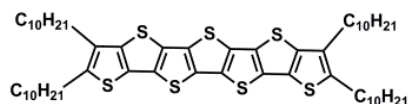


Figura 7.4.1. Estructura química de l'oligotienoacè substituït **D4T7**.

Durant el procés d'estudi de la dimerització a temperatura ambient de l'oligotienoacè (oligòmer de tiofè on els anells es troben fusionats) de set anells α,β -substituït per cadenes laterals, **D4T7** (Figura 7.4.1), s'observen dues espècies intermèdies a través d'espectroscòpia UV-vis. Aquestes espècies, anomenades **T1** i **T2**, experimentalment es manté més la seva aparició de maneres diferents. Per al **T1**, s'obté per acció de disminuir la temperatura durant el procés d'oxidació, mentre que el **T2** es manifesta a través de tenir major concentració de **D4T7** sense oxidar. Davant d'aquestes dades, fem la hipòtesi de que l'intermedi **T1** és una conformació menys estable del π -[**D4T7**]₂²⁺, mentre que l'intermedi **T2** és un dímer de valència mixta catió radical, π -[**D4T7**]₂^{•+}.

Taula 7.4.1. Energia lliure de formació a 298 K obtinguda a nivell M06L/6-31G(d). Tots els càlculs han estat realitzats amb un model continu de solvatació (PCM). S'indica la distància mínima intermolecular.

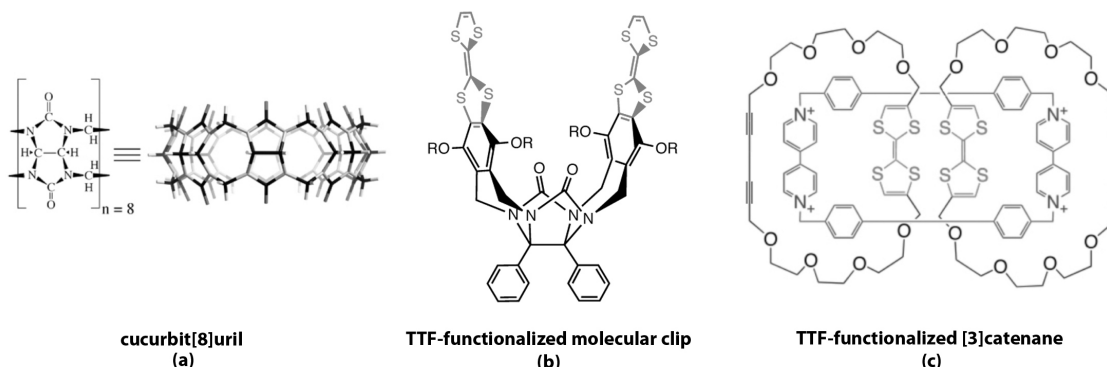
Conformació	r (Å)	ΔG_f° (kcal mol ⁻¹)
[D4T7^{•+}]₂ π-dímer dicatió		
anti [D4T7 ^{•+}] ₂ (CH ₂ Cl ₂) ₈	3.26	-21.0
syn [D4T7 ^{•+}] ₂ (CH ₂ Cl ₂) ₈	3.30	-22.5
forma-X [D4T7 ^{•+}] ₂ (CH ₂ Cl ₂) ₈	3.38	-9.5
[D4T7]₂^{•+} π-dímer catió radical		
anti [D4T7] ₂ ^{•+} (CH ₂ Cl ₂) ₈	3.30	-28.5
syn [D4T7] ₂ ^{•+} (CH ₂ Cl ₂) ₈	3.35	-31.3
forma-X [D4T7] ₂ ^{•+} (CH ₂ Cl ₂) ₈	3.40	-19.0

