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Article

Algorithmic Design of Metal-Free Fully π-Conjugated Organic Polyradicals with Any Ground-State Multiplicity

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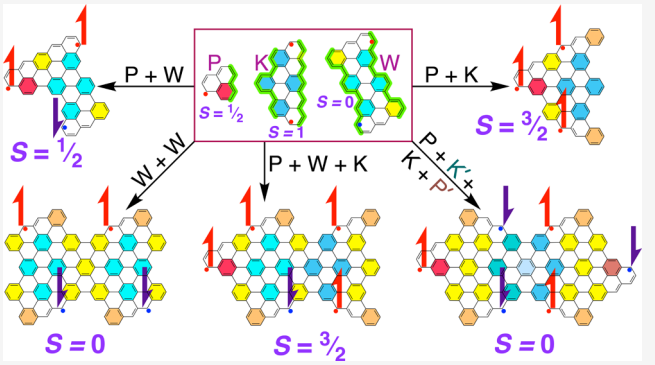
Sergi Betkhoshvili, Ibério de P. R. Moreira,* Jordi Poater,* and Josep Maria Bofill*

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ABSTRACT: Polyradicals, molecules with multiple unpaired electrons, exhibit unique magnetic properties and are promising candidates for applications in organic electronics, photonics, spintronics, and quantum devices. However, polyradicals with more than two unpaired electrons (beyond diradicals) remain underexplored, and the principles governing their design have been elusive. In this work, we develop a comprehensive framework for the rational design of polyradicals with any number of unpaired electrons and a ground-state multiplicity. Our approach allows precise control over the spin state spectrum, including the ability to specify the multiplicity of the highest-energy spin state. Using high-level quantum chemical calculations, we demonstrate how the polyradical character can be tuned based on a set of simple rules, including the topological control of π-conjugation and the use of cross-conjugation to set a lower-bound restriction on polyradical behavior/identity. Our chemical model requires that the designed polyradicals possess a fully conjugated π-system (including unpaired electrons), ensuring stabilization through delocalization and aromaticity. Each pair of directly π-conjugated unpaired electrons should be bridged by a system possessing an aromatic resonance energy equivalent to at least two benzene-like rings, which may be shared among different such pairs. We explore polyradicals built from synthetically accessible building blocks up to hexaradicals with various ground-state multiplicities. Through multiconfigurational quantum chemical validation, we confirm the accuracy of our design rules and show how to systematically tailor the magnetic properties of these systems. Finally, we propose an algorithmic approach to polyradical design and introduce general homologous series that can be extended to generate novel structural frameworks for future research.

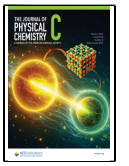


INTRODUCTION

Organic diradicals and polyradicals, due to their unique electronic and magnetic properties, have a wide range of applications, such as in organic electronics and spintronics, *n*-channel or ambipolar field-effect transistors (FETs), organic magnetic materials, molecular switches, singlet fission with solar energy conversion capability, batteries, nonlinear optics, functional dyes, photodynamic therapy, and quantum technologies.[1−20] We define the *order of a polyradical* (*H*) as the number of unpaired electrons in the polyradical. Research on higher-order polyradicals began in 1964 with the first synthesized triradical[21] and tetraradical,[22] after which many theoretical and experimental studies followed.[23−50]

Polyradicals have applications in quantum computing as qubits and qudits (higher-order qubits).[20] For quantum technology applications, organic molecules and frameworks have important advantages compared to metal−organic or crystalline systems due to the possibility of full π-conjugation and stronger correlation/entanglement between different quantum bits and across the local collections (circuits with quantum gates) of these qubits, which can improve the coherence times, the fidelity of the configuration of qubit states, and the fidelity of the unitary transformations (to change the spin state) upon quantum gate operations on these qubits. As a higher number of spin states opens new possibilities in quantum computing and error correction,[51] we propose how to design polyradicals with more than two unpaired electrons and thus more low-energy spin states, which span the well-defined set of qudit states used to expand the wave function of the system.

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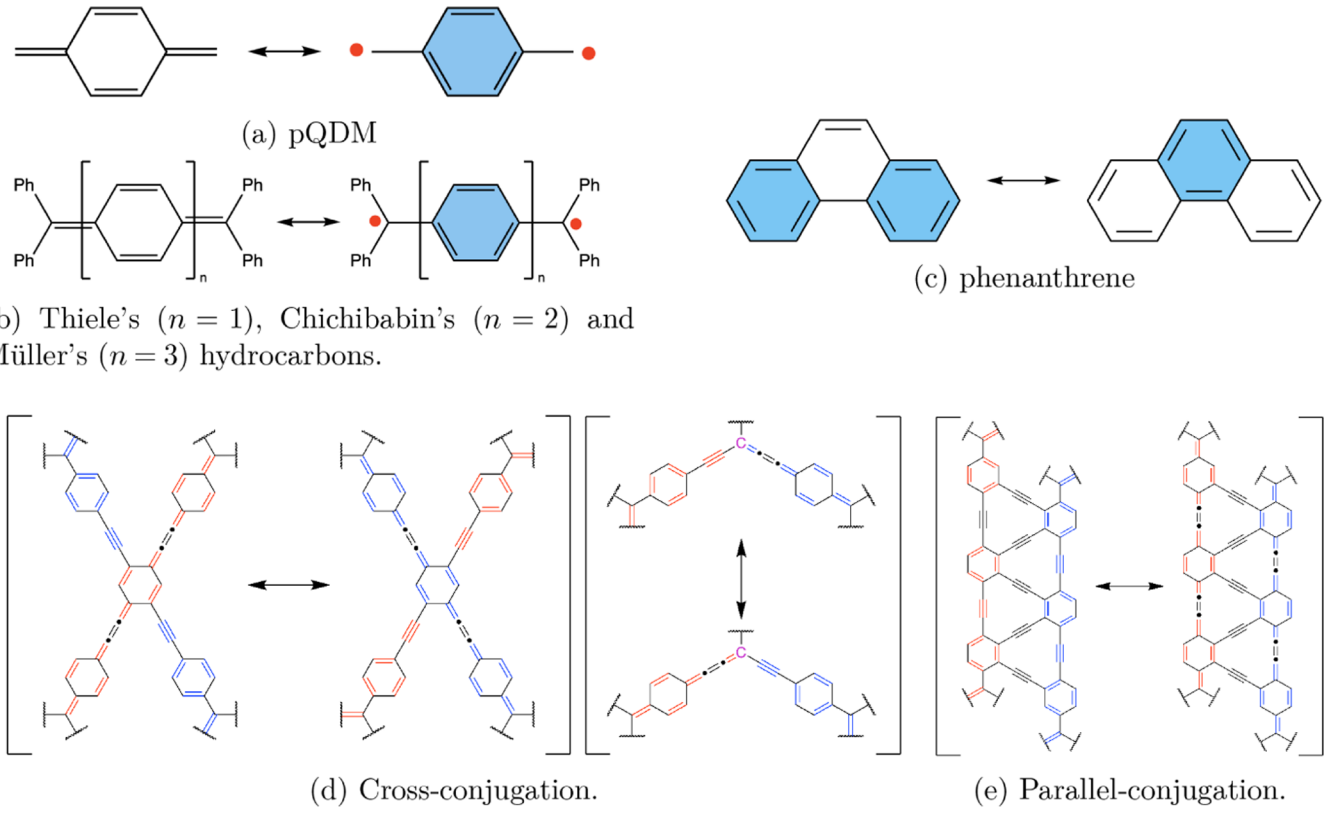


Figure 1. Resonance structures of (a) *para*-quinodimethane (pQDM) and (b) Thiele's, Chichibabin's, and Müller's hydrocarbons. (c) Resonance structures of phenanthrene: structure on the left contributes more to the resonance hybrid according to Clar's rule. (d) Generic cross-conjugated organic frameworks with π-systems shown in red and blue crossing each other in the central benzenoid ring (left) and at the carbon emphasized in purple (right). (e) Generic parallel-conjugated organic framework with parallel but fully conjugated π-systems shown in red and blue, which do not affect each other in terms of rearranging π bonds.

In organic polyradicals, a common stabilizing factor of the open-shell character is delocalization in the π-system and aromaticity. The simple compound that demonstrates this concept is *para*-quinodimethane (pQDM), as shown in Figure 1a. Thiele's hydrocarbon was the first diradicaloid that was synthesized in 1904,[52] soon followed by Chichibabin's hydrocarbon in 1907,[53] and Müller's hydrocarbon in 1941[54] (see Figure 1b). As apparent from Figure 1a,b, the electronic structures of these compounds have contributions from closed-shell quinoidal and diradical aromatic resonance structures. The rings that shift from quinoidal to aromatic configuration in diradical or zwitterionic forms are called pro-aromatic. In our recent publications, we covered how to make a leap from diradicals to tetraradicals by topological control of π-conjugation[50] and we described a planar and fully π-conjugated tetraradical(oid) obtained by merging derivatives of two experimentally characterized diradical(oid)s.[49] In these works, we found that the most important factors that control the polyradical character are aromatic stabilization between radical centers and the topology of π-conjugation, which defines the multiplicity of the ground state and highest-energy spin state within a low-energy spectrum.

In fully π-conjugated organic molecules, we define *cross-conjugation* as follows: if in some valence bond forms (VBFs, i.e., Lewis structures) two terminal sites of the molecule are continuously connected by alternating π bonds (i.e., they are directly π-conjugated), this would forbid a continuous connection via alternating π bonds for *at least* one different pair of terminal sites. As illustrated in Figure 1d by generic (closed-shell) cross-conjugated organic frameworks, these π-systems intersect/*cross* each other, and thus, we call such systems cross-conjugated. The cross-conjugation forbids these π-systems to simultaneously be in both quinoidal or aromatic forms due to the mutual exclusion of the same forms within common groups. For example, such mutual exclusion occurs in the central benzenoid ring where π-systems intersect/cross each other (left in Figure 1d) or at the carbon emphasized in purple (right in Figure 1d) at which terminals of the crossing/intersecting π-chains coincide. In fully π-conjugated polyradicals, which have all of their unpaired electrons conjugated to the π-system of the molecule, this means that if in some VBF a given unpaired electron closes the shell with another unpaired electron by continuous/direct π-conjugation, this would forbid closing *at least* one shell by another pair of directly π-conjugated unpaired electrons.

In fully π-conjugated organic molecules, *parallel conjugation* is defined as when, in some valence bond forms, two terminal sites of the molecule are continuously connected by alternating π bonds, this does *not* forbid a continuous connection via alternating π bonds in other pairs of terminal sites. Notably, linkers bridging these π chains must be fully π-conjugated within and to the π chains that they connect. For illustration, we can refer to Figure 1e, which includes a generic (closed-shell) parallel-conjugated organic framework in which the π-systems are parallel to each other. Contrary to cross-conjugation, the defined parallel conjugation does not forbid these π-systems from both simultaneously being in quinoidal or both in aromatic forms, as both π-systems can assume each configuration

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irrespective of the configuration in the other π-system. Hence, in the context of polyradicals, a parallel-conjugated molecule that has all of the unpaired electrons directly π-conjugated can have a significant contribution from a VBF in which these electrons are paired, and thus, the VBF has a closed-shell configuration. This means the restriction of minimum polyradical character for such a compound does not exist, and it could be a closed-shell molecule. In such cases, in order to increase the open-shell character, one should enhance the aromatic stabilization by including more pro-aromatic rings between radical centers. Hence, in such cases, aromaticity is necessary but sometimes insufficient to achieve high open-shell character.

