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Grau de Química

Treball Final de Grau

Charge transfer in 2D Covalent Organic Frameworks for optoelectronics.
Transferència de càrrega en xarxes orgàniques bidimensionals per a optoelectrònica.

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B:KC Barcelona Knowledge Campus
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Les generacions passen, però les arrels perduren.

Anònim

En primer lloc, voldria agrair de tot cor a la Dra. Maria Fumanal Quintana per guiar-me en aquest projecte amb la dedicació que ho ha fet. La seva manera de transmetre els coneixements amb il·lusió avui em fa estimar encara més la química computacional.

En afegit, voldria donar les gràcies a tota la meva família per recolzar-me sempre. Aquest treball és fruit també dels seus esforços.

REPORT

IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (SDG)

Nowadays, it has become a challenge to meet the global energy requisites while minimizing the damage that obtaining, distributing and consuming it produces on the planet. Therefore, it is essential to develop renewable energy sources that are not only economically viable and safe but also sustainable. In this context, scientists are focused on harnessing the available sunlight to meet global energy demand and, 2D-COFs have interesting properties for photovoltaics. Establishing the structure-property relationship of COFs from computational calculations is essential to focus synthetic efforts, time and cost, only on materials with the most promising properties. [1–3]

The present research carried out has a positive impact on both areas, prosperity and planet. More specifically, at the level of analysis carried out, the results of the computational study mainly present two materials as good candidates for photovoltaics. Ultimately, finding materials with promising light-to-electric optoelectronics applications would make it possible to meet energy requirements through renewable and affordable energy sources (photovoltaics).

Therefore, from what has been mentioned above, this project relates to the following Sustainable Development Goals (SDGs): affordable and clean energy (7), industry, innovation and infrastructure (9), sustainable cities and communities (11) and, climate action (13).

CONTENTS

1. SUMMARY

Currently, the development of novel sustainable nanomaterials that offer high performance in optoelectronics is of great interest not only to the scientific community but also to industry. With the aim of developing state-of-the-art optoelectronics devices, research is being carried out on the properties offered by different materials to be used in either light-to-electric or electric-to-light applications.

Covalent Organic Frameworks (COFs) are a type of nanomaterial with excellent potential to the future of optoelectronics. COFs are a class of organic polymers with permanent porosity and highly ordered crystalline structures. Specifically, COFs have interesting properties for the development not only of solar cells but also for Organic Light-Emitting Diodes (OLEDs). In the case of solar cells, materials are sought that absorb as much solar electromagnetic radiation as possible and convert it into electricity. In the case of OLEDs, materials are sought that generate visible light in the presence of electric current. Establishing the structure-property relationship of COFs from computational calculations is essential to reduce the time, cost and effort of the synthesis process by bringing to it only the candidates with the most promising properties.

In this project, three different families of experimentally reported 2D-COFs have been studied by means of computational chemistry, using Density Functional Theory (DFT) and its Time-Dependent extension (TD-DFT) methods. More specifically, we use the ωB97XD range-corrected functional with the def2-SVP basis set. First, for each system, it has been necessary to determine the most appropriate 0D cluster model (MAM) able to characterize the excited state properties of the periodic 2D-COF monolayer, by cost-effective calculations. Therefore, for each COF, the singlet excited state with the lowest energy has been evaluated for increasing size 0D models of the periodic 2D-COF structure until convergence. This research has been carried out by characterizing the molecular orbitals (MOs) involved in the excitation, the excited state energy and the Charge Transfer (CT) character.

It is concluded that, in order to correctly determine the MAM, it is necessary that the MOs are well surrounded by an environment sufficiently close to that of the periodic monolayer. It has been determined that, a small change in the structure of 2D-COF, which is repeated periodically, give rise to monolayers with different properties. At the level of study carried out, of all systems under study, systems 1 and 3 have the most promising properties for light-to-electric optoelectronics. Both systems have well-defined CT from the linker (the donor) to the ligand (the acceptor).

Keywords: COFs, optoelectronics, TD-DFT, charge transfer

2. RESUM

Actualment, és de gran interès no només per a la comunitat científica, sinó que també ho és per a la industria, el desenvolupament de nous nanomaterials sostenibles que ofereixin alt rendiment en optoelectrònica. Amb l'objectiu de desenvolupar dispositius optoelectrònics de vanguardia, s'estan investigant les propietats que ofereixen diferents materials per a utilitzar-los en aplicacions de tipus *light-to-electric* o *electric-to-light*.

Els *Covalent Organic Frameworks* (COFs) son un tipus de nanomaterial amb un potencial excel·lent pel que fa al futur de la optoelectrònica. Els COFs son una classe de polímers orgànics amb porositat permanent que presenten estructura cristal·lina altament ordenada. Concretament, els COFs presenten propietats interesants per al desenvolupament no només de cel·les solars, sinó que també per al de *Organic Light-Emitting Diodes* (OLEDs). Pel que fa al cas de les cel·les solars, es busquen materials que absorbeixin tanta radiació electromagnètica solar com sigui possible i la transformin en electricitat. En el cas dels OLEDs, es busquen materials que en presència de corrent elèctric, generin llum visible. Establir la relació entre estructura i propietat dels COFs mitjançant càlculs computacionals, és essencial per a reduir el temps, els costos econòmics i l'esforç del procés de síntesis, fent arribar al procés sintètic només als candidats amb les propietats més prometedores.

En aquesta recerca, tres famílies diferents de 2D-COFs experimentals reportats han estat estudiats per mitjans de la química computacional emprant els mètodes *Density Functional Theory* (DFT) i la seva extensió dependent del temps (TD-DFT). Més concretament, s'ha emprat el funcional ωB97XD tipus *range-corrected* i el conjunt de bases def2-SVP. Primerament, per a cada sistema ha estat necessari determinar el model 0D més apropiat (MAM) per a caracteritzar les propietats de l'estat excitat de la monocapa periòdica del 2D-COF, a baix cost computacional. De manera que, per a cada COF, l'estat excitat singlet de menor energia ha estat avaluat mitjançant models 0D de l'estructura del 2D-COF de mida creixent fins a convergir. Aquesta recerca s'ha dut a terme caracteritzant els orbitals molecular (MOs) implicats a l'excitació, l'energia de l'estat excitat i el caràcter de transferència de càrrega (CT).

S'ha conclòs que, per tal de determinar correctament el MAM, és necessari que els MOs estiguin ben envoltats per un entorn suficientment proper al que tenen en la monocapa periòdica. S'ha determinat que, un petit canvi en l'estructura del 2D-COF, el qual es repeteix periòdicament, dona lloc a monocapes amb propietats diferents. Al nivell d'estudi dut a terme, de tots els sistemes objecte d'estudi, els sistemes 1 i 3 son els que tenen les propietats més prometedores per a aplicacions d'optoelectrònica tipus *light-to-electric*. Ambdós sistemes presenten una CT ben definida que va del node (el donador) al lligand (l'acceptor).

Paraules clau: COFs, optoelectrònica, TD-DFT, transferència de càrrega

3. INTRODUCTION

3.1. OPTOELECTRONICS: CURRENT STATUS AND FUTURE PROSPECTS

Optoelectronics has a wide range of applications; both light-to-electric and electric-to-light energy conversion is crucial for applications such as photovoltaics and LEDs, respectively. Work is currently underway to develop novel materials for their use in optoelectronics and the trend is: the smaller the resulting end device, the better. For this reason, nanomaterials such as 2D materials are becoming one of the main objects of study in the field of optoelectronics. [1,4–6] More specifically, the focus of this research is on the optoelectronic properties of 2D covalent organic monolayers.

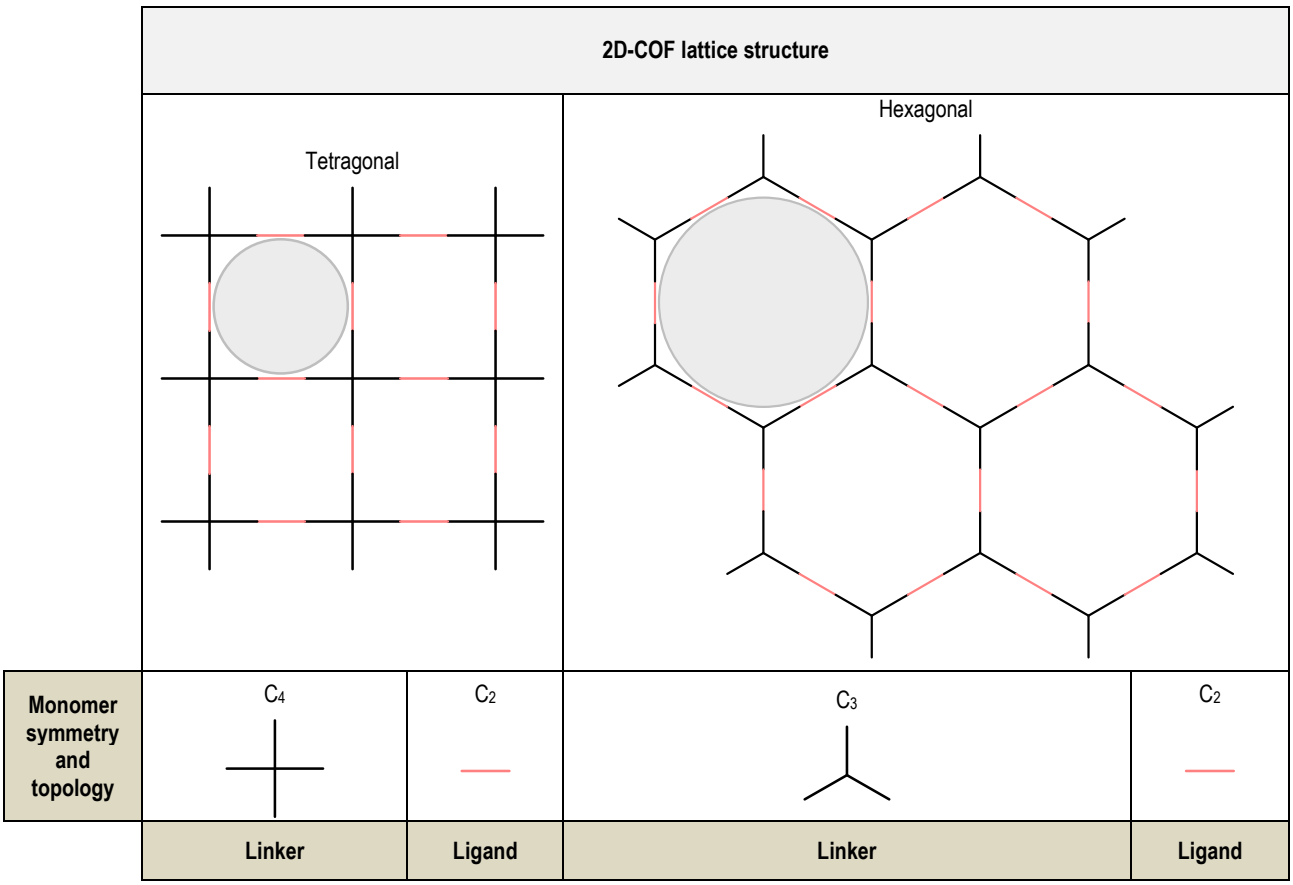
3.1.1. Photovoltaics: solar cells

Nowadays, it has become a challenge to meet the global energy requisites while trying to minimize the negative impact on our planet of generating, distributing and consuming this energy. Therefore, it is vitally important to develop renewable energy sources that are not only economically viable and safe but also sustainable. Scientists are focused on harnessing the available sunlight to meet global energy demand without causing damage to the Earth. Different technologies and methods have been developed with the aim of capturing solar energy. Specifically, photovoltaics cells are the main option for capturing the solar electromagnetic radiation, and for this reason, in the field of solar energy, they are the main object of research not only at the level of academics but also in industry. Finding materials with real promising light-to-electric properties is a challenge. In this context, the higher the efficiency in terms of power generation, the more appropriate the material. Certain organic materials have interesting properties for photovoltaics. However, one of the most important problems of organic photovoltaics is the low efficiency of current generation due to the electron-hole recombination. [1,2,3] In this context, materials with strong donor-acceptor (D-A) character promote efficient charge transfer (CT) improving the energy conversion yield.