La Taula 7.4.1 mostra els valors d'energia lliure de Gibbs a temperatura ambient calculats a nivell M06L/6-31G(d). Els càlculs han estat realitzats per les conformacions més probables per a dos estats d'oxidació, el dímer de valència mixta i el dímer dicatió, el qual forma l'enllaç multicentre a llarga distància. Tal i com es veu, la conformació forma-X és força més estable que les conformacions anti o syn, les quals són pràcticament isoenergètiques. D'altra banda el compost de valència mixta també té una alta estabilitat. A més a més, les transicions electròniques verticals s'han calculat mitjançant càlculs TD-DFT amb el funcional ω B97XD (Taula 7.4.2). D'aquesta manera validem la hipòtesi realitzada sobre la naturalesa de les espècies intermèdies **T1** i **T2**.

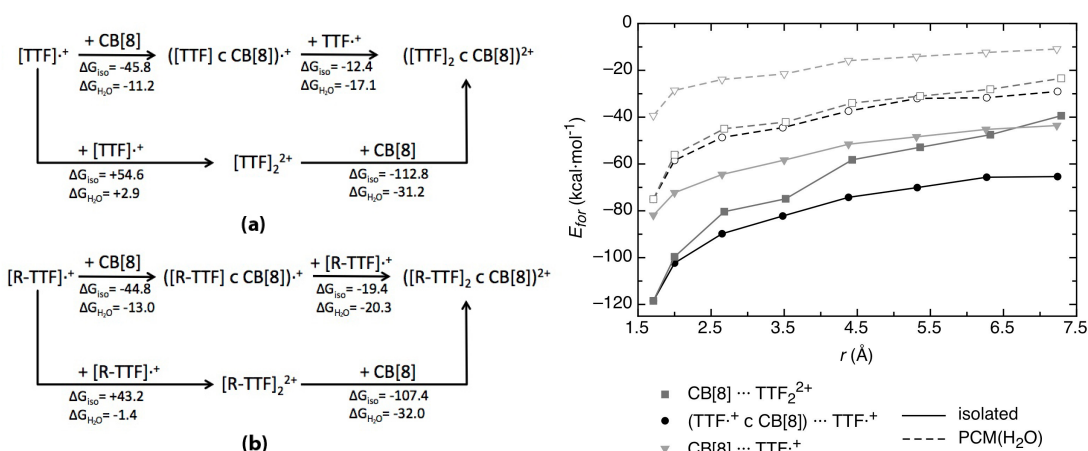
Taula 7.4.2. Transicions electròniques observades experimentalment i calculades a nivell TDDFT amb ω B97XD/6-31G(d).

Compost	$\lambda_{\text{exptl}} \text{ (nm)}$	$\lambda_{\text{calc}} \text{ (nm)}$
D4T7	388,409	378
D4T7^{•+}	582,1116	498,1013
[D4T7^{•+}]₂	~700	765
forma-X [D4T7^{•+}]₂ (= T1)	490,876	497,976
anti [D4T7]₂^{•+} (= T2)	470,620,950	394,574,984

La segona família de compostos que exhibeixen enllaços multicentre a llarga distància són els agregats supramoleculars. El primer exemple fou trobat en la inclusió de dímers de $[\text{TTF}]^{\cdot+}$ dins la cavitat d'un cucurbit[8]uril (CB[8], Figura 7.4.2 a). Posteriorment, una sèrie d'agregats supramolecular han estat caracteritzats exhibint dimerització multicentre a llarga distància a temperatura ambient, com ara la dimerització de clips moleculars (Figura 7.4.2 b) o la formació de $[n]$ catenans (Figura 7.4.2 c). Aquests tres exemples són estudiats a continuació.

**Figura 7.4.2.** Exemples d'agregats supramoleculars involucrant TTF que formen $\pi\text{-}[\text{TTF}]_2^{2+}$ a temperatura ambient.