To describe the presence of aromaticity, a useful chemical concept but *not* an observable, Hückel's rule is most useful for monocyclic compounds. However, for benzenoids (polycyclic aromatic hydrocarbons (PAHs) containing only six-membered rings), a more practical model is the π-sextet rule proposed by Clar in 1972,[55] which considers aromaticity as a local property of the benzene-like six-membered rings with π-sextets that are separated from adjacent rings by C—C single bonds. Clar's rule states that, among structures with an equal number of π bonds, the resonance structure that has the most π-sextets is the most important contributor to the resonance hybrid of a PAH,[56−58] as exemplified by phenanthrene in Figure 1c.

Considering the broad current and future applications of polyradicals, in this work, we establish the essential principles to design and predict the properties of metal-free fully π-conjugated two-dimensional organic polyradicals. Moreover, we formulate an algorithm for polyradical design, based on which one will be able to design polyradicals with any number of unpaired electrons and any ground-state multiplicity. In the presented theory, the fundamental principle for the prediction of spin configurations in polyradicals with different topologies of the π-systems is Ovchinnikov's rule,[59] which can be derived from the premise that alternant hydrocarbons (with alternating π bonds and without odd-membered rings, as in our fully π-conjugated polyradicals) obey the Coulson-Rushbrooke pairing theorem, also known as the "mirror theorem".[60,61]

RESULTS AND DISCUSSION

Essential Theoretical Framework and Definitions. Since the polyradicals are distinguished by the remarkable resemblance between different states close to the ground state and have, on average, one unpaired electron in each radical center, we can approximately represent their wave functions as spin eigenfunctions for a given number of unpaired electrons. Since these states do not significantly differ in electron density distribution (i.e., Heisenberg system with H number of spin-$\frac{1}{2}$ magnetic centers), their difference comes from spin−spin couplings between unpaired electrons. Denoting the number of unpaired electrons in the system as H (same as polyradical order), by taking suitable linear combinations of primitive spin functions, one can obtain spin eigenfunctions belonging to the quantum numbers $S = \frac{1}{2}H, \frac{1}{2}H - 1, ..., M$, where M is 0 if H is even and $\frac{1}{2}$ if H is odd.[62] For a particular value of S, which defines the spin-multiplicity $(2S + 1)$, the number of independent spin states is obtained with eq 1:[62]

$$f(H, S) = \frac{H!}{\left(\frac{1}{2}H - S\right)!\left(\frac{1}{2}H + S\right)!} - \frac{H!}{\left(\frac{1}{2}H - S - 1\right)!\left(\frac{1}{2}H + S + 1\right)!} \quad (1)$$

Such a collection of all states of every allowed spin (S) moment for a given polyradical with H number of unpaired electrons is defined as a low-energy spectrum. Thus, the number of spin states in the low-energy spectrum of a polyradical with H number of unpaired electrons is[62]

$$N = \sum_{S=M}^{H/2} f(H, S) \quad (2)$$

For example, the tetraradical $(H = 4)$ has one quintet state $(S = 2)$ as $f(4,2) = 1$, three triplet $(S = 1)$ states as $f(4,1) = 3$, and two singlet $(S = 0)$ states as $f(4,0) = 2$. Hence, in total, the tetraradical has six spin states in its low-energy spectrum. If the through-bond distances differ sufficiently to result in a clear ordering of coupling strengths in different pairs of radical centers, we can also reliably predict the multiplicity of the highest-excited state (HS) within the low-energy (magnetic) spectrum of the designed polyradicals, which is the Nth lowest-energy state (eq 2). For the ***proper polyradicaloid*** of order K, among the lowest-energy $N = \sum_{S=M}^{K/2} f(K, S)$ number of states of a compound, determined by CASCI/CASSCF (or MRCI/Full CI) calculations in a complete basis set limit, each spin state must have a corresponding spin state in the collection of spin eigenfunctions belonging to the quantum numbers $S = \frac{1}{2}K, \frac{1}{2}K - 1, ..., M$ with K number of spin-$\frac{1}{2}$ magnetic centers. In other words, there should be a one-to-one mapping between the low-energy spectrum of a compound with assumed polyradicaloid order K and the set of spin eigenfunctions belonging to the quantum numbers $S = \frac{1}{2}K, \frac{1}{2}K - 1, ..., M$ with K number of spin-$\frac{1}{2}$ magnetic centers. If this criterion is met and also the state of highest allowed spin multiplicity $(K + 1)$ is thermally accessible, the compound is a ***proper polyradical*** of order K (one must also check numbers $K + 2$ and higher). ***Improper polyradicaloid*** of order K is the compound that does not have a one-to-one mapping from its low-energy spectrum to the spin spectrum of a system with K number of spin-$\frac{1}{2}$ magnetic centers, but the state with the highest allowed multiplicity (of $K + 1$) is within its lowest-energy $N = \sum_{S=M}^{K/2} f(K, S)$ number of states. If this criterion is met and also the state of highest allowed spin multiplicity $(K + 1)$ is thermally accessible, we have an ***improper polyradical*** of the order K (at least). After determining the polyradical(oid) identity, the span ΔE_{Ri} of the low-energy spectrum is the range of energy between the ground state and the highest-energy spin state of the low-energy spectrum. For example, for a tetraradical(oid), the energy span of the low-energy spectrum of spin states is ΔE_{R4}, the energy difference between the sixth lowest-energy state and the ground state. In the algorithmic design that we present, the designed compounds are all proper polyradical(oid)s of the given order, as verified by the CASSCF/CASCI calculations. For the sake of simplicity, the structures of presented polyradical design templates fall into the alternant hydrocarbon category to ensure the prediction of only one dominant spin configuration according to Ovchinnikov's

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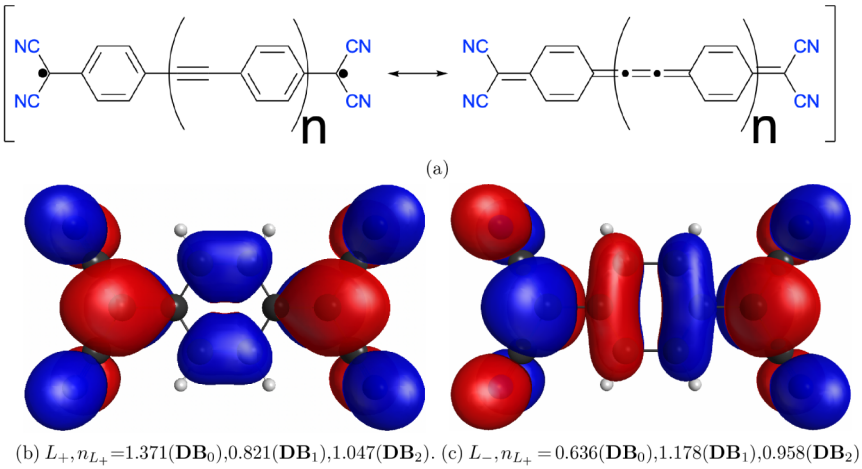


Figure 2. (a) Resonance structures of diradical(oid) series $\mathbf{DB}_{0-2}$ differing by ethynylphenyl residue: n = 0, 1, 2. (b−c) CASSCF frontier natural orbitals (NOs) of $\mathbf{DB}_0$ analogical with frontier NOs of $\mathbf{DB}_{1-2}$ with symbolic assignations and occupation numbers in the ground state for each compound.

rule, which maintains the general character and the predictive power of the theory as polyradicals grow upon application of the algorithm. Nonetheless, the rules of our theory of polyradical design can extend to nonalternant conjugated hydrocarbons if the presented topological principles are properly applied.

Theory for the Rational Design of Polyradicals. Before we computationally demonstrate the rules and guidelines that we established in our previous publications[49,50] and extended in this work, we must formulate the rules that define our general theory for designing fully π-conjugated metal-free organic polyradicals:

Rule (0). Ovchinnikov's rule:[59] In an alternant hydrocarbon (a conjugated hydrocarbon without odd-membered rings), atoms can be subdivided into two groups, arbitrarily denoted by types A and A*, so that each atom of type A is surrounded only by atoms of type A*, and vice versa. In the ground state, the total spin $S = |n_A - n_A*|/2$ and multiplicity is $2S + 1 = |n_A - n_A*| + 1$, where n_A and n_A* are numbers of such atoms.

Rule (1). Within an arbitrary organic system, any encompassed polyradical subsystem with a defined number of unpaired electrons must have all of its π_z (including unpaired) electrons conjugated to the continuous π_z-system. This ensures stabilization by delocalization and conjugation. Also, this ensures that the prediction of the ground-state multiplicity of a given polyradical subsystem is possible and reliable.

Rule (2). In fully conjugated parts of a given compound, there is a specific maximum number of topologically allowed proper π bonds ($N_{\pi\text{-b.}}(\max)$) and a minimum number of unpaired electrons ($N_{e^-\text{-unp.}}(\min)$). In a given valence bond form (VBF_i) contributing to the electronic structure of the π-system, the number of π bonds and unpaired electrons are related as $N_{\pi-\mathrm{b.}}(\max) = N_{\pi-\mathrm{b.}}(\mathrm{VBF}_i) + \frac{1}{2}[N_{\bar{e}-\mathrm{unp.}}(\mathrm{VBF}_i) - N_{\bar{e}-\mathrm{unp.}}(\min)]$. Hence, for every new pair of unpaired electrons after the minimum number ($N_{e^-\text{-unp.}}(\min)$), one π bond is broken. To assume high open-shell character, i.e., to offset the energy of the broken π bond, each **pair of directly π-conjugated unpaired electrons** must be appropriately bridged by at least two or (more favorably) three more benzene rings (Clar's π-sextets) or *a set of generic aromatic rings with the same total resonance energy* in open-shell VBFs compared to the VBFs in which these two electrons are paired and form the closed-shell configuration. If a given number of aromatic rings is not sufficient to support a high open-shell character, one should insert more pro-aromatic rings between these unpaired electrons to ensure proper stabilization of the open-shell VBFs in which these rings assume aromatic configurations (e.g., Clar's π-sextet or other aromatic configuration) relative to VBFs in which the corresponding shell is closed and pro-aromatic rings assume nonaromatic electronic configurations.

Rule (3). Aromatic rings can be shared between different pairs of directly π-conjugated unpaired electrons within a polyradical to offset the energy of each broken π bond that leads to each open-shell subsystem.