3.2 COVALENT ORGANIC FRAMEWORKS (COFS)

Covalent Organic Frameworks (COFs) are a type of nanomaterial composed of organic molecules linked by covalent bonds. More specifically, COFs are a class of organic polymer with permanent porosity and highly ordered crystalline structures. COFs are prepared by the linkage of molecular building blocks and nodes in order to form 2D or 3D crystalline frameworks with well-defined porous architectures. The structure of building blocks and nodes as a pair has an essential effect on the properties of the material as a whole. 2D-COFs are being studied in the field of optoelectronics due to their ability to form highly crystalline periodic networks with the potential to improve the semiconducting properties offered by less ordered 1D polymers. [6–9]

In the field of COFs, it is also common to refer to the molecular building block as a ligand and the node as a linker. The node can be a small molecule such as benzene, but this linker can also be a large molecule like a metal-containing porphyrin. As for the ligand, there are also many possibilities. In addition, there are different possible topologies. Therefore, there is a wide diversity around the composition of COFs. The concept of geometric topology focuses on the relative structure positions instead of the specific components and it provides a helpful approach to designing and interpret COFs structures. In this context, COFs structures are represented by simplified skeletons formed by vertices (which represent atoms, functional groups or molecular units) and edges (which represent the bonds between vertices). In all cases, the lattice structure is highly ordered with well-defined porous. Tetragonal and hexagonal 2D-COFs lattices are among the most common. See Figure 1. [7–9]

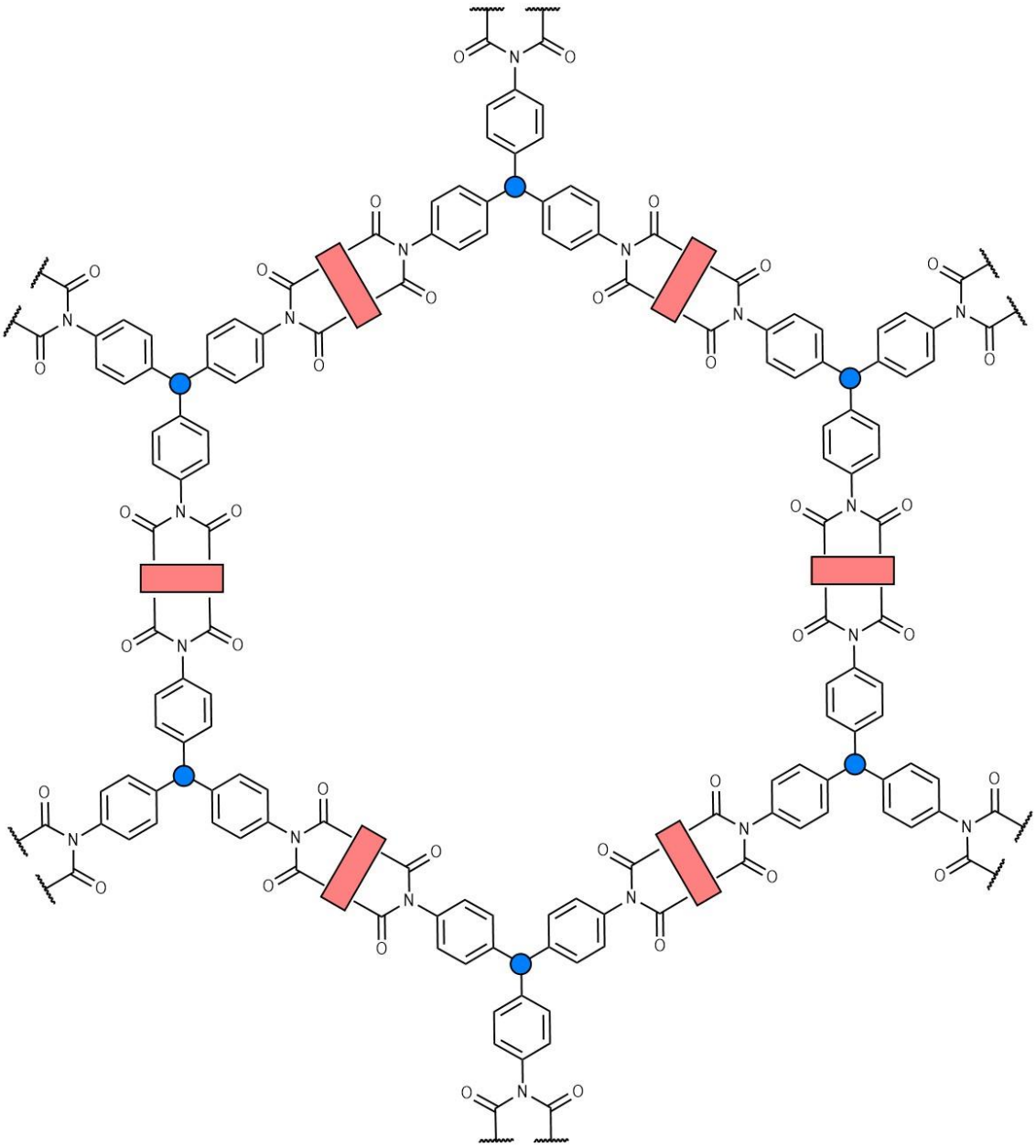


i. Grey circles identify well-defined pores size.

Figure 1. Tetragonal and hexagonal 2D-COFs structures: topological representations.

3.2.1 The 2D-COFs studied in this research: nomenclature and structure

In this project, three different families of experimentally reported 2D-COFs have been studied: G1[10], G2[11] and G3[12]. The systems that are part of the same family are similar in terms of composition and structure. In total, 14 different systems have been studied, which are part of the CURATED database.[13] See Appendix 1. In order to simplify the nomenclature throughout the research, a system number (1-14) has been assigned to each COF studied. See Figures 2, 3 and 4.



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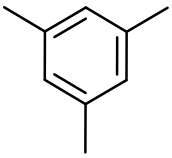
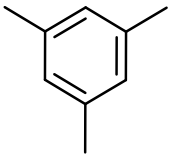
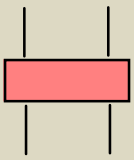
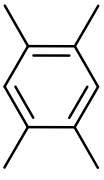
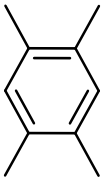
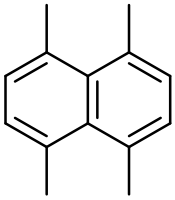
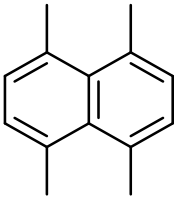
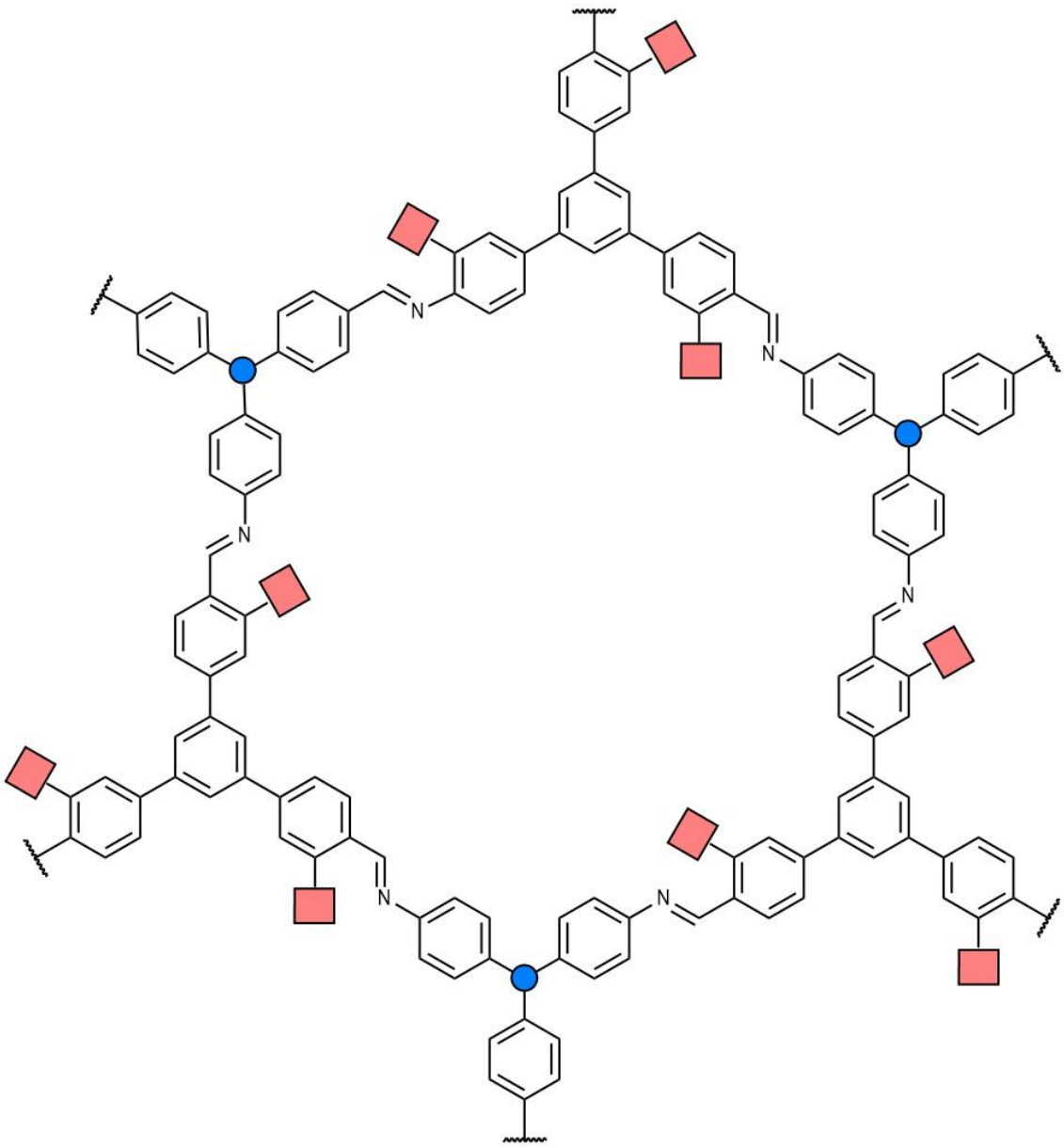
				
				

Figure 2. G1 monolayer structures.