La Figura 7.4.3 (esquerra) mostra la termodinàmica del procés. Es veu que tant la inclusió d'un $[\text{TTF}]^{\cdot+}$ com la del dímer $\pi\text{-}[\text{TTF}]_2^{2+}$ estan afavorides termodinàmicament. També es veu que l'efecte de tenir TTF substituït o sense substituir no varia la termodinàmica del procés. Per altra banda, la Figura 7.4.4 (dreta) mostra la cinètica del procés, per als dos mecanismes d'inserció, els quals tots mostren l'estabilitat del procés i l'absència de barreres energètiques.

**Figura 7.4.3.** Esquerra: energies lliures de formació a 298 K. Dreta: corbes d'energia de formació, per als mecanismes d'un-pas i de dos-pasos. Càlculs realitzats a nivell M06L/6-31G(d). Efectes de dissolvent inclosos amb model de solvatació continu.

Per les dades de la Figura 7.4.3 s'aprecia que l'estabilització és prou important com per a romandre a temperatura ambient. Una aproximació de les components de dispersió i electrostàtica de l'energia d'interacció mostra que la dispersió té un valor de $-63.4 \text{ kcal}\cdot\text{mol}^{-1}$, mentre que l'electrostàtica és de $-108.5 \text{ kcal}\cdot\text{mol}^{-1}$ en medi aquós. Aquesta estabilització electrostàtica visualment pot estimar-se a través dels mapes de potencial electrostàtic (Figura 7.4.4).

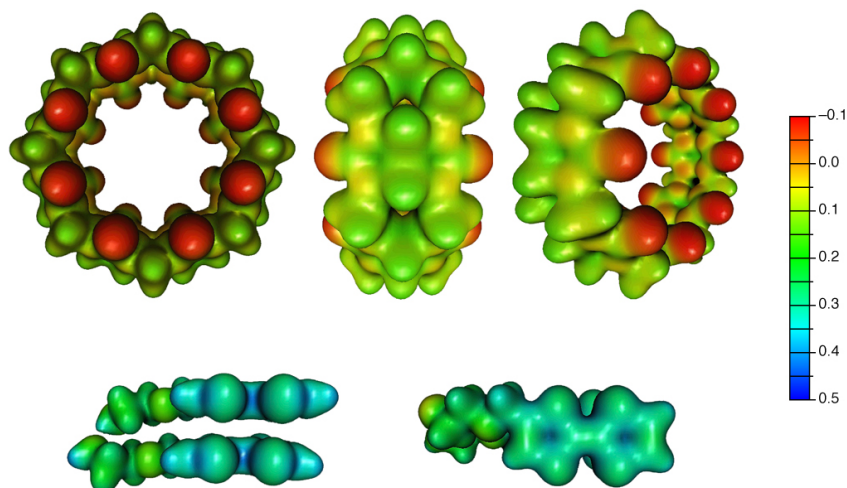


Figura 7.4.4. Mapes de potencial electrostàtic (MEP) del CB[8] i el π -[R-TTF] $_2^{2+}$.

El segon exemple d'agregat supramolecular estudiat en aquesta tesi és la dimerització de clips moleculars (Figura 7.4.2 b). A cada extrem final del clip molecular (d'ara en endavant, clip) hi ha enllaçat un TTF. Degut a la pròpia geometria del clip, aquest pot dimeritzar formant una estructura central on es troben quatre TTF encarats. Això permet, després de les quatre oxidacions pertinents, la formació de dos dímers π -[TTF] $_2^{2+}$. La Taula 7.4.3 conté els valors d'energia de formació i d'energia lliure de Gibbs a temperatura ambient per als diferents estats d'oxidació del dímer clip $_2^{n+}$. Com es veu, la formació de fins al clip $_2^{4+}$ és estable a 298 K.