Rule (4). Upon designing a polyradical, one can restrict the lower bound of polyradical character by cross-conjugation so that the closed-shell electronic structure is topologically forbidden.[49,50]

Rule (5). For an alternant hydrocarbon-based polyradical, in determining the spin multiplicity of the highest-energy state within a low-energy spectrum, which is the Nth ($N = \sum_{S=M}^{K/2} f(K, S)$) lowest-energy state for a polyradical of order K, the relative spin configuration for any two unpaired electrons should be as follows: two electrons on two carbon atoms have the same spin if the number of carbon atoms within the continuous π-conjugated chain that connects these carbons is even, and have the opposite spin if that number is odd. Thus, the relative spin configuration of the radical centers (defining the multiplicity) in the highest-excited state in a low-energy spectrum of the polyradical can be predicted based on the application of Ovchinnikov's rule in reverse. If, due to molecular configuration, it is impossible to have every coupling mode opposite to that of the ground state, the spin configuration of the highest-excited state should have as many significant opposite interactions compared to the pairs of radical centers in the ground state as possible, where the hierarchy of significance is determined by through-bond distances and the presence of direct π-conjugation.

Computational Verification of the Proposed Rules for Polyradical Design. First, we provide computational verification for rules (1)−(4) that we have proposed. Afterward, we define (di)radical building blocks that can result in an algorithmic solution and general mixed homologous series, by

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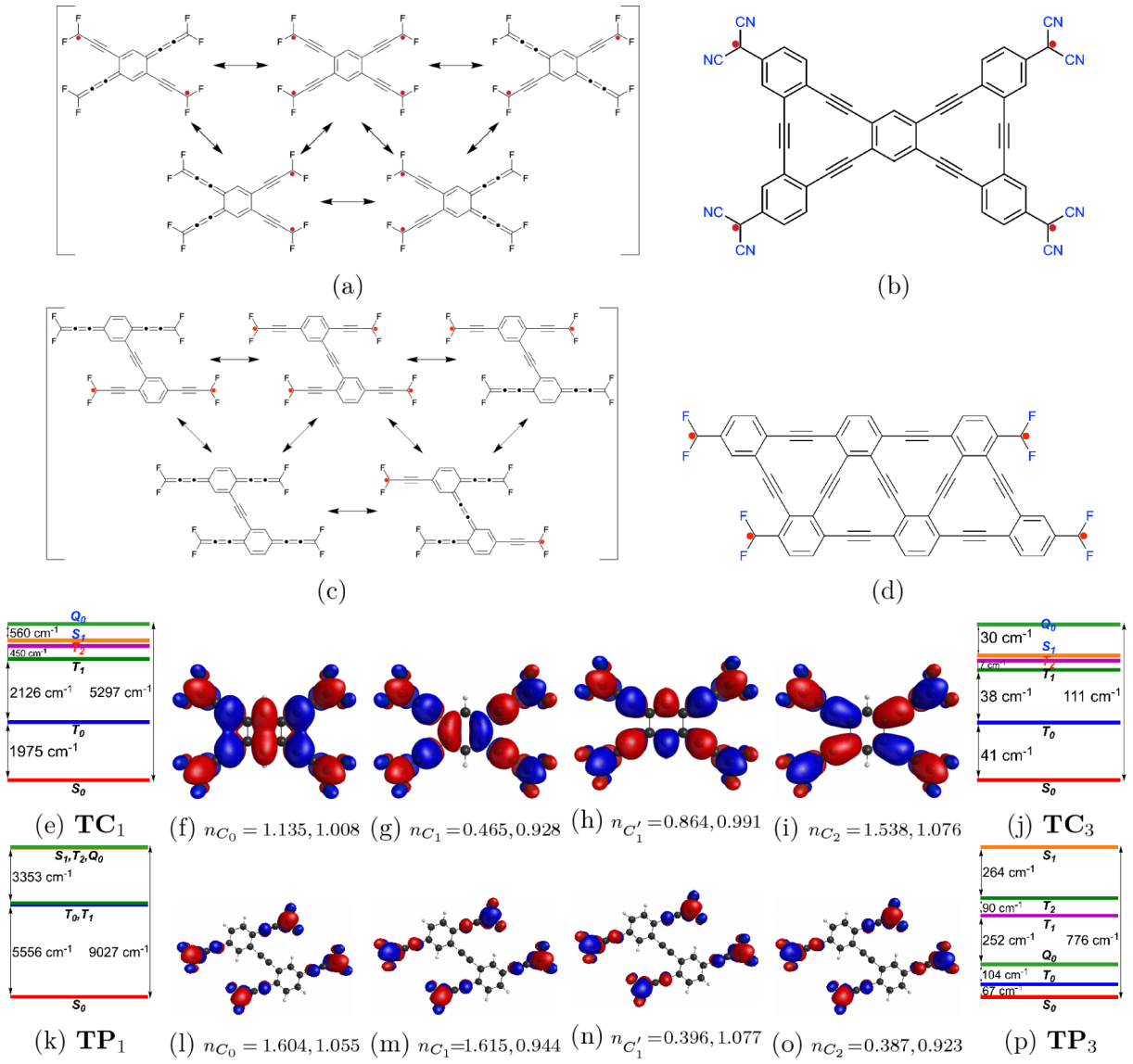


Figure 3. Resonance structures of (a) cross-conjugated $\mathbf{TC}_1$ and (c) parallel-conjugated $\mathbf{TP}_1$ tetraradical(oid)s with one benzenoid ring for each diradical subunit. (b) Tetraradical valence bond forms of cross-conjugated $\mathbf{TC}_3$ and (d) parallel-conjugated $\mathbf{TP}_3$ tetraradical(oid)s with (at least) three benzenoid rings for each diradical subunits. CASSCF frontier natural orbitals (NOs): (f–i) $\mathbf{TC}_1$ and (analogically) $\mathbf{TC}_3$, and (l–o) $\mathbf{TP}_1$ and (analogically) $\mathbf{TP}_3$ with symbolic assignations and NO occupation numbers (n_{NO}) for $\mathbf{TC}/\mathbf{TP}_{1,3}$, respectively. CASCI spectrum of (e) $\mathbf{TC}_1$, (k) $\mathbf{TP}_1$, (j) $\mathbf{TC}_3$, and (p) $\mathbf{TP}_3$.

which one can design polyradicals with any number of unpaired electrons and any ground-state multiplicity. Hence, the strategy of polyradical design is translated to structural formulas, enabling us to write an algorithm to generate polyradicals with desired qualitative properties. After characterizing the presented polyradicals assembled from the (di)radical building blocks, we rationalize the multiplicity of the highest spin state in the low-energy spectrum of a polyradical in order to demonstrate rule (**5**). *Remarkably, experimental scientists can use this general theory to design polyradicals with the desired number of unpaired electrons and ordering of spin states and properties, without having to investigate electronic structure with multiconfigurational quantum chemistry calculations. In addition to strong theoretical and experimental foundations, we show the validity of our rules with multiconfigurational calculations.*

We optimized the geometries of the presented compounds using unrestricted Kohn–Sham density functional theory (DFT), with the BLYP exchange-correlation functional[63,64] and a Slater-type all-electron triple-ζ basis set,[65] and computed the electronic structure of these compounds using Complete Active Space Self-Consistent Field (CASSCF)[66−72] and Complete Active Space Configuration Interaction (CASCI) methods with Dunning's correlation-consistent double-ζ basis set (cc-pVDZ),[73] or smaller basis sets STO-3G[74] and 4−31G[75] considering molecular sizes. Methods and computational details are thoroughly described in Section S2. Diradical character y_0 as a special case of polyradical character y_n varies from $y_n = 0$ (fully closed shell) to $y_n = 1$ (fully open shell). The method of calculating polyradical character indices[76] is given in Section S2.2.

We can demonstrate an increase in diradical character as we include more benzenoid rings (Clar's π-sextets) between radical centers (rule (**2**)) using very simple derivatives of Thiele's, Chichibabin's, and Müller's hydrocarbons[52−54] shown in Figure 1b. The structure of this homologous series named $\mathbf{DB}_{0-2}$ differing by an ethynylphenyl moiety, is given in Figure 2a and

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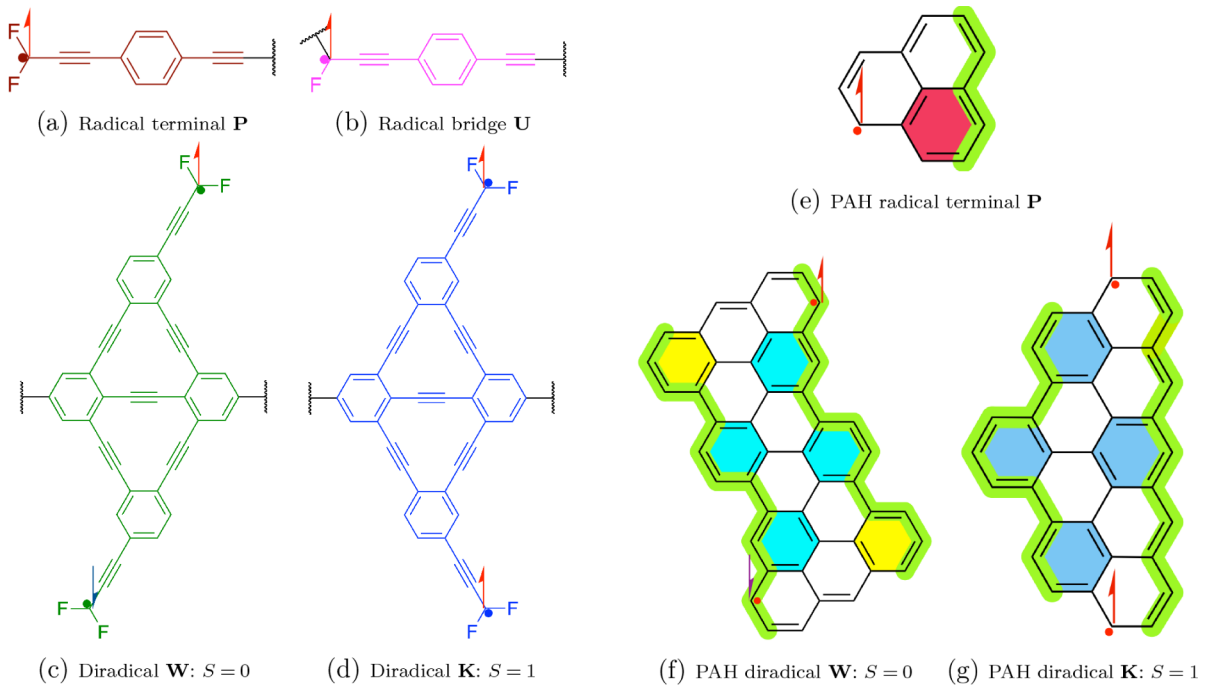


Figure 4. Primitive building blocks with defined connection sites for assembling polyradicals of any order and ground-state multiplicity, based on (a–d) difluoromethylene-terminated γ-graphyne fragments referred to as the generic set, (e–g) polycyclic aromatic hydrocarbons (PAHs).