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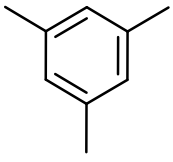
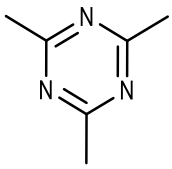
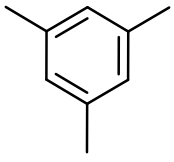
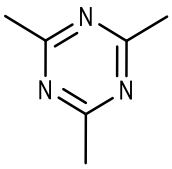
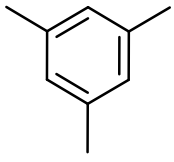
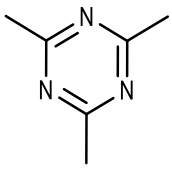
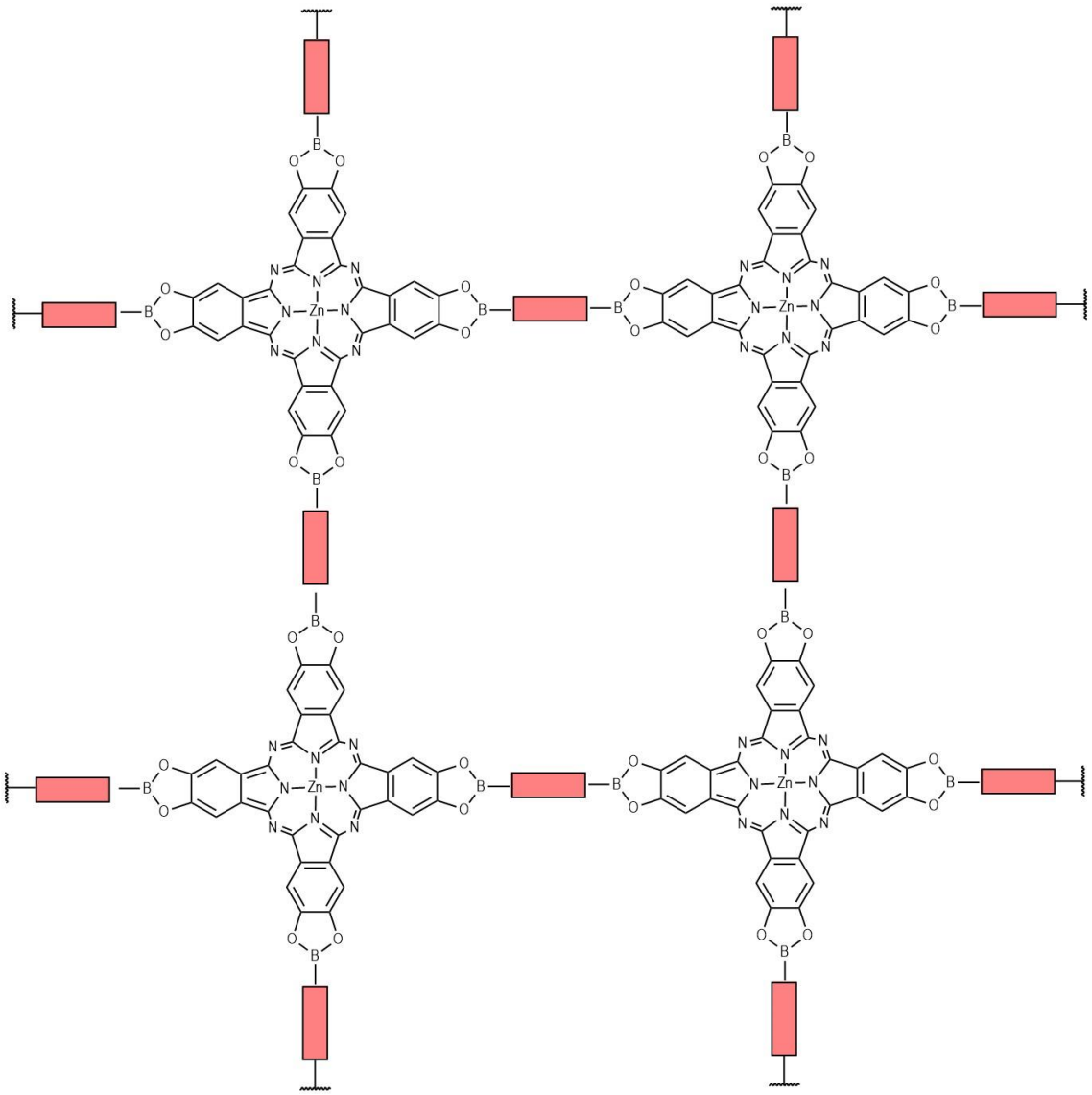
						
	H	H	CF_3	CF_3	OH	OH

Figure 3. G2 monolayer structures.



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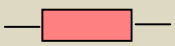
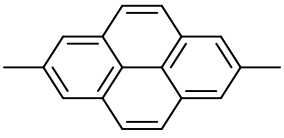
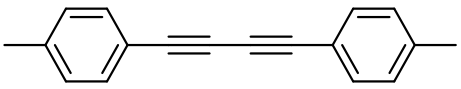
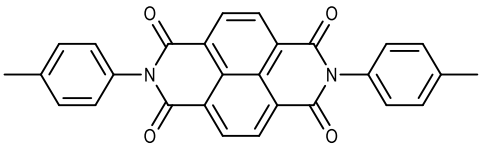
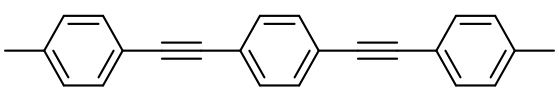
		
	13	**14**
		

Figure 4. G3 monolayer structure.

3.2.2 2D Donor-Acceptor COFs and their photoinduced charge transfer

D-A COFs are a type of COF composed by donor-acceptor pairs. More specifically, intraplane D-A combinations are used to construct 2D-COFs with interesting properties for light-to-electric optoelectronics. The main differentiated feature of D-A COFs is their photoinduced charge transfer (CT). The photoinduced CT process involves transferring an electron from the donor to the acceptor after the system irradiation, where these two molecules are covalently-bonded. See Figure 5. Photoinduced CT between D-A pairs occurs under a specific electromagnetic radiation and it confers these D-A COFs with promising applications in organic photovoltaics. Photoinduced CT aims to solve one of the most important problems of organic photovoltaics, which is the low efficiency of current generation due to the electron-hole recombination, which happens when the electron (-) and hole (+) generated through the excitation quickly recombine through radiative and nonradiative processes.[3,5,9]

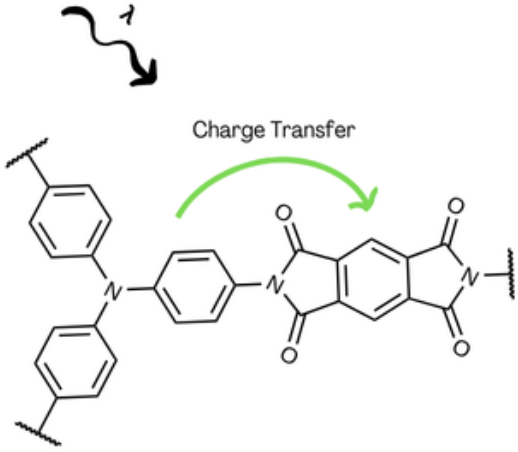


Figure 5. System 1 (21081N2 CURATED COF) photoinduced CT involves transferring an electron from the donor to the acceptor after the system irradiation. In this case, the donor is the linker and the acceptor is the ligand but this is not a rule for all systems.

When an electron is transferred from the Highest Occupied Molecular Orbital (HOMO) located on the donor to the Lowest Unoccupied Molecular Orbital (LUMO) also located on the donor, it is a local excitation. Charge transfer, on the other hand, takes place when an electron is transferred from the HOMO located on the donor to the LUMO located on the acceptor. See Figure 6. However, it is important to note that it is not always the HOMO and LUMO orbitals that are involved in charge transfer. That is, these molecular orbitals are normally taken as a reference to define the CT but it depends on the specific system. In some cases, it is true that HOMO and LUMO are the orbitals involved in the CT process. In other cases, other molecular orbitals close to these in energy give rise to the CT process. [6,9,14]

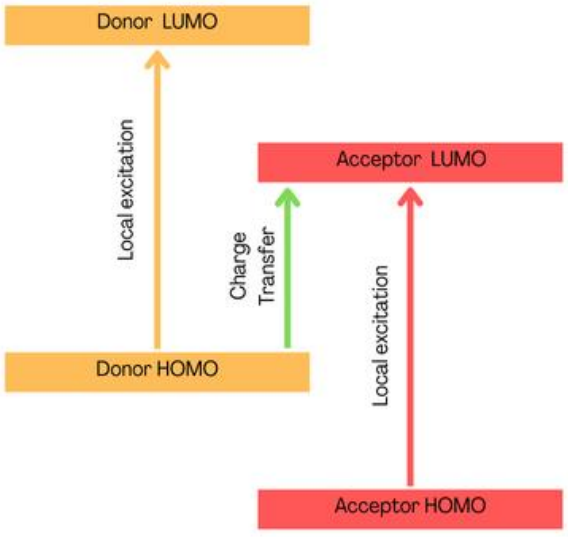


Figure 6. Scheme of the HOMO and LUMO orbital energies of the Donor and the Acceptor involved in non-local CT excitation.

3.3. COMPUTATIONAL FUNDAMENTS

3.3.1. Time-Dependent extension of Density Functional Theory (TD-DFT)

Time-Dependent Density Functional Theory (TD-DFT) methods are widely used for the computations of the properties of electronically excited states (ES). When performing TD-DFT calculations, it is necessary to select an exchange–correlation functional (XCF) and this is not trivial. XCF significantly influences how the accurate the results are. To help in the selection of a given XCF, many TD-DFT benchmarks have appeared during the last two decades.[15,16] In this work, we use the ωB97XD range-corrected functional with the def2-SVP basis set. This method correctly predicts CT in D-A systems.[4]

3.3.2. TheoDORE package

TheoDORE is a package for Theoretical Density, Orbital Relaxation and Exciton analysis. It is used for the analysis of the excited states obtained from quantum chemical excited state calculations. The main types of analysis that can be performed by TheoDORE: charge transfer numbers, natural transition orbitals, and an exciton size analysis. In this work, we use TheoDORE to characterize the CT of the first excited state of our 2D-COF monolayers.

4. OBJECTIVES

Predicting 2D-COFs monolayer properties through computational studies is essential to focus synthetic efforts only on materials with the most promising properties. The aim of this computational research is to study three different families of experimentally reported 2D-COFs: G1, G2 and G3. First, for each system, it is necessary to determine the 0D cluster model able to characterize the excited state properties of the periodic 2D-COF monolayer by cost-effective calculations. Then, the final goal is to determine which 2D-COFs have the most promising properties for light-to-electric optoelectronics applications based on our calculations.

5. EXPERIMENTAL SECTION

5.1 METHODOLOGY

As mentioned above, the first goal of this study is to determine the 0D cluster model able to characterize the excited state properties of the periodic 2D-COF monolayer. For each system, the singlet excited state with the lowest energy has been evaluated for increasing size 0D models of the periodic 2D-COF structure until convergence. The 0D cluster model that has been considered the most appropriate to characterize the properties of the excited state of the periodic 2D-COF monolayer is the one that best meets the following conditions:

1st. Be correctly representative of the 2D-COF monolayer giving results close enough to those of the complete structure not only in terms of energy but also in the shape and location of the orbitals.

2nd. Be a small model to achieve accurate results by computational cost-effective calculations.