Taula 7.4.3. Energia de formació i energia lliure de Gibbs a 298 K per als diferents estat d'oxidació. Càlculs a nivell M06L/6-31G(d).

	clip $_2^0$	clip $_2^+$	clip $_2^{2+}$	clip $_2^{3+}$	clip $_2^{4+}$	clip $_2^{6+}$	clip $_2^{8+}$
E_{for}	-45.9	-52.8	-52.6	-50.7	-41.2	-16.5	+0.8
ΔG (298 K)	-12.2	-20.7	-20.6	-18.1	-9.5	+16.9	+29.5

L'estabilitat a temperatura ambient és deguda a una forta component electrostàtica, com es pot veure a la Figura 7.4.5 i la Taula 7.4.4. La Figura 7.4.5 mostra una distribució zwitteriònica per al clip sigui quin sigui el seu estat d'oxidació, el qual mostra un anell central on hi resideix una càrrega negativa de -1 u.a. Aquest fet es tradueix en una forta atracció electrostàtica entre el TTF carregat del clip veí, tal i com es veu en l'anàlisi de components de la Taula 7.4.4 (columnes 3 i 4).

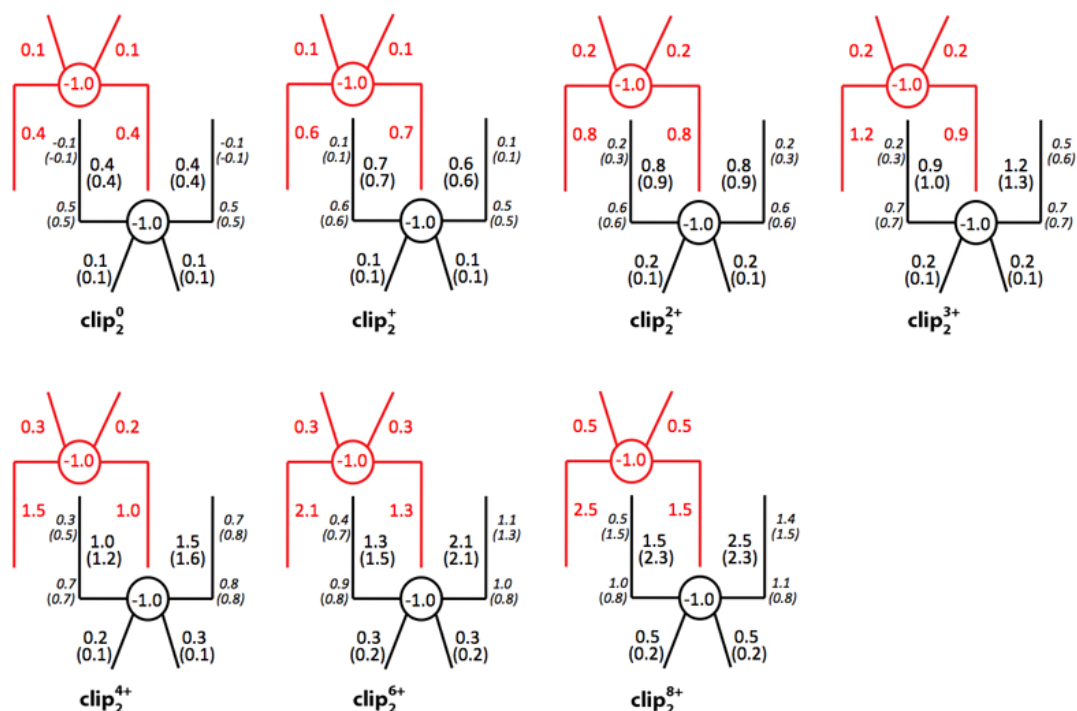


Figura 7.4.5. Distribució de càrrega dels dímers clip_2^{n+} per als diferents estat d'oxidació. Càlculs M06L/6-31G(d), anàlisi de població de Mulliken.

Taula 7.4.4. Anàlisi de components dels dímers clip_2^{n+} , on BR es refereix al fragment del clip sense els TTF. Càlculs realitzats a nivell M06L/6-31G(d). Es fa notar l'ajust de la partició el coincideix les energies E_{sum} i E_{int} .