CASSCF frontier natural orbitals are given in Figure 2b,c. Natural orbitals (NOs) are eigenvectors of the first-order density matrix, and the corresponding eigenvalues are occupation numbers (n_{NO}).[77] As a simple notion, each of these orbitals shows the electron density distribution of the average number of electrons occupying the orbital, as given by the occupation number. From the CASSCF results, we can calculate that diradical character (always between $y_0 = 0$ and 1) changes from $y_0 = 0.127$ for $n = 0$, to $y_0 = 0.654$ for $n = 1$, to $y_0 = 0.911$ for $n = 2$, corresponding to aromatic stabilization by one, two, and three Clar's aromatic π-sextets, respectively. As rule **(2)** in our theory states, there must be an aromatic stabilization from at least two Clar's π-sextets, but the stabilization from three π-sextets is more favorable as it increases the diradical character to about 90%. This rule is fully supported by a multitude of experimental studies, where for Kekulé diradical(oid)s, the greater aromatic stabilization, provided by an increasing number of aromatic rings between radical centers, increases the diradical character of the species.[4,5,78]

In order to computationally demonstrate rule **(4)**, we compare electronic structures of tetraradical(oid)s that are cross-conjugated and parallel-conjugated (see Figure 1d,e for definitions) with one and three benzenoid rings (Clar's π-sextets) for stabilization of diradical subunits. The potential tetraradical(oid) $\mathbf{TC_1}$ with one benzenoid ring given in Figure 3a is cross-conjugated such that it is impossible to draw the valence bond form (VBF) which is closed-shell. Hence, it must be *at least* diradical. In contrast, the potential tetraradical(oid) $\mathbf{TP_1}$ with one benzenoid ring for each diradical(oid) subunit given in Figure 3c is parallel-conjugated, and we are able to draw the VBF that is completely closed-shell, as in each diradical subunit the shell can be closed independently from another. This means that a given cross-conjugated molecule with the same number of aromatic π-sextets for each diradical subunit as its parallel-conjugated counterpart must have the higher diradical character, as the only allowed diradical character for cross-conjugated polyradicals is exactly $y_0 = 1$, while there is no lower bound restriction on the polyradical identity for parallel-conjugated molecules. They have diradical character always between 0 and 1, and at best asymptotically approach $y_0 = 1$. Hence, cross-conjugation is a sufficient but not a necessary condition to achieve a high diradical character. To make the comparison accurately, it suffices to compare diradical character indices of cross- and parallel-conjugated tetraradical(oid)s. According to CASSCF results, the diradical characters are $y_0 =$ 0.733, 0.115, 0.983, 0.889 for $\mathbf{TC_1}$, $\mathbf{TP_1}$, $\mathbf{TC_3}$, and $\mathbf{TP_3}$, respectively. Evidently, the diradical character of cross-conjugated polyradicals surpasses the diradical character of parallel-conjugated polyradicals. Calculated indices of cross-conjugated diradicals are never exactly 1, due to the use of occupation numbers of frontier natural orbitals of state S_0, which do not exactly equal 1.000. The detailed data for the CASSCF calculations of these compounds are given in Section S3.2. The demonstration of rules **(1)** and **(3)** is trivial if we note that we satisfy the defined scope as every polyradical we described is fully π-conjugated (rule **(1)**) and in $\mathbf{TC_1}$ and $\mathbf{TC_3}$ some benzenoid rings (Clar's π-sextets) are shared among more than one diradical subunit (rule **(3)**). The effect of charge transfer from radical centers to electron-withdrawing groups does not diminish open-shell characters, as shown for small diradicals in Section S3.5.

Polyradicals Built from Primitive Building (Di)Radical Blocks. Having demonstrated rules **(1)**–**(4)**, we define the organic primitive building blocks that are common, synthetically viable, structurally rigid, and stable. The compounds and extended systems with similar constituent scaffolds that we used as primitive building blocks have been synthesized and characterized by Haley and coworkers,[79−81] and methods of synthesis of polycyclic aromatic hydrocarbons (PAHs) have been extensively documented in the chemical literature. These methods allow for sufficient flexibility to synthesize open-shell molecules within these classes of compounds.

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The set of primitive building blocks with precisely defined sites of connection eventually enables us to design polyradicals with any number of unpaired electrons and any allowed ground-state multiplicity for a given number of unpaired electrons. Generally, to achieve this, we need subunits to adjust the total spin moment of the systems incrementally or leave the total spin moment of the system unchanged but increase the number of unpaired electrons. The simplest building blocks for polyradicals with these features can be (di)radical residues, which can be connected to other (poly)radical subunits. To show that the topological principles that allow the rational design of fully π-conjugated polyradicals transcend chemical groups, we propose two different sets of subunits which can be mapped to the other set one-to-one due to principal topological similarity. The radical terminal subunit exemplified by subunit type **P** for generic and PAH-based subunits in Figure 4a,e can be connected to other radical centers either ferromagnetically (spin-parallel) to change the total magnetic moment S of the system by $+\frac{1}{2}$ and antiferromagnetically (spin-antiparallel) to change S by $-\frac{1}{2}$ based on the regioisomerism. In polyradical design, it is also convenient to use diradical subunits, which can be connected to other subunits and change the total S of the system by +1 if one uses a diradical with a triplet ground state (subunits type **K** shown in Figure 4d,g) ferromagnetically coupled to the rest of the system or −1 if we use a diradical with a triplet ground state antiferromagnetically coupled to the rest of the system. We can also change total S by 0 if one uses any polyradical with a singlet ground state, which in our case of primitive building blocks is the diradical subunit type **W** with a singlet ground state shown in Figure 4c,f. These subunits can be connected from different sides with respect to other subunits than directions that are drawn (for example, upon reflection with respect to a horizontal mirror, the triplet diradical subunit is connected from its other side). These building blocks are radical terminal subunit type, denoted as **P** (as drawn) and **M** (if the subunit is on the opposite side of another subunit); diradical subunit type with a singlet ground state (antiferromagnetically coupled radical centers) denoted as **W** (as drawn) and **V** (if on the opposite side of the connected subunit); diradical subunit type with a triplet ground state (ferromagnetically coupled radical centers) denoted as **K** (as drawn) and **L** (if on the opposite side of the connected subunit); and a radical bridge subunit type, denoted as **U**. Even though the radical bridge type shown in Figure 4b is not used in the presented compounds, for extensions and generalizations of the design principles and possible structures, it can be a crucial building block type to control the directions of chain growth and avoid steric hindrance if the structure grows in multiple directions. In the defined sets of the subunits, the terminal radical subunits can only connect to one other subunit, while diradical subunits and the radical bridge can be connected to two other subunits as shown in Figure 4. Also, the terminal subunits can be connected both ferromagnetically and antiferromagnetically to different ends of the polyradical chain, which allows further flexibility in the variety of designing the polyradical with a specific number of unpaired electrons and ground-state multiplicity.

Algorithm of Polyradical Design. The main principle of the algorithmic design of polyradicals is to grow the polyradical chain with subunits that change the number of unpaired electrons and total spin moment incrementally. Since the formulated theory of rational design of polyradicals is general within the defined scope, we can propose various solutions to the problem of designing polyradicals with any number of unpaired electrons and any ground-state multiplicity. We can start, grow, and terminate the polyradical chains with the subunits presented in Figure 4 and thus, with them, one of the algorithmic solutions of polyradical design can be constructed. Since, based on Ovchinnikov's rule, we can predict the spin configuration within and across these subunits, we can also create a simple representation of these (di)radical subunits, which reflects their most important attributes upon designing the polyradical. The essential attributes of these (di)radical subunits are the number of unpaired electrons, their internal relative spin configuration, their spin configuration with respect to other subunits, and sites of connection to other subunits. Radical units **P** and **M** are terminal units and have a single connection to other subunits, while diradical units **L**, **K**, **W**, and **V** have two connection points/sides. Since **W** contributes $S = 0$, the two connection points/sides are equivalent in terms of modifying the spin. In contrast, for subunit **K**, the connection points/sides are not equivalent, and we take one of two connection points/sides to define subunit **K**, and if connected to the growing chain with another point/side, we refer to it as subunit **L**, as they contribute opposite magnetic moments to the growing polyradical chain, +1 and −1, respectively. The branching diagram for designing the growing polyradicals using these primitive (di)radical subunits is given in Figure 5.

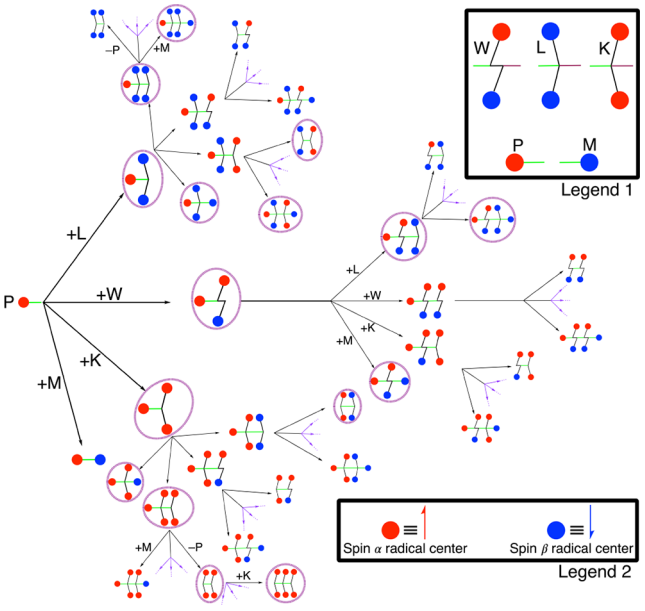


Figure 5. Algorithm of designing π-conjugated polyradicals with the subunits given in Figure 4. Black lines denote bonds within subunits, and green lines denote bonds between subunits. In **Legend 1**, subunits are defined by connection sites and radical centers with specified spin configuration. The green lines are connections made upon growing the polyradical chain with a given subunit, while purple lines denote connections to subunits to be added afterward. **Legend 2** shows the color code for α and β spin centers. Encircled structures correspond to the polyradicals described in this work.

We start with a radical subunit **P**, taking its spin arbitrarily as α, and the spin configuration of other radical centers is determined by referring to the spin moment in subunit **P** and applying Ovchinnikov's rule to determine the relative spin configuration of a particular radical center. The spin moments of radical centers in defined subunits are drawn in accordance with

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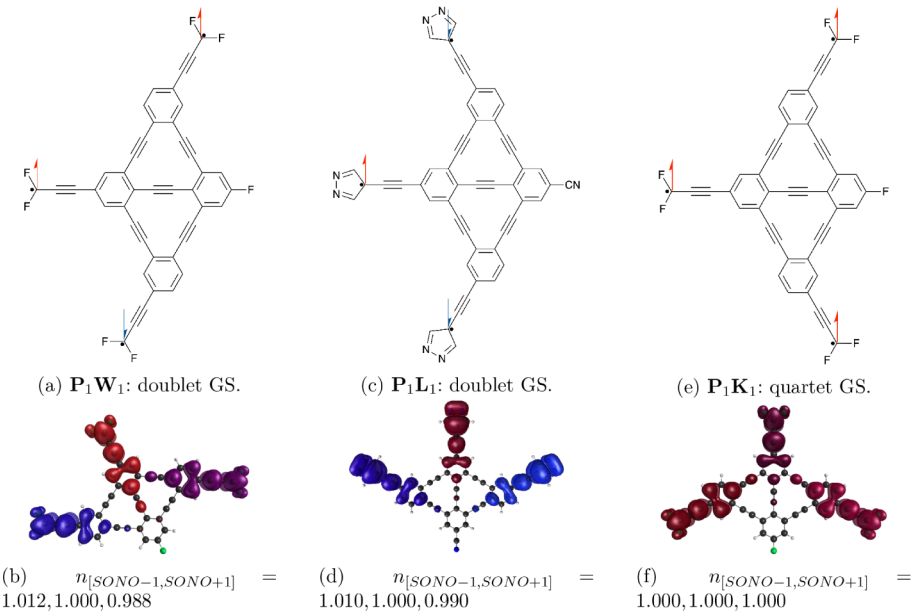


Figure 6. Triradicals with (a, e) doublet and (i) quartet ground states. Sum of CASSCF frontier localized orbitals with colors for each radical center and ground-state occupation numbers of frontier natural orbitals of (b) $\mathbf{P_1W_1}$, (d) $\mathbf{P_1L_1}$, and (f) $\mathbf{P_1K_1}$.