This research has been carried out first by characterizing the orbitals involved in the excitation and the excited state energy. As mentioned previously, the excited state analysed is the singlet with lowest energy. More specifically, the excited state is a linear combination of different one-electron transitions between an occupied and a virtual molecular orbital. In this context, we refer to these different one-electron transitions as contributions. The excited state has been characterized by calculating the coefficients of each of

the contributions and by analysing the orbitals involved in the contributions with highest coefficients. An essential point of this molecular orbitals characterization, is to make sure that they are located in an area of the 0D model surrounded by an environment as close as possible to that of the periodic 2D-COF monolayer (1st condition). Moreover, between two models with very similar excited state energy values, the model formed by a lower number of atoms has been chosen as the most appropriate model (MAM) (2nd condition). Once the most appropriate model has been selected, the charge transfer property of each system has been studied using TheoDORE. Thus, in subsequent comparisons between different COFs, it is the results of the most appropriate model of each system that have been compared.

To carry out the present study, a sequence of different calculations has been made for the 0D cluster models, which are represented in Scheme 1 below:

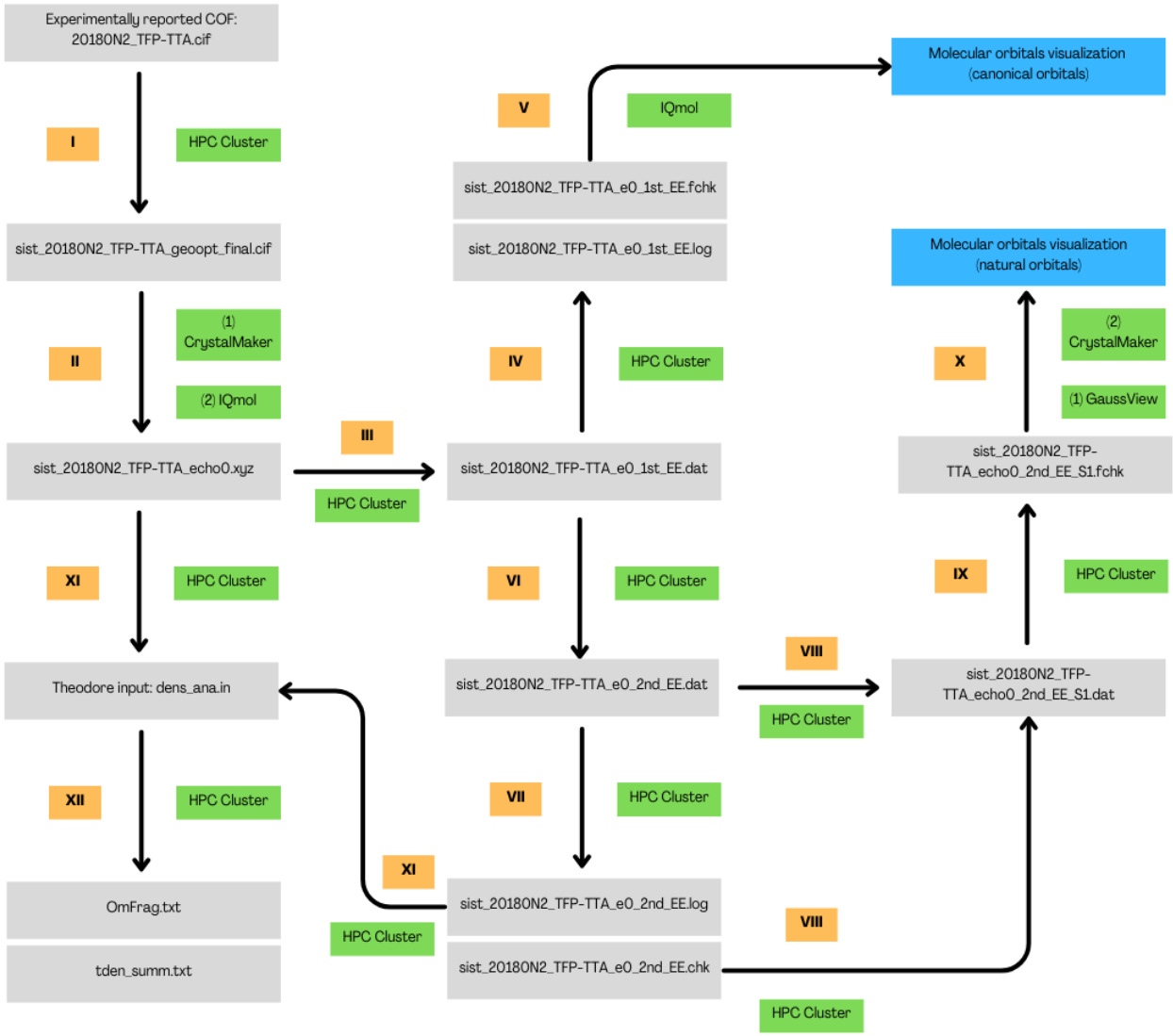
(Step-1) the coefficients of the different contributions (working with canonical orbitals) and the excited state energy have been obtained with TD-DFT calculations,

(Step-2) the results have been collected in a specific way in order to be readable with the TheoDORE program,

(Step-3) in some cases, the coefficients of the different contributions have been evaluated working with natural orbitals and,

(Step-4) the numerical value of charge transfer and the characterization of the fragments involved in this process has been done.

The different steps carried out, as well as the different software and environments used in this study, are shown in Scheme 1 using the example of model e0 of system 6.



Scheme 1. Scheme of the methodology used for the characterization of the singlet with lowest energy of system 6 model e0.

I. From the experimentally reported COF (.cif) the optimization of the monolayer is carried out (previous work).

II. (1) From the COF monolayer a region of the structure is selected and exported. (2) Hydrogens are added where appropriate to complete the structure of the 0D model. The goal is to obtain a document containing the atoms coordinates.

III. The calculation input document for Step-1 is prepared using the coordinate data and appropriated keywords.

IV. First, the Step-1 calculation is performed. Second, from the output document with a (.chk) extension, the (.fchk) is generated.

V. Firstly, the coefficients obtained for the different contributions in Step-1 (.log) are analysed. Then, the orbitals involved in the contributions with higher coefficients are visualized.

VI. The calculation input document for Step-2 is prepared using the coordinate data and appropriated keywords.

VII. The Step-2 calculation is performed.

VIII. The calculation input document for Step-3 is prepared using the appropriate data and keywords.

IX. First, the Step-3 calculation is performed. Second, from the output document with a (.chk) extension, the (.fchk) is generated.

X. (1) The coefficients obtained for the different contributions are analysed. (2) Then, the orbitals involved in the contributions with higher coefficients are visualized.

XI. The calculation input document for Step-4 is prepared using the coordinate data, appropriated keywords and indicating by numbering which atoms make up each fragment.

XII. First, the Step-4 calculation is performed. Then, the results are analysed, not only the value obtained for CT character (tden_summ.txt), but also, which fragments and how much are they involved in the CT process (OmFrag.txt).

5.2 COMPUTATIONAL DETAILS

The three excited state singlets with lowest energy calculations were performed with TD-DFT using the range corrected ωB97X-D functional and def2SVP basis set. The computations were done with Gaussian 16 (Steps 1-3). The COFs monolayers geometry optimizations were obtained in previous work at the same level of theory using ground state DFT.

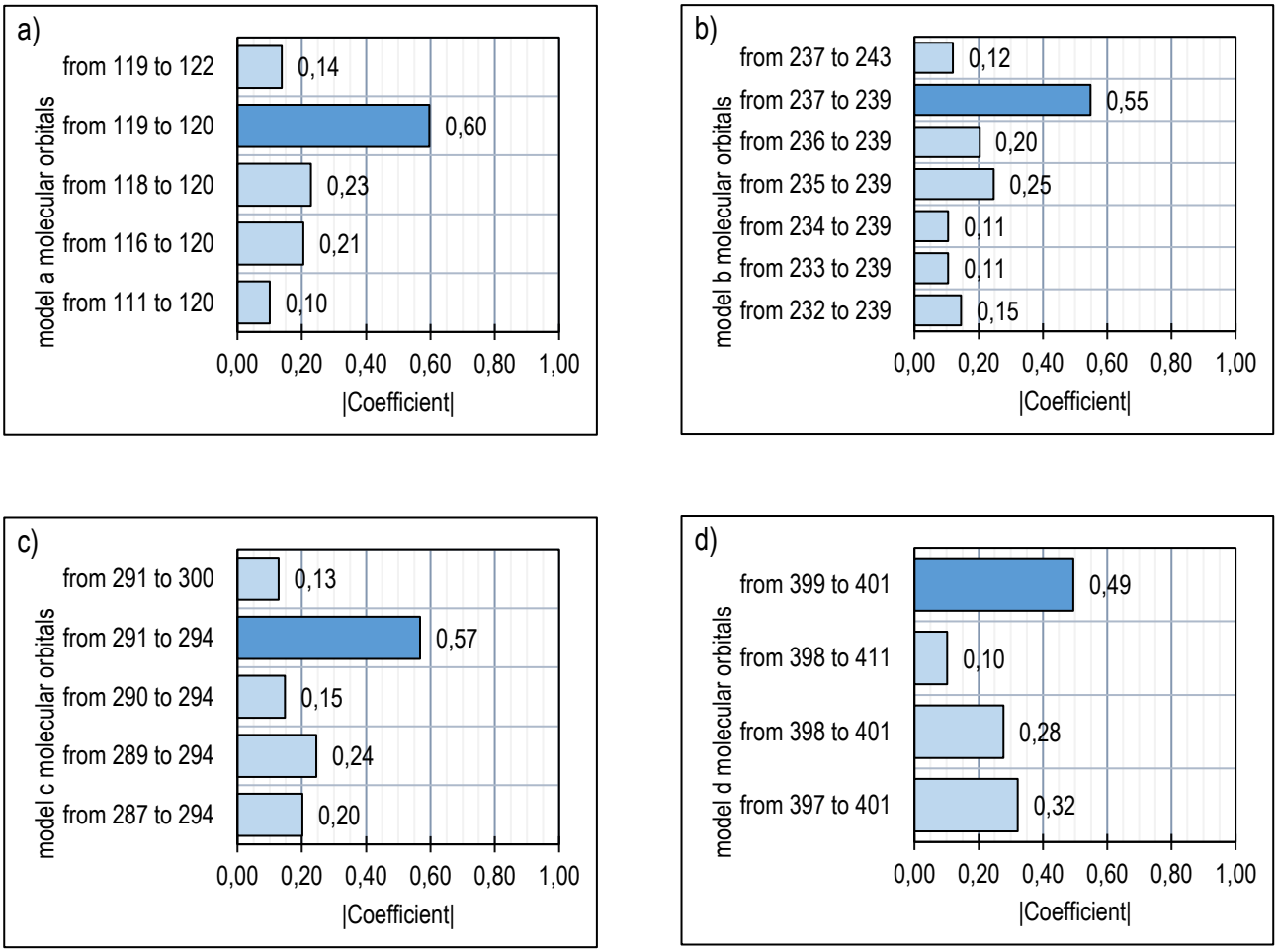
Charge transfer character and electron-hole separation calculations haven been done by TheoDORE program (Step-4). The charge transfer numbers are computed as partial summations over squared transition density matrix elements of molecular fragments. The key point for the charge transfer analysis is to divide the structure into meaningful fragments: linker and ligand. We have considered the linker and ligand fragments following the synthetic route reported in the experimental articles.