	$E(2\text{TTF}_1-2\text{TTF}_2)$	$E(\text{BR}_1-\text{BR}_2)$	$E(2\text{TTF}_1-\text{BR}_2)$	$E(\text{BR}_1-2\text{TTF}_2)$	E_{sum}	E_{int}
clip_2^0	0/0	0/0	0/0	0/0		0/0
	-16.1	+0.01	-16.4	-16.4	-48.7	-49.5
clip_2^+	0/1+	0/0	0/0	0/1+		0/1+
	-28.5	+0.01	-16.7	-21.4	-66.5	-64.2
clip_2^{2+}	1+/1+	0/0	1+/0	0/1+		1+/1+
	+20.3	+0.01	-21.5	-21.5	-22.6	-25.5
clip_2^{3+}	1+/2+	0/0	1+/0	0/2+		1+/2+
	+56.7	+0.01	-21.0	-36.3	-0.5	-2.7
clip_2^{4+}	2+/2+	0/0	2+/0	0/2+		2+/2+
	+156.6	+0.01	-36.6	-36.6	+83.5	+80.9
clip_2^{6+}	3+/3+	0/0	3+/0	0/3+		3+/3+
	+264.7	+0.05	-75.3	-73.4	+116.1	+189.5
clip_2^{8+}	4+/4+	0/0	4+/0	0/4+		4+/4+
	+522.0	+0.05	-100.8	-103.8	+317.7	+370.5

Finalment, el tercer exemple de la Figura 7.4.2 (l'exemple c) fou estudiat, el [3]catenan. Aquest compost presenta tres macrocicles entrelaçats entre ells, així parla d'arquitectures moleculars mecànicament entrelaçades. En aquest exemple, els dos macrocicles externs contenen un TTF com a part constituent del macrocicle, els quals poden ser oxidats fins a tenir $[\text{TTF}]^{2+}$, mentre que el macrocicle central (CBPQT) es troba carregat 4+ (és a dir, CBPQT^{4+}). Quan el complex es troba dioxidat respecte el seu estat inicial, és a dir, de $[\text{3}]catenan^{4+}$ a $[\text{3}]catenan^{6+}$, els dos macrocicles externs poden formar un dímer $\pi\text{-}[\text{TTF}]_2^{2+}$ en la cavitat del macrocicle central (Figura 7.4.6).