Ovchinnikov's rule with specified connection sites and directions upon the growth of the polyradical chain. This scheme can generate all possible permutations for a chain of diradical subunits **W**, **K**, and **L** for a given number of unpaired electrons, and each such permutation can always be added with **P** and/or **M** at terminal sites. *Since the scheme in* Figure 5 *allows one to design polyradicals with any number of unpaired electrons and any ground-state multiplicity, it represents one of the general solutions of the algorithmic design of polyradicals.* One can note that we can also change the relative spin moment of each radical center of terminal subunits relative to other subunits by simple regioisomerism and incrementally adjust the spin moment of the ground state.

By using the presented primitive (di)radical subunits and the algorithmic scheme, we built polyradicals of successive orders and every allowed ground-state multiplicity to illustrate the versatility of the structures obtained from this procedure, for which the multiple symbolic combinations from triradicals to hexaradicals are given in Section S3.1. We explore the polyradicals with every allowed ground-state multiplicity from triradicals to hexaradicals, as shown in Figure 5. Furthermore, we propose other (perhaps simpler) generalization schemes of these design principles as general mixed homologous series of generic conjugated groups and PAHs to design fully π-conjugated organic polyradicals with any order and ground-state multiplicity without using theoretical calculations or any complicated procedure. In generic series, notably, the number of benzene and acetylene residues is always adjustable to avoid steric hindrance between any groups and ensure the resulting structure will have a planar ground-state geometry. For PAHs, the filler benzenoid rings can also be used for a similar purpose if necessary. In this work, such a modification does not affect the naming of the built polyradicals. If steric hindrance is avoided, the planarity of these structures is ensured since they have fully π-conjugated systems that stabilize the polyradical electronic structure, highly connected backbone, and thus acquired planar rigidity. Molecules constructed according to this general template strictly follow the rules we formulated for the polyradical design and usually involve cross-conjugation. For PAH polyradicals, by carefully tailoring the connections between subunits, we ensured that upon growing the polyradical with the algorithmic principle, the unpaired electrons do not close the shell. Technically, this is achieved by using filler and auxiliary aromatic rings connected at specific sites of these subunits, colored in yellow and orange in figures depicting PAH polyradicals, respectively.

Besides, in order to stabilize a polyradical, it is better to connect subunits such that they have direct π-conjugation and antiferromagnetic coupling between radical centers of different subunits, if possible. With this consideration, in addition to Ovchinnikov's rule and our five rules that define the rational design of polyradicals and allow the algorithmic design of the polyradicals, let us connect the subunits in order to produce polyradicals with an increasing number of unpaired electrons. These polyradicals can be found in dashed purple circles in Figure 5. The naming style of the **generic set** of presented compounds will be such that the letters denoting primitive building blocks in Figures 4 and 5 indicate the presence of a particular subunit, while subscript numbers describe how many of this subunit is present at that section of the chain in the given polyradical. The ordering of the letters with their corresponding subscripts specifies connectivity in the direction of the chain growth of the polyradical, as shown in Figure 5 and thus the name of a given polyradical is a well-defined sequence of letters with subscripts. For the same sequence of subunits in the **PAH set** of polyradicals, the name is **X**-[**sequence**].

Note that in some cases, the terminal (usually electron-withdrawing) groups can be fluorine atoms or many other groups, such as other halogen atoms, cyano groups, hydrogen atoms, pyrazolyl groups, etc. Since the main factors to control the open-shell characters of polyradicals are aromatic stabilization and the topology of π-conjugation, the slight modification of the electron-withdrawing group does not cause any significant qualitative change in expected properties, as justified below for triradicals and tetraradicals with CASSCF calculations.

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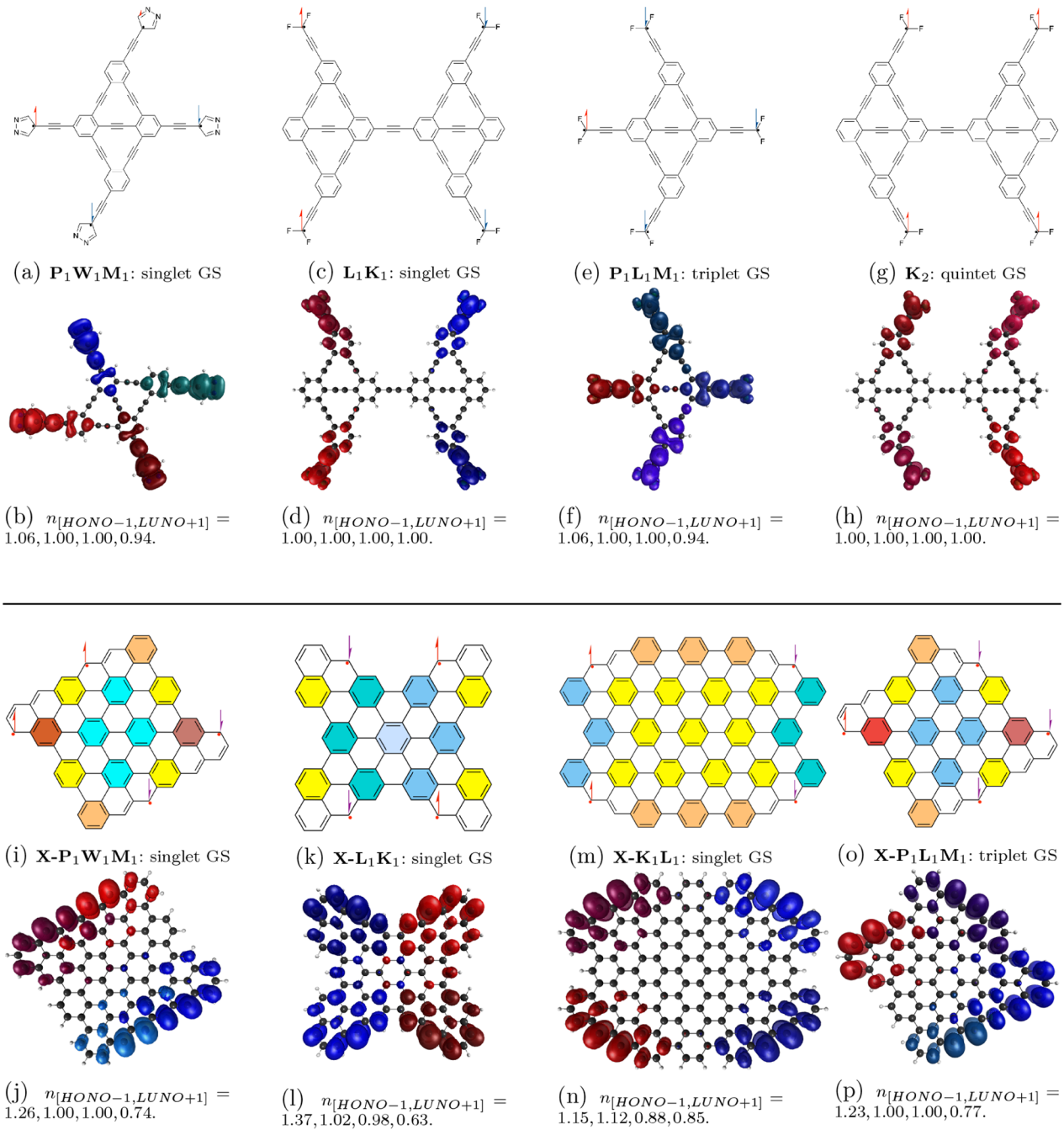


Figure 7. Structures of the generic set and PAH-based tetraradicals with singlet, triplet, and quintet ground states, along with subfigure of each compound depicting the sum of ground-state CASSCF frontier localized orbitals with colors for each radical center and ground-state occupation numbers of CASSCF frontier natural orbitals in the captions.

Triradicals. We can design two different triradicals with a doublet ground state, $\mathbf{P_1W_1}$ and $\mathbf{P_1L_1}$, which both have one radical subunit **P** and one diradical subunit, **W** and **L**, respectively. As shown in Figure 6a for $\mathbf{P_1W_1}$ and in Figure 6c for $\mathbf{P_1L_1}$, Ovchinnikov's rule predicts the doublet ground state as the arrow arrangement shows $S = \frac{1}{2}$, and multiplicity $2S + 1$, which in this case is 2 (a doublet). To design the triradical with a quartet ground state, we need to couple radical (spin) centers ferromagnetically. This is achieved by connecting subunit **P** with subunit **K** so that we obtain the triradical $\mathbf{P_1K_1}$ with a quartet ground state. In order to demonstrate the predicted triradical identity of these compounds and the ground-state multiplicity, we performed multiconfigurational CASSCF calculations with optimal active spaces within computational limits. Their triradical resonance structures with arrows to indicate the spin configuration of the radical centers according to Ovchinnikov's rule, the sum of each localized CASSCF frontier orbital (in different colors) and CASSCF frontier natural orbital occupation numbers in the ground state are given in Figure 6. To simplify the comprehension of these results, we can use the triradical character index, which would be, according to the method of Yamaguchi,[76] $y_{1/2}$ calculated from occupation numbers of the natural orbitals encompassing the singly occupied natural orbital (SONO). These triradical characters are $y_{1/2}$= 0.976 for $\mathbf{P_1W_1}$, $y_{1/2}$= 0.962 for $\mathbf{P_1L_1}$ and $y_{1/2}$= 1.000 for

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$\mathbf{P_1K_1}$, with cc-pVDZ basis set and CASSCF(15,15), CASSCF-(15,15), and CASSCF(13,13), respectively. For $\mathbf{P_1W_1}$, the state ordering is doublet D_0, followed by another doublet D_1 (+27.3 cm^{-1}) and quartet Q_0 (+38.0 cm^{-1}), with every energy change shown relative to the ground state (GS). For $\mathbf{P_1L_1}$, the state ordering is D_0, D_1 (+7.6 cm^{-1}), and Q_0 (+10.6 cm^{-1}). For $\mathbf{P_1K_1}$, the state ordering is Q_0, D_0 (+3623.2 cm^{-1}), and D_1 (+3684.9 cm^{-1}). These results verify the predicted ground-state multiplicities based on Ovchinnikov's rule and also demonstrate that design principles based on our rules produce triradicals with very high open-shell character. In the structures from Figure 6, each pair of spin-antiparallel unpaired electrons has at least three benzene rings between radical centers if we follow the path of the direct π-conjugation, through which these unpaired electrons can close the shell. Also, these triradicals are fully π-conjugated and exhibit cross-conjugation.