6. MOLECULAR ORBITALS CHARACTERIZATION

The excited state analysed is the singlet with lowest energy and, as mentioned previously, it is a linear combination of different one-electron transitions between an occupied and a virtual molecular orbital. In this context, we refer to these different one-electron transitions as contributions. For each model of each system, the coefficients of the different contributions (working with canonical orbitals) have been obtained with TD-DFT calculations (Step-1) and they have been analysed. Then, the orbitals involved in the contribution with highest coefficient are visualized in order to find out in which model they are located in an area of the 0D model surrounded by an environment as close as possible to that of the periodic 2D-COF monolayer (1st condition). For G2 it has also been necessary to calculate the coefficients of the contributions in terms of natural orbitals (Step-3). This is because with canonical orbitals a large number of contributions are obtained and none of them has a significantly higher coefficient than the rest. For G1, G3 (canonical orbitals) and G2 (natural orbitals), once the coefficients have been obtained, the characterization of the orbitals involved in the most important contribution of each model has been done in the same way. Through the example of system number 1 it is shown in more detail how the characterization of molecular orbitals has been carried out and which results have been obtained.

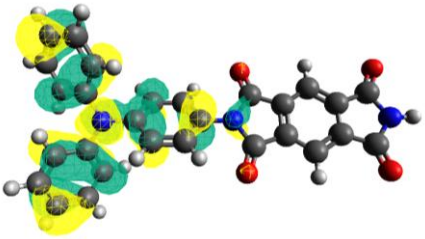
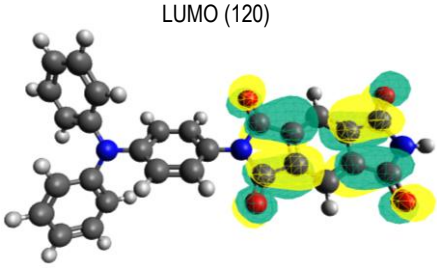
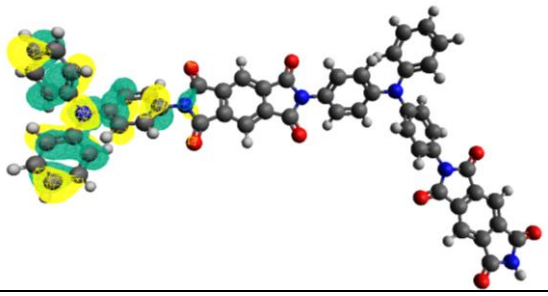
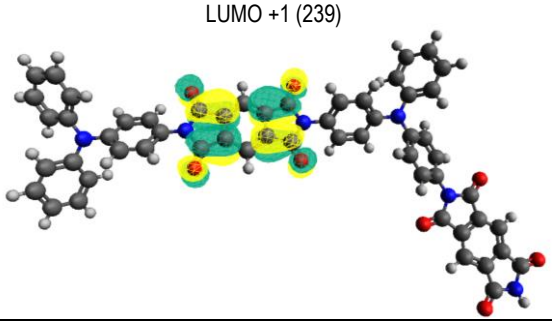
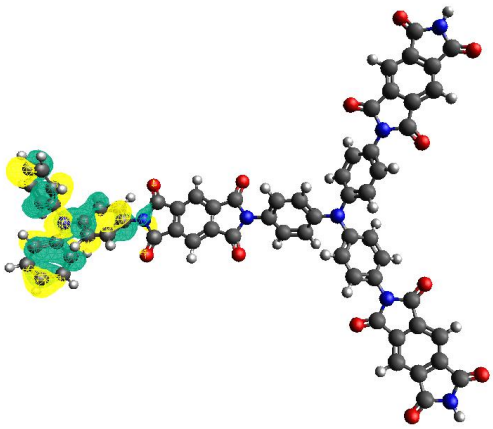
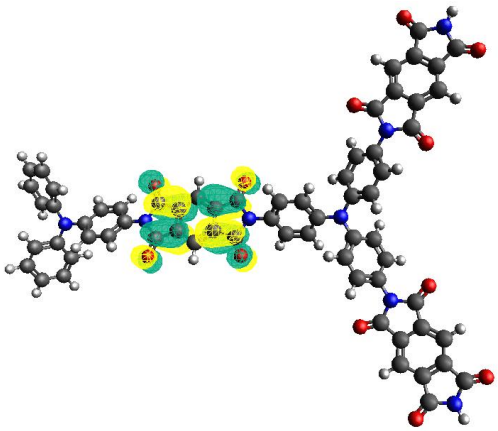
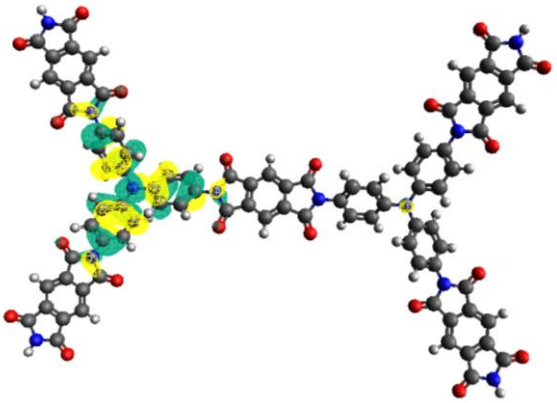
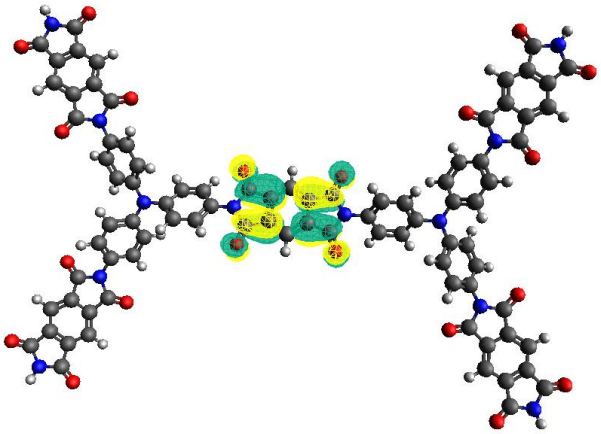
6.1 SYSTEM 1: MOLECULAR ORBITALS CHARACTERIZATION RESULTS

Firstly, for each model of system 1, the coefficients of the different contributions obtained with TD-DFT calculations (Step-1) are analysed. Thus, for each case, the contribution with the highest coefficient is identified. The most important contribution for models: a, b, c, and d, is from HOMO (119) to LUMO (120), from HOMO (237) to LUMO+1 (239), from HOMO (291) to LUMO+2 (294), and from HOMO (399) to LUMO+1 (401), respectively. See Figure 7. Secondly, for each model, the orbitals involved in the contributions with highest coefficient are visualized. It has been identified the d model presents both the starting and the arrival orbital, not only the arrival orbital as is the case of the b and c models, surrounded by an environment closer to that of the complete monolayer. This means that with regard to (1st condition), model d is the best candidate to be the MAM. See Figure 8.



i. The numbers associated with the molecular orbitals increase as the energy of the orbitals increases.
ii. The darker blue identifies the contribution with the highest coefficient.

Figure 7. System 1 models: the coefficient associated with each contribution obtained with TD-DFT calculations (Step-1).

Model	Starting occupied molecular orbitals	Arrival virtual molecular orbitals
a	HOMO (119) 	LUMO (120) 
b	HOMO (237) 	LUMO +1 (239) 
c	HOMO (291) 	LUMO +2 (294) 
d	HOMO (399) 	LUMO +1 (401) 

i. The orbitals are represented by two colors: green and yellow, which correspond to positive and negative signs, respectively.

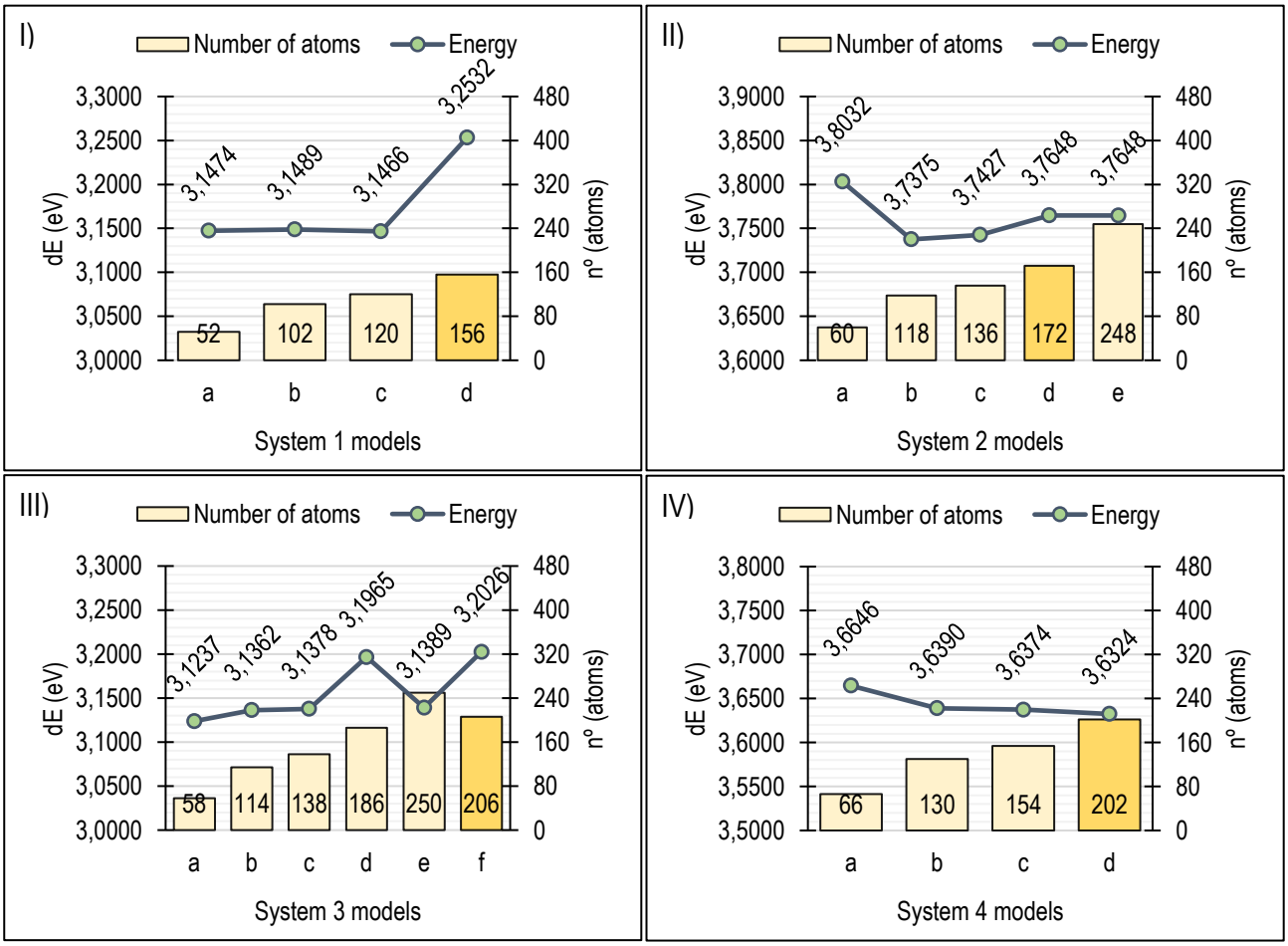
Figure 8. System 1 models: the molecular orbitals involved in the contribution with highest coefficient.