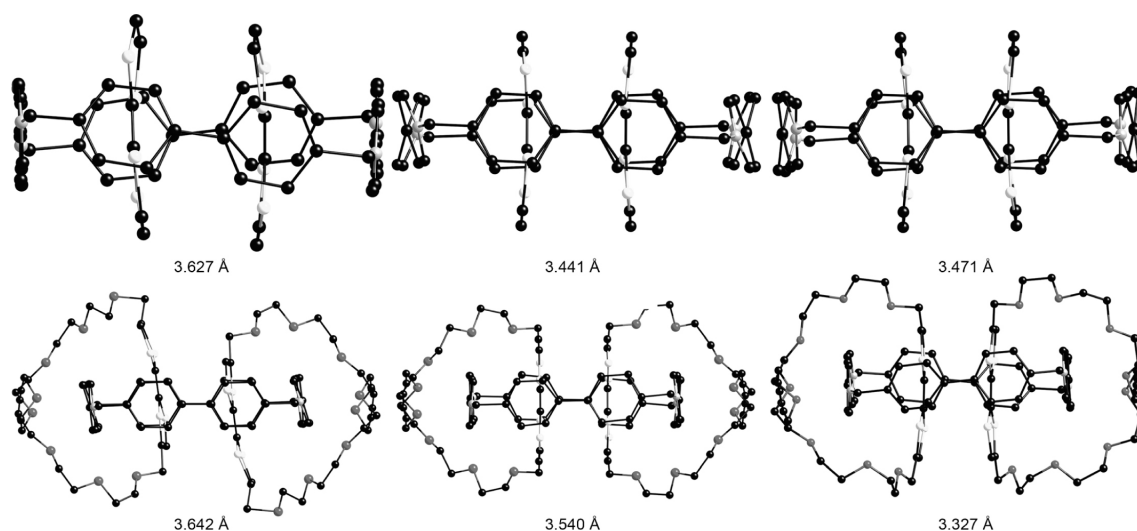


Figura 7.4.6. Geometries òptimes dels compostos $[(\text{TTF})_2^{n+} \subset \text{CBPQT}^{4+(n+4)+}]$ i $[3]\text{catenan}^{n+}$ per a $n = 0, 1+, 2+$. Càlculs realitzats a nivell M06L/6-31G.

A través de càlculs a nivell M06L/6-31G(d,p) veiem com pels diversos estats d'oxidació la càrrega majoritàriament es troba en els TTF. A més a més, la Taula 7.4.5 mostra com el dissolvent juga un paper transcendent dins l'estabilització d'aquest sistema.

Taula 7.4.5. Energies d'interacció (en $\text{kcal} \cdot \text{mol}^{-1}$) obtingudes a nivell M06L/6-31G(d,p).

Sistema	$(\text{TTF})_1^{n+} \dots$ $(\text{TTF})_2^m$	$(\text{TTF})_1^{n+} \dots$ CBPQT^{4+}	$(\text{TTF})_2^{n+} \dots$ CBPQT^{4+}	E_{tot}	E_{int} $E_{\text{int, MeCN}}$
$[(\text{TTF})_2 \subset \text{CBPQT}^{4+}]^{4+}$	-7.0 -7.1	-37.9	-36.3	-81.2	-82.3 -61.6
$[(\text{TTF})_2^+ \subset \text{CBPQT}^{4+}]^{5+}$	-28.8 -18.9	154.3	-29.8	95.7	100.6 -47.5
$[(\text{TTF})_2^{2+} \subset \text{CBPQT}^{4+}]^{6+}$	38.2 -11.3	149.5	152.6	340.3	336.8 -31.2
Sistema	$(\text{BPP-TTF})_1^{n+} \dots$ $(\text{BPP-TTF})_2^m$	$(\text{BPP-TTF})_1^{n+} \dots$ CBPQT^{4+}	$(\text{BPP-TTF})_2^{n+} \dots$ CBPQT^{4+}	E_{tot}	E_{int} $E_{\text{int, MeCN}}$
$[3]\text{catenan}^{4+}$	-8.4 -7.7	-111.3	-114.5	-234.2	-228.3 -113.3
$[3]\text{catenan}^{5+}$	-27.9 -17.6	73.2	-115.0	-69.7	-48.7 -109.3
$[3]\text{catenan}^{6+}$	23.9 -14.6	65.2	60.8	149.9	147.8 -95.5
$[3]\text{catenan}^{6+}$ rotat	16.7 4.8	27.7	20.8	65.2	54.1 -32.8
$[3]\text{catenan}^{8+}$	<i>neum</i> ^a	<i>neum</i> ^a	<i>neum</i> ^a	<i>neum</i> ^a	<i>neum</i> ^a
$[3]\text{catenan}^{8+}$ rotat	59.0 1.4	140.0	142.7	341.7	324.2 -50.2

^a *neum*: no és un mínim en la superfície d'energia potencial.