Tetraradicals. Having characterized triradicals with different multiplicities, we can select tetraradicals with allowed ground-state (GS) multiplicities (singlet (S), triplet (T) and quintet (Q)) designed by the same set of (di)radical subunits as the presented triradicals. In a generic set, selected tetraradicals with the predicted singlet ground state are $\mathbf{P_1W_1M_1}$ and $\mathbf{L_1K_1}$, with the triplet ground state is $\mathbf{P_1L_1M_1}$, and with the quintet ground state is $\mathbf{K_2}$. Their tetraradical resonance structures, with arrows to indicate the spin configuration of the radical centers according to Ovchinnikov's rule, the sum of each localized CASSCF frontier orbitals (in different colors) and CASSCF frontier natural orbital occupation numbers in the ground state are given in Figure 7. Diradical and tetraradical character indices calculated with CASSCF results for $\mathbf{P_1W_1M_1}$ are $y_0 = 0.998$ and $y_1 = 0.880$, for $\mathbf{L_1K_1}$ are $y_0 = 1.000$ and $y_1 = 1.000$, for $\mathbf{P_1L_1M_1}$ are $y_0 = 1.000$ and $y_1 = 0.874$, and for $\mathbf{K_2}$ are $y_0 = 1.000$ and $y_1 = 1.000$.

Notably, for $\mathbf{P_1W_1M_1}$, one cannot draw the fully closed-shell valence bond form (VBF)/resonance structure, since $\mathbf{P_1W_1M_1}$ is cross-conjugated and the lower bound polyradical identity is diradical. This is why the calculated diradical character is essentially 1. Despite full π-conjugation in $\mathbf{L_1K_1}$ and pairs of radical centers that couple antiferromagnetically, closing the shell between any two unpaired electrons that give rise to these radical centers is forbidden by the topology of the π-conjugation. Hence, the lower bound of the polyradical identity of $\mathbf{L_1K_1}$ is tetraradical. If the connectivity is opposite (compound $\mathbf{K_1L_1}$ described in Section S3.3), the ground state is still a singlet, closing the shell for different pairs of unpaired electrons is allowed, and the lower bound polyradical identity of such a compound is diradical. We present the case of $\mathbf{L_1K_1}$ to demonstrate the predictability of the ground-state multiplicity even when there is no way to close the shell by direct π-conjugation in any pairs of unpaired electrons in the fully π-conjugated compound. Similarly to $\mathbf{P_1W_1M_1}$, the lower bound polyradical identity of $\mathbf{P_1L_1M_1}$ is diradical, while it has a triplet ground state. As a fully ferromagnetically coupled and an alternant hydrocarbon-type tetraradical, closing any shell via direct π-conjugation in $\mathbf{K_2}$ is forbidden, and its lower bound polyradical identity is tetraradical, which has a quintet ground state as predicted by Ovchinnikov's rule and verified by CASSCF calculations.

The low-energy spectrum calculated from CASSCF(12,12)/cc-pVDZ for $\mathbf{P_1W_1M_1}$ is S_0 GS, followed by the states in the order of increasing energy relative to the GS in the units of cm^{-1} T_0 (+2.88), Q_0 (+67.50), T_1 (+74.39), T_2 (+77.99), S_1 (+87.38). For $\mathbf{L_1K_1}$, according to CASSCF(16,16)/STO-3G, the state ordering is S_0, T_0 (+0.00), Q_0 (+0.00), T_1 (+0.13), T_2 (+0.13), and S_1 (+0.26). Energy gaps in the latter case are underestimated because of the minimal basis set STO-3G, but it correctly describes the ground-state multiplicity and ordering of the spin states of the presented systems. This is also verified by CASCI(16,16)/4−31G, which results in the ordering of states as S_0, T_0 (+0.46), Q_0 (+1.38), T_1 (+333.87), T_2 (+333.87), and S_1 (+666.83). For $\mathbf{P_1L_1M_1}$ calculated from CASSCF(16,16)/cc-pVDZ, the state ordering is T_0, S_0 (+28.76), Q_0 (+82.46), T_1 (+124.11), T_2 (+171.08), and S_1 (+180.28). For $\mathbf{K_2}$ calculated from CASCI(12,12)/cc-pVDZ, the state ordering is Q_0, T_0 (+24.61), S_0 (+36.92), T_1 (+152.60), T_2 (+154.20), and S_1 (+294.50). The rationalization of the highest spin multiplicity by applying rule (**5**) of the formulated theory for these tetraradicals is given in Section S3.3.

For the PAH-based tetraradicals $\mathbf{X\text{-}P_1W_1M_1}$, $\mathbf{X\text{-}L_1K_1}$, and $\mathbf{X\text{-}K_1L_1}$ (singlet GS) and $\mathbf{X\text{-}P_1L_1M_1}$ (triplet GS), the singlet−triplet gaps are $\Delta E_{S\text{-}T}$ = 263, 507, 225, −192 cm^{-1}, diradical characters are y_0 = 0.997, 0.963, 0.756, 1.000, and tetraradical characters are y_1 = 0.521, 0.352, 0.711, 0.564, respectively, computed with the CASSCF(12,12)/4−31G level of theory. Apparently, due to higher delocalization and internal connectivity, the tetraradical characters in these PAHs are diminished compared to the generic set. However, this is readily controllable upon design by using more Clar's π-sextets bridging the directly π-conjugated unpaired electrons as stated in rule (**2**).

It is also important to analyze similarities and differences in modes of conjugation between different classes of topologically similar (same modes of spin−spin couplings and some equivalent paths of direct conjugation) polyradicals. We can compare the modes of conjugation between pairs of antiferromagnetically coupled unpaired electrons in generic $\mathbf{P_1W_1M_1}$ and PAH-based $\mathbf{X\text{-}P_1W_1M_1}$ as exemplified by resonance structures and color-emphasized groups in Figure 8 that are affected upon closing the shell along the paths of direct conjugation between these unpaired electrons. The paths of

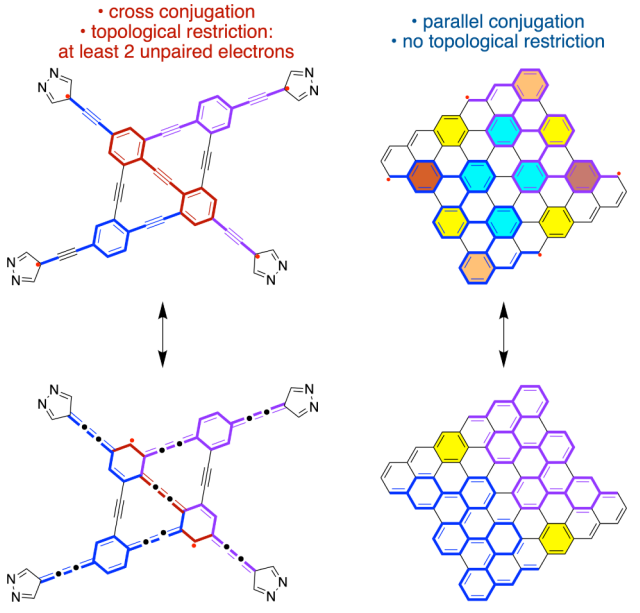


Figure 8. Comparison of the mode of conjugation among unpaired electrons giving rise to four radical centers in γ-graphyne fragment-based and PAH-based tetraradicals.

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direct conjugation that allow the closure of the shell between different pairs of antiferromagnetically coupled unpaired electrons necessarily *converge* in the case of $\mathbf{P_1W_1M_1}$, which prevents the possibility of closing both shells in the same configuration, while they can *diverge* in $\mathbf{X\text{-}P_1W_1M_1}$, which allows closing both shells in the same configuration. This is because the PAH-based $\mathbf{X\text{-}P_1W_1M_1}$ is more internally connected than $\mathbf{P_1W_1M_1}$. The filler and auxiliary aromatic rings (shown in yellow and orange, respectively, in Figure 7i) allow the alternate paths of direct conjugation for antiferromagnetically coupled unpaired electrons, and paths of different pairs do not necessarily converge in $\mathbf{X\text{-}P_1W_1M_1}$ as opposed to paths in generic $\mathbf{P_1W_1M_1}$, which lacks these filler groups. This is why the diradical character of $\mathbf{P_1W_1M_1}$ must be greater than or equal to that of $\mathbf{X\text{-}P_1W_1M_1}$, while the tetraradical characters do not have such restrictions. If we use the filler groups for **a generic set**, we can create additional paths of direct conjugation that can allow removal or softening of the restriction on the lower bound number of unpaired electrons. Hence, the freedom given by the topological principles, whether or not to use the filler and auxiliary aromatic rings, can serve as an additional method of controlling the polyradical characters of the designed compounds.

Pentaradicals. For pentaradicals, the allowed ground-state (GS) multiplicities are doublet (D), quartet (Q) and sextet (S). The selected pentaradical with the predicted doublet GS is $\mathbf{P_1W_1L_1}$, with the quartet GS is $\mathbf{P_1L_2}$ and with the sextet GS is $\mathbf{P_1K_2}$. The highest allowed polyradical order resonance structures with the spin configuration predicted by Ovchinnikov's rule, an approximate frontier-orbitals density (from unpaired electrons) distribution, and CASCI low-energy spectrum of spin states are given in Figure 9. The frontier-orbitals density distribution (due to unpaired electrons) is shown with the CASSCF natural orbital belonging to a fully symmetric irreducible representation, which has approximately equal amplitudes at each radical center. This orbital is quasi-degenerate with four other frontier orbitals that bear four other unpaired electrons. Triradical and pentaradical character indices

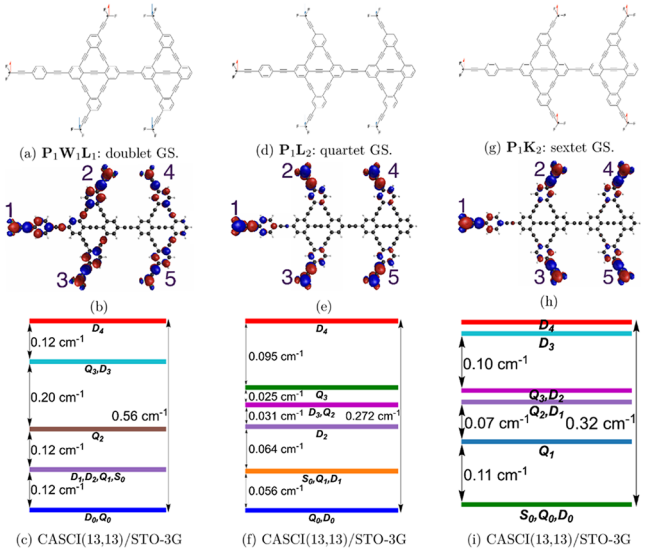


Figure 9. Pentaradicals with (a) doublet, (d) quartet, and (g) sextet ground states. Electron density distribution from CASSCF frontier natural orbitals due to unpaired electrons and CASCI spectrum of (b–c) $\mathbf{P_1W_1L_1}$, (e–f) $\mathbf{P_1L_2}$, and (h–i) $\mathbf{P_1K_2}$.

calculated for $\mathbf{P_1W_1L_1}$ (CASCI(13,13)/STO-3G) are $y_{1/2}$ = 1.000 and $y_{3/2}$ = 0.997, for $\mathbf{P_1L_2}$ (CASSCF(16,16)/STO-3G) are $y_{1/2}$ = 1.000 and $y_{3/2}$ = 0.997, and for $\mathbf{P_1K_2}$ (CASSCF-(16,16)/STO-3G) are $y_{1/2}$ = 1.000 and $y_{3/2}$ = 1.000. We observe the expected spin-density distribution according to the resonance structures of these polyradicals. CASCI results show that the ground-state multiplicity had been predicted correctly according to connectivity between specific subunits, as given in Figure 4. The rationalization of the highest spin multiplicity by applying rule **(5)** of the formulated theory for these pentaradicals is given in Section S3.3.