7. THE EXCITED STATE ENERGY CHARACTERIZATION

For each system, the singlet excited state with the lowest energy has been evaluated for increasing size 0D models of the periodic 2D-COF structure. The energy value associated with the excited state has been calculated with TD-DFT (Step-1). Taking into account the molecular orbitals characterization results and the energy values associated with excitation, for each system, it has been determined which model is the most appropriate (MAM) to predict the properties of the complete monolayer.

7.1 G1: THE EXCITED STATE ENERGY RESULTS

For G1 systems the excited state energies are: system **1** 3,2532 eV (381,12 nm), system **2** 3,7648 eV (329,33 nm), system **3** 3,2026 eV (387,14 nm) and system **4** 3,6324 eV (341,33 nm). See Figure 9. In the case of system **1**, it is not until model d that the excited energy is close enough to that of the complete structure. This is because models a-c do not have the starting and/or the arrival orbital well-surrounded. See Figures 8 and 9. In the case of system **2**, the model d is the MAM because it has well-surrounded orbitals, provides the same excited energy than model e (energy has converge), and it has a lower number of atoms than model e (2nd condition). In the case of system **3**: the model f is the MAM, because presents the best results in terms of well-surrounded orbitals. Therefore, a bigger model (e) does not always lead to better results. In the case of system **4**: the model d is the MAM. This is because, energy is converging (decreasing from model a to model d) and model d is the best described in terms of orbitals. See Figure 9.



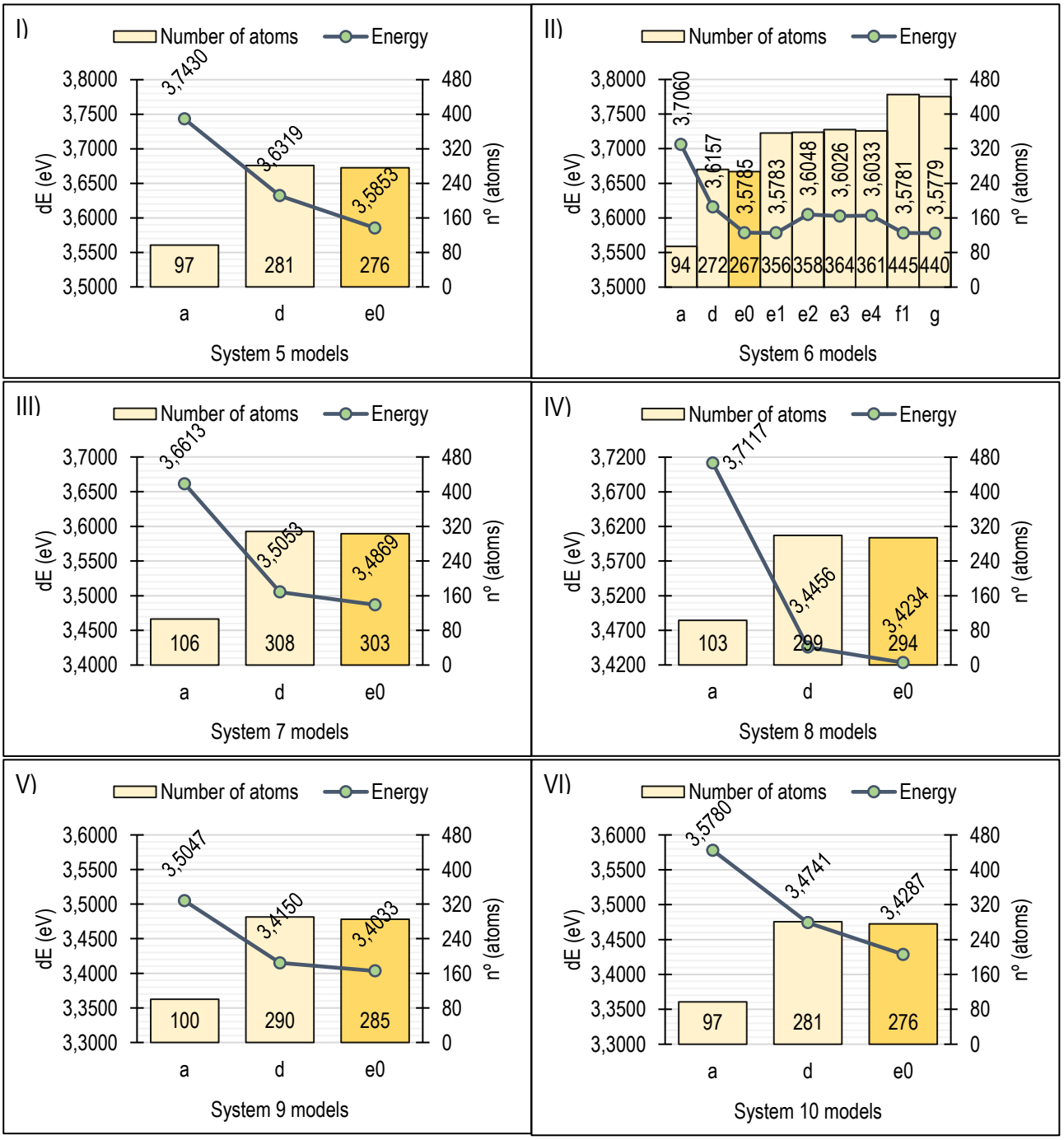
i. The darker yellow identifies the most appropriated model (MAM).

Figure 9. G1 systems: energy associated with the lowest energy excited state obtained with TD-DFT calculations (Step-1).

7.2 G2: THE EXCITED STATE ENERGY RESULTS

For G2 systems the excited energies are: system **5** 3,5853 eV (345,81 nm), system **6** 3,5785eV (346,47 nm), system **7** 3,4869 eV (355,58 nm), system **8** 3,4234 eV (362,17 nm), system **9** 3,4033 eV (364,31 nm) and system **10** 3,4287 eV (361,61 nm). See Figure 10.

System 6 was first studied in order to determine which structure is the MAM for any G2 system. System 6 was chosen because it has only the blue circle fragment replaced (by 1,3,5-triazine ring). Therefore, it has been considered the best option because it contains a certain functionality at the same time it has a conservative structure. See Figure 3. In this way, for each other G2 system it has only been considered necessary to study models a, d and e_0. In the case of system **6**: the models that best describe the system (e_0, e_1, f_1 and g) are those that are made up of at least one complete hexagon. The model e_0 is the MAM. This is because, having well-surrounded orbitals and providing similar energy results (energy convergence), has a lower number of atoms than other models (2nd condition). In the case of system **5** and systems **7**-to-**10**: the model e0 is the MAM. This is because, energy is converging (decreasing from model a to model e_0) and model e_0 is the best described in terms of orbitals.

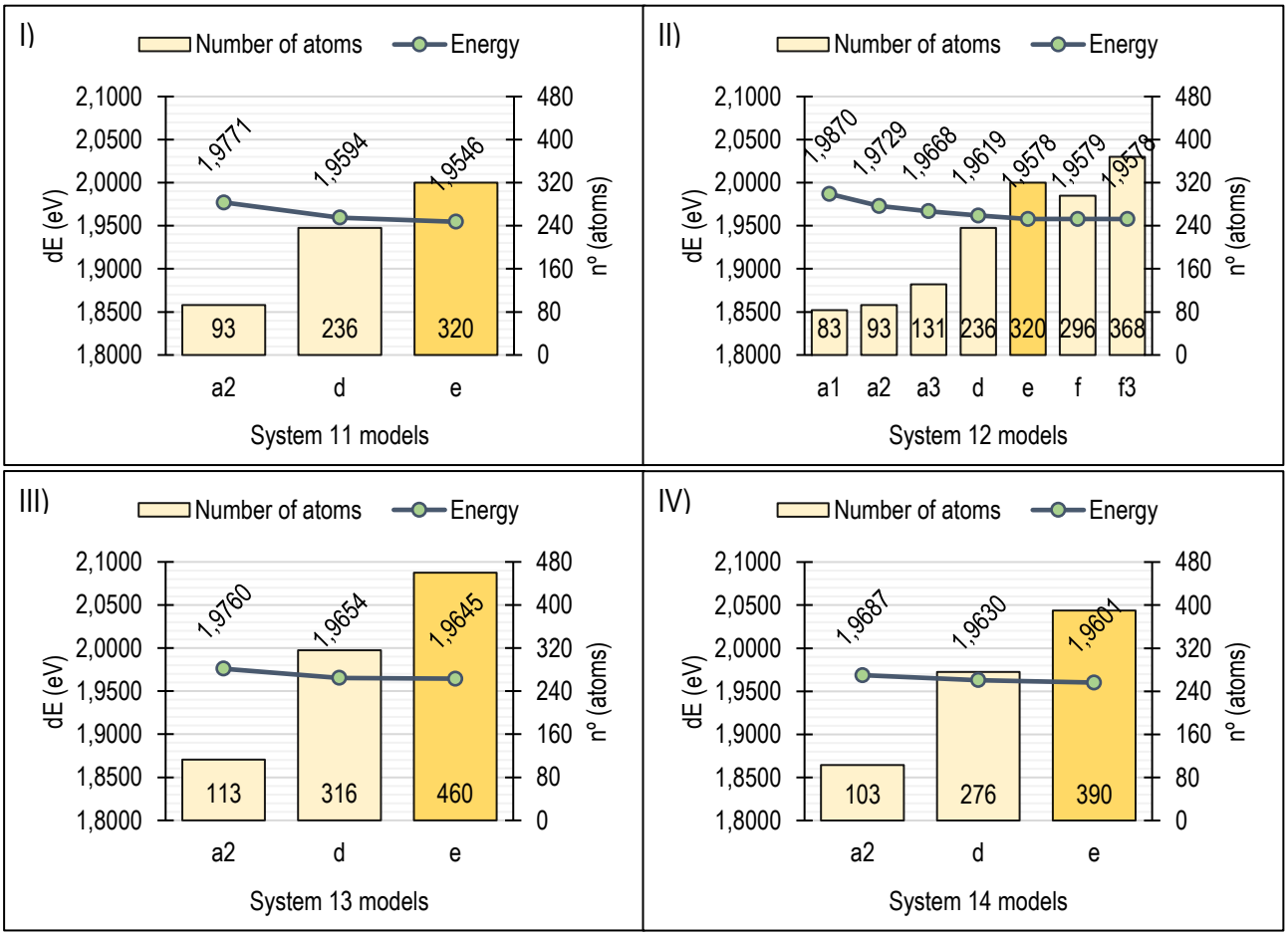


i. The darker yellow identifies the most appropriated model (MAM).

Figure 10. G2 systems: energy associated with the lowest energy excited state obtained with TD-DFT calculations (Step-1).