7.5. Conclusions

Les següent conclusions han estat obtingudes durant el transcurs de la present tesi doctoral:

- L'espai actiu mínim (2,2) proporciona una descripció qualitativa de la funció d'ona del dímer, tot i que per a obtenir energies quantitatives cal introduir l'espai- π directe paral·lel a l'eix d'enllaç. L'espai- π actiu complert paral·lel a l'eix d'enllaç és necessari per tal de descriure el procés de dissociació de manera quantitativa.
- Correccions de dispersió han de ser considerades per a una adequada (qualitativa) descripció dels enllaços multicentre a llarga distància. Els funcionals híbrids de rang separat són incapaços de descriure aquests enllaços, inclús quan correccions de dispersió hi són incloses.
- La naturalesa dels enllaços multicentre a llarga distància és predominantment electrostàtica. El terme estabilitzant més important és la dispersió, tot i que el terme d'enllaç té una major influència a l'hora de determinar l'orientació relativa dels fragments.
- La preferència en l'orientació dels enllaços multicentre a llarga distància en estat sòlid ve en última i major instància determinada pels contraions (i, per tant, per l'empaquetament cristal·lí).
- La prèvia assignació dels dímers π -[TCNE] $_2^{2-}$ L_c fou un error d'interpretació. En lloc, es formen π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] enllaçats multicentre a llarga distància.
- L'enllaç multicentre a llarga distància en π -[TTF $^{\delta+}$...TCNE $^{\delta-}$] es manté (en lloc de formar enllaç σ) degut a les altes interaccions de repulsió-bescanvi, malgrat la naturalesa atraient dels fragments.
- Els cations no prenen un paper crucial en l'estabilització de π -[TCNE] $_2^{2-}$ en dissolucions de diclorometà.
- La primera esfera de solvatació de π -[TCNE] $_2^{2-}$ és formada per 20 molècules de diclorometà, tot i que les 8 molècules que envolten la regió equidistant d'ambdós monòmers proporcionen una major estabilització. Les molècules de CH₂Cl₂ estabilitzen el π -[TCNE] $_2^{2-}$ a través de contactes H...N.
- La geometria de π -[TCNE] $_2^{2-}$ es manté en dissolució, mostrant únicament petites fluctuacions respecte a la coneguda estructura experimental. El perfil d'energia lliure a 175 K mostra un mínim estable per -5.5 kcal·mol⁻¹, amb una barrera energètica enfront la dissociació de 9.6 kcal·mol⁻¹.
- Cadenes laterals i un gran excés de contraions en la dissolució són factors que intensifiquen l'estabilitat dels enllaços multicentre a llarga distància.
- La formació de dímers multicentre a llarga distància entre cations radicals d'oligotienoacens presenten un mecanisme on dos intermedis són identificats: un dímer catió radical de valència mixta es forma durant el procés d'oxidació, així com un dímer dicatíon de conformació menys estable que finalment acaba convertint-se en els més estables π -dímers *anti* o *syn*.
- Totes les propietats associades als enllaços multicentre a llarga distància es mantenen després de la formació d'agregats supramoleculars.

- Els efectes electrostàtics són crucials a l'hora d'estabilitzar la formació d'enllaços multicentre a llarga distància entre ions radicals.
- La distribució polaritzada del cucurbit[8]uril, CB[8], és responsable de l'alta estabilització del complex d'inclusió $(\pi\text{-[R-TTF]}_2 \subset \text{CB[8]})^{2+}$, complementat per una estabilització de dispersió. La formació del complex d'inclusió és espontània i el procés no presenta barreres energètiques.
- El clip molecular estudiat presenta una distribució de càrrega zwitteriònica (on una càrrega -1 u.a. es troba localitzada en l'anell central, indistintament de l'estat d'oxidació), que estabilitza la càrrega positiva de les unitats de TTF quan l'agregat supramolecular és format.
- La formació de dímers $\pi\text{-[TTF]}_2^{2+}$ en el [3]catenan que conté unitats de TTF en els seus macrocicles externs és altament repulsiu quan es troba aïllat, i induiria una rotació d'aquests macrocicles externs. Els efectes de solvatació atenuen dràsticament la repulsió electrostàtica i permeten la formació del dímer.
- El funcionat de la densitat M06L s'ha avaluat intensament i s'ha comprovat que és un mètode fiable per a la predicció de propietats i tendències involucrant enllaços multicentre a llarga distància i complexos supramoleculars.

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