Hexaradicals. For hexaradicals, the allowed ground-state multiplicities are singlet (S), triplet (T), quintet (Q) and septet/heptet (H). The selected hexaradical with the predicted singlet ground state is $\mathbf{P_1L_1K_1M_1}$, with triplet GS: $\mathbf{P_1W_1L_1M_1}$, with quintet GS: $\mathbf{P_1L_2M_1}$, and with septet/heptet GS: $\mathbf{K_3}$. The highest allowed polyradical order resonance structures with the spin configuration, the frontier-orbitals density (due to unpaired electrons) distribution, and CASCI low-energy spectrum of spin states of these hexaradicals are given in Figure 10, which are correctly predicted by our theory. According to CASCI results with large active spaces, for $\mathbf{P_1L_1K_1M_1}$, diradical, tetraradical, and hexaradical characters are y_0 = 1.000, y_1 = 0.993, y_2 = 0.993; for $\mathbf{P_1W_1L_1M_1}$, y_0 = 1.000, y_1 = 1.000, y_2 = 0.989; for $\mathbf{P_1L_2M_1}$, y_0 = 1.000, y_1 = 1.000, y_2 = 0.973; and for $\mathbf{K_3}$, y_0 = 1.000, y_1 = 1.000, y_2 = 1.000. Detailed results and rationalizations of the multiplicity of highest spin states are presented in Section S3.3.

Therefore, we rationally designed, characterized, and verified the predicted properties of these various fully π-conjugated organic triradicals, tetraradicals, pentaradicals, and hexaradicals with high polyradical character and showed the reliability of the presented theory in controlling the ground-state multiplicity, which is modified through the topological control of π-conjugation by regioisomerism, i.e., modifying the relative positions of the radical centers. Henceforth, one can design polyradicals using the general algorithmic scheme shown in Figure 5 or other generalized structural templates shown in Figure 11a,b that are assembled from building blocks shown in Figure 4. Arrows in Figure 11 indicate the spin configuration in the ground state according to Ovchinnikov's rule. Notably, the set of structures generated from this generalized structural template is a subset of structures that can be generated by the algorithmic scheme shown in Figure 5 if we also use subunit **V** in the algorithm, which also contributes two unpaired electrons and S = 0 as subunit **W**. These template structures can be even more generalized by extending them in multiple directions in two dimensions, as given in Figure S1. As we see from the spin configuration of the generalized structures in Figure 11 and in **Legend 1** of Figure 5, the subunit **P** contributes one unpaired electron (H = +1) and $S = +\frac{1}{2}$ upon building polyradical, while **W** contributes two unpaired electrons (H = +2) and S = 0, subunit **K** contributes two unpaired electrons (H = +2) and S = +1, **L** contributes two unpaired electrons (H = +2) and S = −1, subunit **V** contributes two unpaired electrons (H = +2) and S = 0, and subunit **M** contributes one unpaired electron (H = +1) and $S = -\frac{1}{2}$.

Hence, for these general structures, the order of polyradical (H) can be expressed as shown in eq 3:

$$H = P + M + 2(W + L + K + V) \tag{3}$$

where these numbers denote how many of the subunits are present in the designed polyradical. The ground-state multi-

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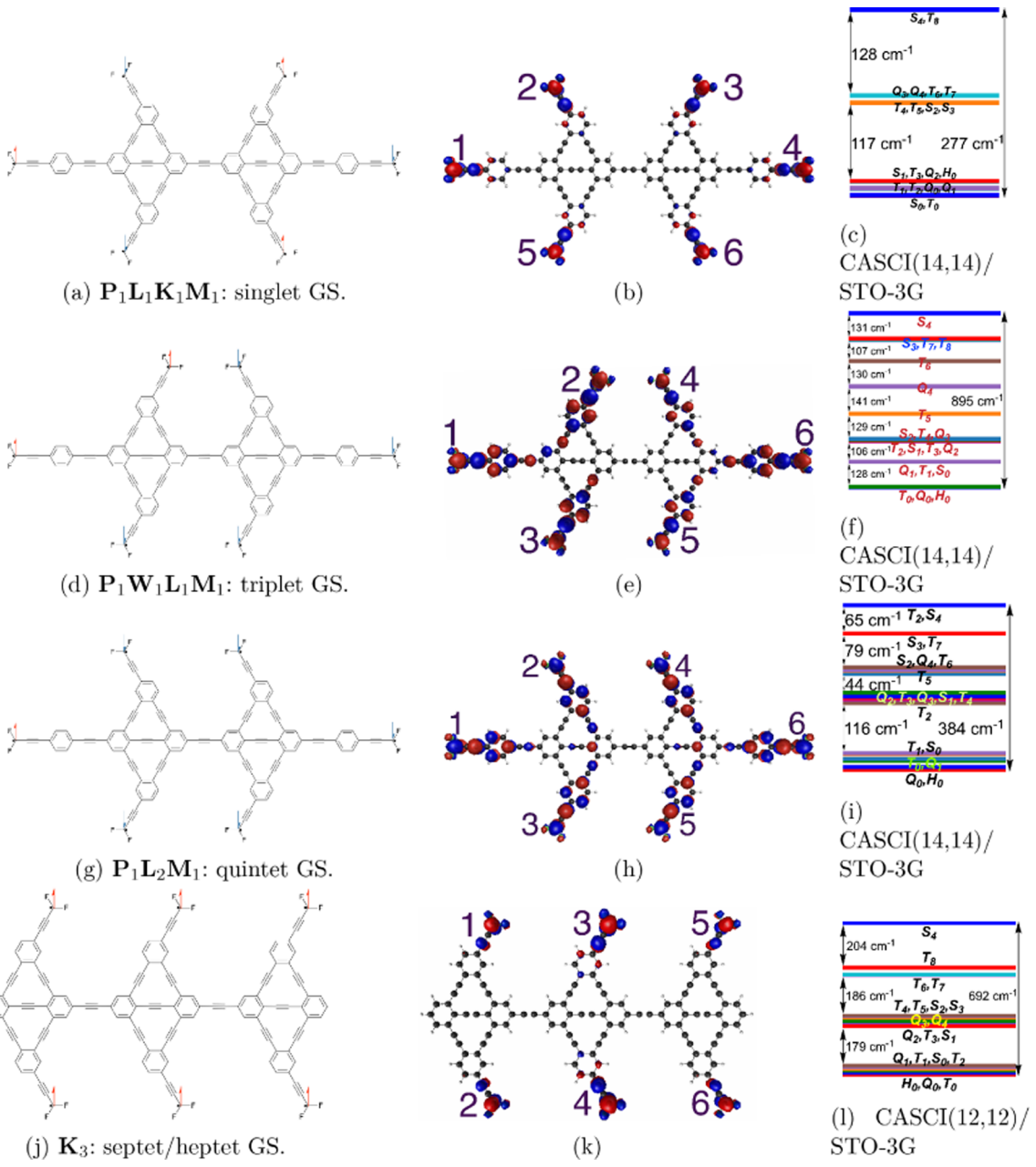


Figure 10. Hexaradicals with (a) singlet (S), (d) triplet (T), (g) quintet (Q), and (j) septet/heptet (H) ground states. Electron density distribution from CASSCF frontier natural orbitals due to unpaired electrons and CASCI spectrum of (b–c) $\mathbf{P_1L_1K_1M_1}$, (e–f) $\mathbf{P_1W_1L_1M_1}$, (h–i) $\mathbf{P_1L_2M_1}$, and (k–l) $\mathbf{K_3}$.

plicity ($2S + 1$) for the polyradical designed from this general structure is given in eq 4:

$$2S + 1 = |P + 2K - 2L - M| + 1 \quad (4)$$

With the algorithmic scheme and generalized structural templates, experimental scientists can create polyradicals with any number of unpaired electrons and ground-state multiplicity, as long as they are synthetically feasible.

Rational Design of Various Polyradicals. In addition to template-based polyradicals, our theory allows the rational design of compounds with the same specificity for the ground-state multiplicity for a given order of polyradical. Using these principles, we designed a hexaradical(oid) derivative of triphenylene named **TH** with a singlet ground state (GS) and septet/heptet highest-energy spin state (HS), a hexaradical(oid) derivative of dibenzo[fg,op]tetracene **DT** with a singlet GS and triplet HS, and an octaradical(oid) **BC** resembling cross-conjugated $\mathbf{TC_3}$ with a singlet GS and nonet HS, all given in Figure 12. These structurally small polyradicals are partially cross-conjugated with Clar's π-sextets shared between several diradical subunits and have high polyradical characters and a narrow spectral range of low-energy spectrum with thermally accessible paramagnetic states. For **TH**, diradical, tetraradical, and hexaradical characters are $y_0 = 0.653$, $y_1 = 0.644$, and $y_2 = 0.644$, respectively, while the spectral range of 20 low-energy spin states is 2202 cm^{-1}. For **DT**, diradical, tetraradical, and hexaradical characters were computed to be $y_0 = 0.867$, $y_1 = 0.507$, $y_2 = 0.502$, respectively, and the range of the low-energy spectrum of the 20 spin states is 1768 cm^{-1}. The octaradical(oid) **BC** has 70 spin states in the low-energy spectrum with a

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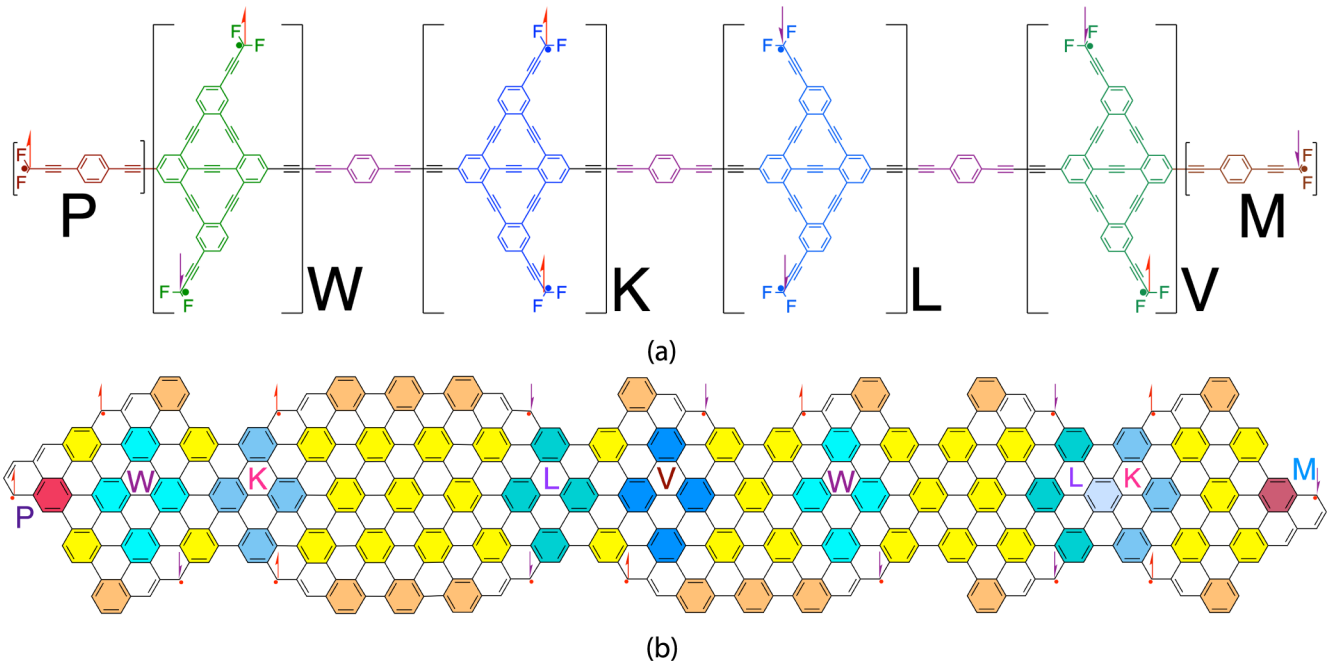


Figure 11. General mixed homologous series with a controlled ground-state multiplicity for a polyradical of a given order as expressed in eqs 3 and 4: (a) γ-graphyne separate fragments connected along a single chain with difluoromethylene terminal radical groups and (b) polycyclic aromatic hydrocarbon (PAH) polyradical.