7.3 G3: THE EXCITED STATE ENERGY RESULTS

For G3 systems the excited energies are: system **11** 1,9546 eV (634,30 nm), system **12** 1,9578 eV (633,29 nm), system **13** 1,9645 eV (631,13 nm) and system **14** 1,9601 eV (632,55 nm). See Figure 11. For the G3 family, the system 12 was the first system studied. This system was chosen to determine which structure could be expected for the MAM for any G3 system. System 12 was chosen because it has a low-complexity ligand compared to other G3 systems and allows working with smaller models than the equivalents for the other G3 systems with more complex ligands. For each other G3 system, it has only considered necessary to study models a_2, d and e which have the same type of structure ends. In the case of system **12**: models a_1, a_2 and a_3 differ one from each other in how the 0D structure ends have been finished. The model e is the MAM. This is because, having well-surrounded orbitals and providing the same energy results (energy convergence), it has a lower number of atoms than model f_3 (2nd condition). The model f, which is smaller than model e, has well-described orbitals and provides really similar energy results. However, it is not the MAM because it has different structure ends. In the case of systems **11**, **13** and **14**: the model e is the MAM. This is because energy is converging (decreasing from model a to model e) and model e is the best described in terms of orbitals.



i. The darker yellow identifies the most appropriated model (MAM).

Figure 11. G3 systems: energy associated with the lowest energy excited state obtained with TD-DFT calculations (Step-1).

8. CHARGE TRANSFER CHARACTERIZATION

For each system, the charge transfer character associated to the excitation has been studied for the most representative 0D cluster model (Step-4). The CT character have been analysed from the donor to the acceptor monomer, not only in terms of the total value, but also which fragments and how much are they involved in the CT process. The CT values can go from 0 (no CT) to 1 (maximum CT). In this context, we refer to appreciable CT character when CT total value > 0,1. The other contributions up to 1 correspond then to local excitations. The root-mean-square electron-hole separation value (RMSeh) has also been analysed, which shows how effective the separation of charges between electron (-) and hole (+) is.

8.1 G1: CHARGE TRANSFER CHARACTERIZATION

In the case of systems **1**, **2** and **3**: the total CT character is appreciable. In the case of systems **1** and **3** (systems containing nitrogen in the centre of the linker): they have higher CT character, RMSeh and wavelength than those with the centre of the node replaced by a benzene ring. See Figure 12. This follows the trend that has been found in the MOs involved in the contribution with the largest coefficient See Figure 13. On the one side, there are no significant differences in terms of energy between the virtual OMs of the different G1 systems. On the other side, in the case of systems 1 and 3 the occupied OMs have higher energies. As a consequence, the CT is enhanced for these systems. In the case of system **4**: CT global character is not appreciable (CT total value < 0,1). However, the electron-hole separation is significant. This is because this e-h separation occurs locally in the ligand See Figure 14.

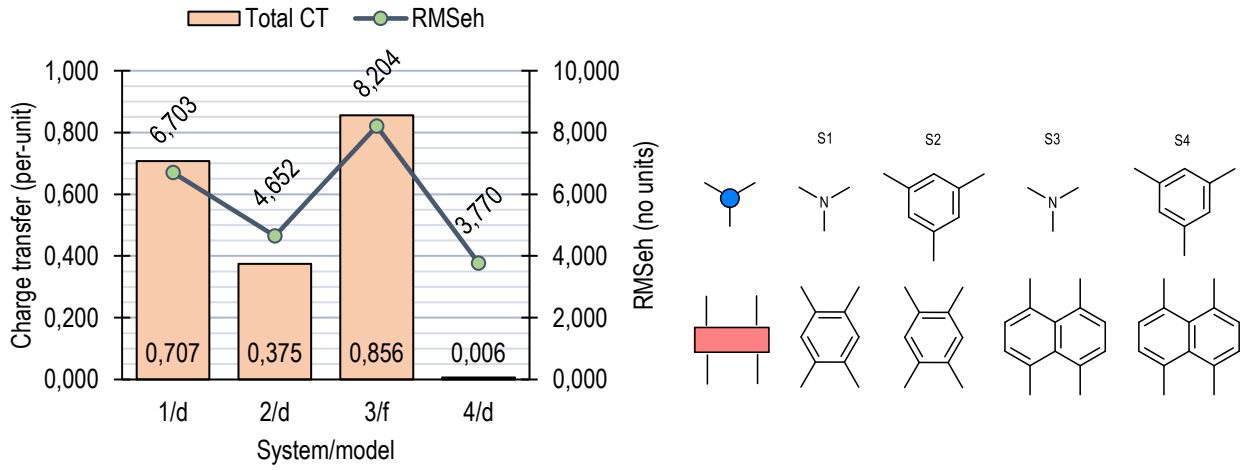


Figure 12. MAM of each G1 system: total charge transfer character and the root-mean-square electron-hole separation values.

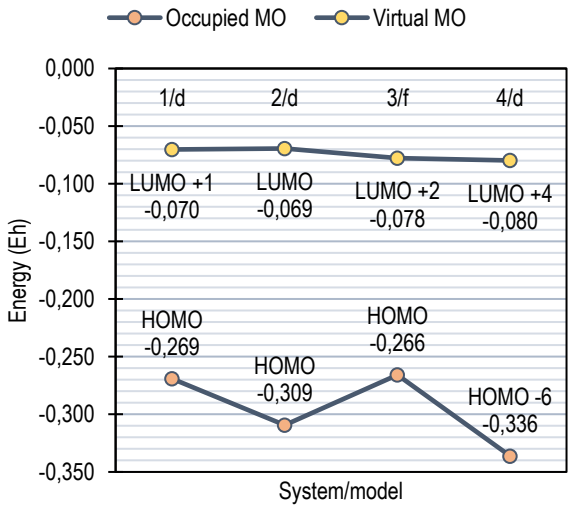


Figure 13. MAM of each G1 system: energy values of molecular orbitals involved in the contribution with highest coefficient both; starting occupied MOs and arrival virtual MOs.

The global charge transfer has been broken down into its different participations in order to characterise in more detail the CT character of each system See Figure 14. In the case of systems **1** and **3** there are two appreciable contributions: linker-ligand (the highest) and, ligand-ligand, which is a local excitation. In the case of system **2** there are two appreciable contributions: ligand-ligand (the highest) and, linker-ligand. In the case of system **4** there is only one appreciable contribution: local excitation ligand-ligand.

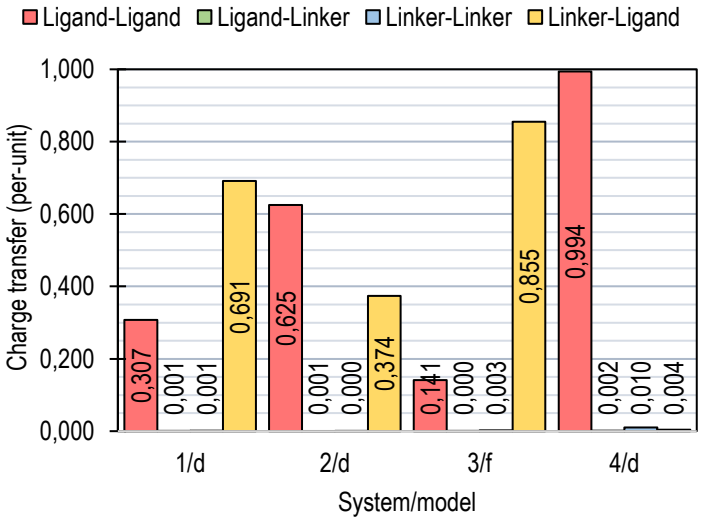


Figure 14. MAM of each G1 system: breakdown of the different participations in the global charge transfer.

8.2 G2: CHARGE TRANSFER CHARACTERIZATION

In all G2 systems the CT character is appreciable. G2 systems are classified into 3 pairs according to the substitution of the position represented by a red box: systems **5** and **6 (-H)**, **7** and **8 (-CF_3)** and **9** and **10 (-OH)**. At the same time, G2 systems are classified into 2 groups according to the substitution of the position represented by a blue circle: systems **5**, **7** and **9 (benzene ring)** and systems **6**, **8** and **10 (1,3,5-triazine ring)**. See Figure 15.

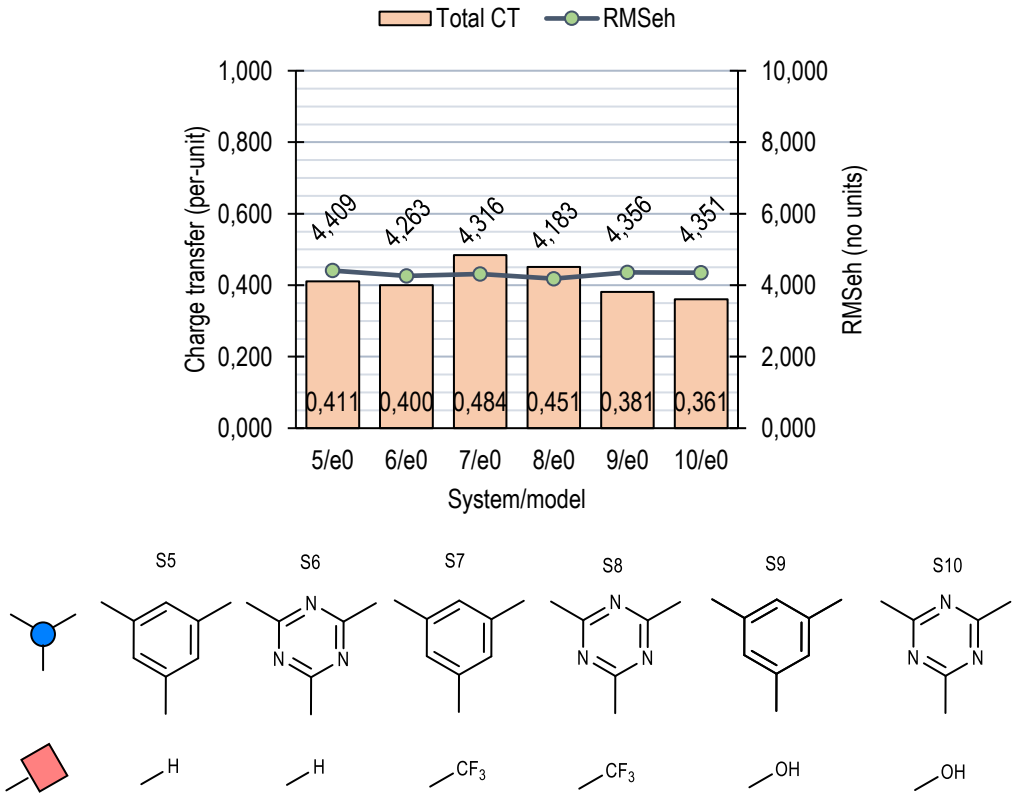
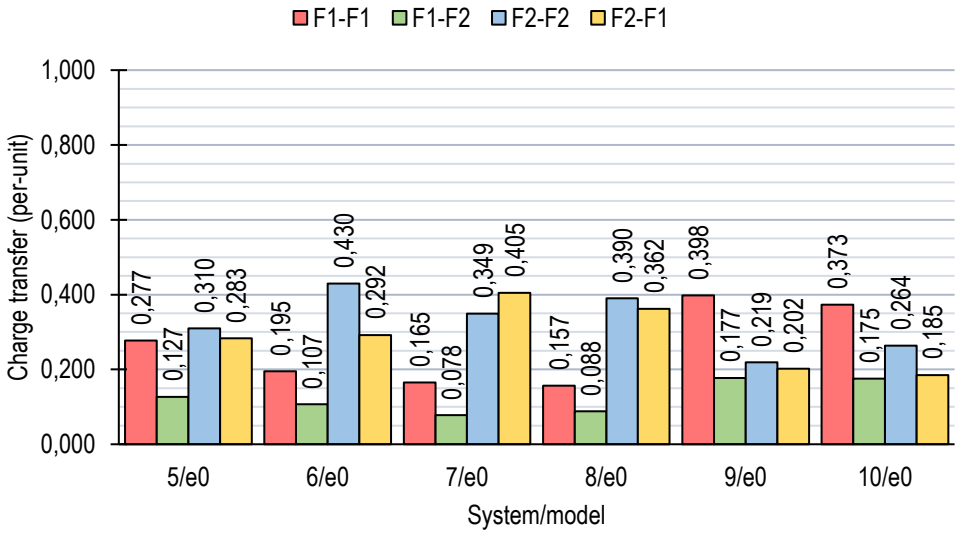


Figure 15. MAM of each G2 system: total charge transfer character and the root-mean-square electron-hole separation values.