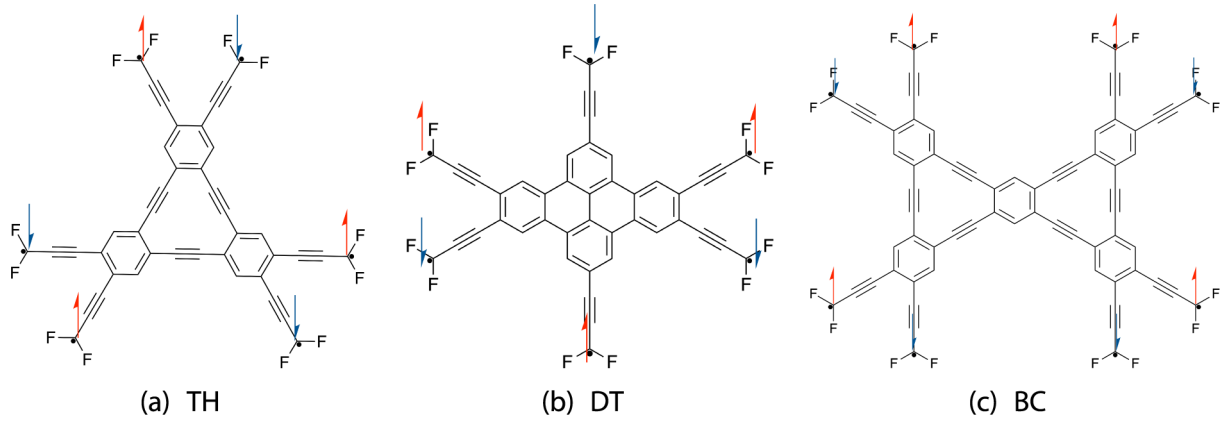


Figure 12. Hexaradical(oid)s **TH** and **DT** and octaradical(oid) **BC** are given with singlet (S) ground states.

spectral range of 2510 cm^{-1} and its open-shell characters are y_0 = 0.648, y_1 = 0.647, y_2 = 0.631, and y_3 = 0.628.

Detailed CASSCF/CASCI results for these polyradicals are given in Section S3.4, with the justification of the highest spin states for hexaradical(oid)s **TH** (H_0) and **DT** (T_8) and octaradical(oid) **BC** (N_0), which exemplify how to predict the highest-excited spin state in the low-energy spectrum by taking opposite couplings to the one predicted by Ovchinnikov's rule in the ground state, which demonstrates rule **(5)** of the presented theory. For example, the highest spin state of **TH** can be predicted by noting that pairs with radical centers closest to each other (in *ortho* relative positions in the same benzenoid rings) and pairs with collinear radical centers (along directly π-conjugated chain) connected to different benzene rings will shift from antiferromagnetic coupling in the ground state to ferromagnetic coupling in the highest spin state, considering the stabilization effects of different coupling modes and through-bond distances. This results in a fully ferromagnetic configuration in the highest spin state defining the multiplicity of septet. Thus, one can design polyradicals with controlled magnetic properties upon defining the states of specific multiplicity to be the highest-excited state, relatively lower-excited state, or the ground state. Specifically, this implies that we can also design polyradicals of order H with ground-state multiplicity of H + 1 corresponding to the highest allowed magnetic moment of the molecule. Since the primary factors of control are the topology of π-conjugation and aromatic stabilization, one can use various functional groups to modify other properties of polyradicals without affecting open-shell characters and GS or HS multiplicities. We stress that functional groups do not significantly affect these properties as long as they do not change the topology of the π-conjugation.[50,82]

With this framework, we gain significant control over the structure of the low-energy spectrum (ordering of the states with different spin multiplicity) by considering the combinations of coupling modes in each spin state to determine its relative stability compared to other states in a low-energy spectrum. First, we can start by applying other rules **(2)**-**(4)** to estimate the

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polyradical(oid) order of a fully π-conjugated compound. This is based on the resonance theory, which can reveal topological restrictions on the lower-bound number of unpaired electrons. Then, counting the aromatic Clar's π-sextets (or estimating the resonance energy of a generic aromatic system) in each relevant valence bond form provides a way to estimate the contribution of different VBFs in the resonance hybrid. Having determined the polyradical order within an accuracy of two unpaired electrons (we can still find the correspondence between the higher-order and lower-order polyradical(oid) spectra, since they apply to the same molecule), we can consider the coupling modes between spin centers in the molecule to predict the structure of the low-energy spectrum. First, we apply Ovchinnikov's rule to determine the ground state configuration of spin centers. For each pair, we must estimate the strength of coupling based on the topology of the π-conjugation and through-bond distance. For instance, if two unpaired electrons that give rise to the pair of spin centers can close the shell in some VBFs, then they are directly π-conjugated spin centers and have much stronger coupling than those spin centers with a similar through-bond distance but lacking such direct conjugation.[49] We note that in nonalternant systems, two spin centers that are induced by two directly π-conjugated unpaired electrons do not have to be antiferromagnetically coupled, because there might be at least two nonequivalent paths of conjugation: one allowing the closure of the shell between these electrons and another (perhaps shorter) controlling their relative spin alignment. In such cases, greater care must be taken to study the hierarchy of the through-bond paths to determine the relative strengths of coupling between different through-bond paths and, consequently, the mode of coupling between the radical centers. In principle, if a certain through-bond path is significantly shorter than other paths, this path will control the spin alignment of the unpaired electrons, giving rise to the radical centers. Henceforth, in most cases, we can generate the ordering of the excited spin states within the low-energy spectrum based on single or double spin flips and estimate its relative energy based on induced coupling modes. One must note that a set of a few spin states might have different coupling modes but similar energies, leading to quasi- or full degeneracy among spin states if the interactions between spin centers are very weak. This approach at least partly substitutes the necessity to diagonalize the Heisenberg model Hamiltonian (if it is applicable to the magnetic system) and thus reduces the effort to predict the properties qualitatively. Therefore, the described theory of polyradical design represents a powerful toolkit for the creation and tuning of properties of a vast variety of polyradicals.

CONCLUSIONS

In this work, we established a theoretical framework for the rational design of metal-free, planar, and fully π-conjugated polyradicals with any number of unpaired electrons and any ground-state/highest-energy spin state multiplicity. These polyradicals are stabilized by the delocalization and aromaticity of a system with an equivalent resonance energy of at least two benzene-like rings for each diradical subunit, with this system possibly shared among different pairs of directly π-conjugated unpaired electrons within the fully conjugated π-system. Such precise control over the polyradical character, number of unpaired electrons, and ground-state/highest-state multiplicity has not been previously achieved for fully π-conjugated organic molecules. By unifying observations from previous experiments with our past and current computational studies, we identified new factors and principles for the rational design of polyradicals. We formulated a theory with specific rules that enable one to reach an algorithm of polyradical design (Figure 5) and to construct general polyradical series with controlled ground-state multiplicity (Figure 11a,b). These polyradicals can grow in multiple directions in two dimensions, potentially filling most of the plane within the perimeter of the polyradical (Figure S1).

The primitive building blocks used to construct these polyradicals combine common groups in organic chemistry, are structurally rigid and stable, and are synthetically viable.[79−81] By increasing structural complexity in two dimensions, one can use the presented principles and specific constraints to generate a significant portion of the chemical space for two-dimensional fully π-conjugated organic polyradicals with various properties. This can be achieved using the (di)radical building blocks shown in Figure 4 or other primitive blocks based on the presented theory.

These organic molecules have many advantageous properties for quantum technology and computing. They are less costly to produce and less hazardous than heavy-metal-based devices and many semiconductors, and they exhibit stronger correlation and entanglement between radical centers. This might result in longer coherence times,[20] improved fidelity of the spin configuration, and greater specificity of unitary transformations of the qubit states when operating with quantum gates. Moreover, the presented principles of modulating properties of polyradicals could be applied to understand the open-shell border states of tailored graphenic materials and PAHs. The applications of polyradicals designed by using the principles we present can lead to significant technological breakthroughs. Our research group is actively exploring this frontier to further enhance the potential of these materials.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.4c07513.

General view of the general polyradical series and algorithmic design, computational details of geometry optimization, computational details of CASSCF and CASCI calculations, CASSCF/CASCI results for every presented triradical, tetraradical, pentaradical, hexaradical, and octaradical, rationalization of the highest spin state for every presented polyradical, study of effects of charge transfer from radical centers to electron-withdrawing groups in diradicals with small tetraradical characters, optimized geometries for every relevant state of all the compounds presented in this study (PDF)

AUTHOR INFORMATION

Corresponding Authors

Ibério de P. R. Moreira − *Departament de Ciència de Materials i Química Física & IQTCUB, Universitat de Barcelona, Barcelona 08028, Spain;* orcid.org/0000-0002-2684-6982; Email: i.moreira@ub.edu

Jordi Poater − *Departament de Química Inorgànica i Orgànica & IQTCUB, Universitat de Barcelona, Barcelona 08028, Spain; ICREA, Barcelona 08010, Spain;* orcid.org/0000-0002-0814-5074; Email: jordi.poater@ub.edu

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Josep Maria Bofill − *Departament de Química Inorgànica i Orgànica & IQTCUB, Universitat de Barcelona, Barcelona 08028, Spain;* orcid.org/0000-0002-0974-4618; Email: jmbofill@ub.edu

Author

Sergi Betkhoshvili − *Departament de Química Inorgànica i Orgànica & IQTCUB, Universitat de Barcelona, Barcelona 08028, Spain;* orcid.org/0009-0004-1160-3613

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.4c07513

Notes

The authors declare no competing financial interest.

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