In the case of systems **5** *vs* **6**, **7** *vs* **8** and **9** *vs* **10**: the results show that between two systems with the same substituent in the position represented by the red box, the system whose position represented by the blue circle is substituted by a benzene ring, has slightly higher CT character and RMSeh than the system with 1,3,5-triazine ring. See Figure 15.

In the case of systems with the same blue circle comparation: the effect of the red box substituent (substituents with different electronegativity), is more appreciated. Specifically, between the systems that have with the same blue circle: CT global character goes **(-CF_3)** > CT global character **(-H)** > CT global character **(-OH)**. See Figure 15.

The global charge transfer haven been broken down into its different participations in order to characterise in more detail the CT character of each system. In all G2 systems: F1-F2 is the smallest contribution. In the case of systems **5** and **6** (-H) there are four appreciable contributions with the same trend in both systems: F2-F2 (the highest) which is a local excitation > F2-F1 > F1-F1 > F1-F2. In the case of system **7**: there are three appreciable contributions: F2-F1 (the highest) > F2-F2 > F1-F1. In the case of system **8**: there are three appreciable contributions: F2-F2 (the highest) which is a local excitation> F2-F1 > F1-F1. In the case of systems **9** and **10**: (-OH) there are four appreciable contributions with the same trend in both systems: F1-F1 (the highest) which is a local excitation > F2-F2 > F2-F1 > F1-F2. See Figure 16.



i. F1 corresponds to the monomer that contains the fragment of the red box.
ii. F2 corresponds to the monomer that contains the fragment of the blue circle.

Figure 16. MAM of each G2 system: breakdown of the different participations in the global charge transfer.

8.3 G3: CHARGE TRANSFER CHARACTERIZATION

No system in G3 has appreciable CT character. However, all systems have effective electron-hole separation (RMSeh results). Therefore, electron-hole separation is due to a local excitation and not to a CT between ligand and linker. The global charge transfer has been broken down into its different participations in order to characterise in more detail the excited state character of each system. In all G3 there is only one appreciable contribution: local excitation linker-linker. In conclusion, in all G3 systems, electron-hole separation is due to a local excitation located in the metal-containing porphyrin. See Figures 17 and 18.

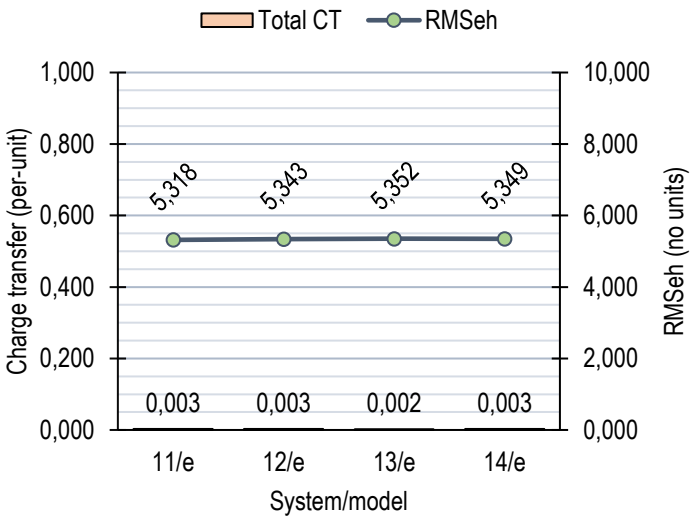


Figure 17. MAM of each G3 system: total charge transfer character and the root-mean-square electron-hole separation values.

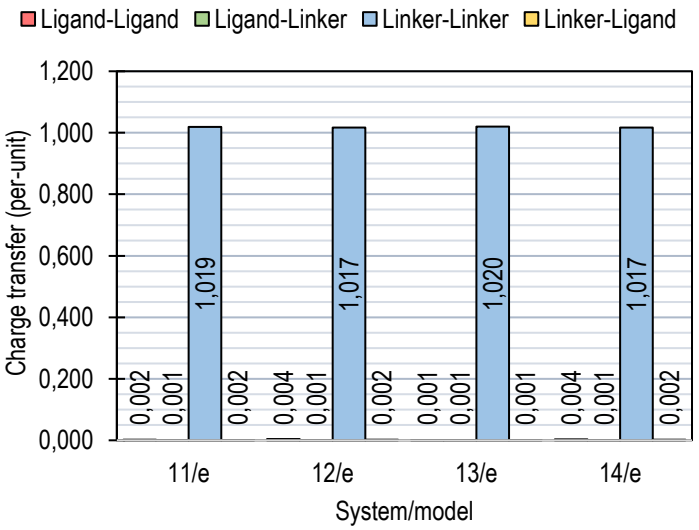


Figure 18. MAM of each G3 system: breakdown of the different participations in the global charge transfer.

9. CONCLUSIONS

9.1 GENERAL CONCLUSIONS

Predicting 2D-COFs monolayer properties through computational studies is crucial to focus synthetic efforts only on materials with the most promising properties. First, it is necessary to find the MAM on which to deepen the studies, not only to correctly characterize the excited state properties of the periodic 2D-COF monolayer but also to keep cost-effective calculations. For the 2D-COFs studied, in order to correctly determine the MAM, it is concluded that it is necessary for the MOs involved in the excitation with highest contribution coefficient, surrounded by an environment close enough to that of the complete monolayer. Complying with the above, in general terms, the smaller the model the better.

It has been determined that, a small change in the structure of 2D-COF, which is repeated periodically, give rise to monolayers with different features. Therefore, there are many possible combinations to study in order to find materials with promising optoelectronics properties.

9.2 G1 CONCLUSIONS

Systems 1 and 3 are the G1 systems (a family of 2D-COFs with hexagonal lattice structure) that have the most promising properties for light-to-electric optoelectronics applications. Furthermore, systems 1 and 3 are the best candidates for light-to-electric optoelectronics, not only of the G1 but of the all studied families. Both systems have well-defined CT from the linker (the donor) to the ligand (the acceptor).

In the context of MOs involved in the contribution with highest coefficient: there are no significant differences in terms of energy between the virtual OMs of G1 systems. However, among the occupied OMs it has been determined that in the case of systems 1 and 3, these OMs have higher energies (because their linker composition). It is concluded, non-local CT is favoured when the occupied MO (which is located on one monomer) and the virtual MO (which is located on the other monomer) are close in terms of energy.

9.3 G2 CONCLUSIONS

System 7 is the G2 system (a family of 2D-COFs with hexagonal lattice structure) that has the most promising properties for light-to-electric optoelectronics applications. System 7 has well-defined CT from the donor to the acceptor. However, systems 1 and 3 from the previous G1 group, have better non-local charge transfer properties.

9.4 G3 CONCLUSIONS

No system in G3 (a family of 2D-COFs with tetragonal lattice structure) is a good candidate for light-to-electric optoelectronics applications in terms of appreciable donor-to-acceptor CT. In all G3 systems, electron-hole separation is due to a local excitation located to the metal-containing porphyrin (the linker).

10. REFERENCES AND NOTES

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11. ACRONYMS

COFs: Covalent Organic Frameworks

CT: Charge Transfer

CURATED COFs database: Clean, Uniform, and Refined with Automatic Tracking from Experimental Database of Covalent Organic Frameworks

D-A COFs: Donor-Acceptor Covalent Organic Frameworks

DFT: Density Functional Theory

ES: Excited State

HOMO: Highest Occupied Molecular Orbital

HPC cluster: High-Performance Computing cluster

LEDs: Light-Emitting Diodes

LUMO: Lowest Unoccupied Molecular Orbital

MAM: Most Appropriate Model

MOs: Molecular Orbitals

OLEDs: Organic Light-Emitting Diodes

SDGs: Sustainable Development Goals

TD-DFT: Time-Dependent Density Functional Theory

TheoDORE: Theoretical Density, Orbital Relaxation and Exciton analysis

XCF: Exchange–Correlation Functional

2D: Bidimensional

APPENDICES

APPENDIX 1: COFS NOMENCLATURE; CURATED COFS DATABASE

Clean, Uniform, and Refined with Automatic Tracking from Experimental Database of Covalent Organic Frameworks (CURATED COFs database) contains COFs structures reported from the literature and with refined geometry. These structures are named CURATED COFs. The database includes one set of CURATED COF structures which contains the original frameworks as reported in the literature and another set containing the structures that succeeded the DFT optimization. In this database, COFs are labelled using 7-character strings that encode information not only about their provenance but also their structure. See Figure 19.[13]

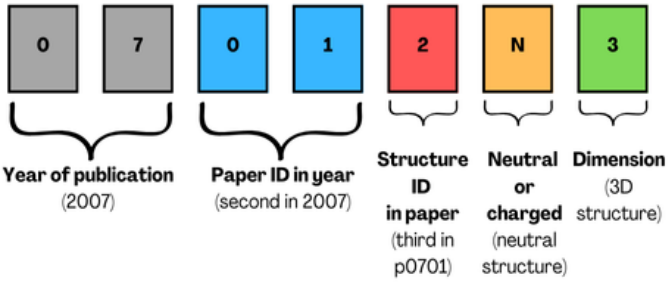

Figure 19. CURATED COFs label information. The first four characters are an index for the reference paper. So, the label of any CURATED COF from the same paper has the same first four numbers. Paper ID and structure ID are progressive counters starting from zero and following the order of insertion into the database (not the chronological order of publication). [13]

In total, 14 different systems have been studied, which are part of the CURATED COFs database. In order to simplify the nomenclature throughout the research, a system number (1-14) has been assigned to each COF studied. See Table 1.

Table 1. 2D-COFs studied throughout the project.

Group or family	System number assigned	CURATED COF code
G1[10]	1	21081N2
	2	21080N2
	3	21083N2
	4	21082N2
G2[11]	5	20180N2_TFP-TAPB
	6	20180N2_TFP-TTA
	7	20181N2_CF3-TFP-TAPB
	8	20181N2_CF3-TFP-TTA
	9	20182N2_OH-TFP-TAPB
	10	20182N2_OH-TFP-TTA
G3[12]	11	12020N2
	12	12022N2
	13	12023N2
	14	12024N2

i. 1,3,5-tri(4-formylphenyl)-benzene (TFP).[11]
ii. 1,3,5-tris(4-aminophenyl)benzene (TAPB).[11]
iii. 4, 4', 4''-(1,3,5-triazine-2,4,6-triyl)trianiline (TTA).[11]
iv. 1,3,5-tris(4-formyl-3-trifluoromethyl)benzene (CF3-TFP).[11]
v. 1,3,5-tris(4-formyl-3-hydroxyphenyl)benzene (OH-TFP).[11]