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Designing stable π-radicals

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π-Conjugated radicals, molecules with unpaired electrons, have been known since Gomberg's discovery of the persistent triphenylmethyl in 1900. First considered a curiosity, π-radicals have helped to refine the electronic structure theory and better understand the reactivity of organic compounds, and for the last 40 years have been actively pursued as functional materials: single component organic conductors, semiconductors for field-effect transistors, organic magnets, and most recently, as electroluminescent and quantum materials. This tutorial review provides the essential quantum-chemical background and practical lessons learned from 125 years of the history of developing stable π-radicals, aiming to inspire and inform new researchers entering this field. We discuss the cause of the reactivity of π-radicals and the methods to suppress this reactivity in the design of stable π-radicals. Without any intent of comprehensive coverage, we systematise and highlight the most important examples of stable neutral π-radicals, covering arylmethyl, polycyclic hydrocarbon, conjugated heteroatomic radicals, di- and polyradicals while also briefly covering radical ions. We show how the presence of unpaired electrons in these molecules is manifested in their unusual electronic, optical and magnetic properties, and summarise the most important applications of π-radicals explored to date. Our overall goal is to bring the accumulated knowledge of the field to the attention of a new generation of researchers designing stable π-radicals in pursuit of various applications.

Key learning points

(1) π-radicals are a family of conjugated open-shell molecules with unusual electronic properties, studied for the last 125 years but still not well-understood.
(2) Key chemical design approaches to create stable π-radicals, alongside quantum mehcanics background for understanding their electronic structures.
(3) Diverse examples of stable π-radicals, showing the evolution of structural complexity and properties, from 1900 to recently developed structures.
(4) Beyond stability, how can one design for emerging applications of π-radicals.

1 Early history

At the turn of the 20th century, Moses Gomberg at the University of Michigan was attempting the synthesis of the sterically congested hexaphenylethane *via* Wurtz coupling of triphenylmethyl chloride. Under an inert atmosphere, he observed the formation of a deeply coloured species that was highly reactive but could persist for months in the absence of air. Gomberg concluded that this compound is a trivalent carbon species, the triphenylmethyl (trityl) radical **1** (Fig. 1), considering that it formed a white solid peroxide **2** under air.[1]

This first described persistent radical challenged the prevailing notion that carbon must be tetravalent. Despite the awkward statement "This work will be continued and I wish to reserve the field for myself" in Gomberg's seminal paper, other chemists joined the discussion merely weeks after.[3] Cryoscopic molecular weight measurements showed that >95% of the material in solution corresponded to a dimeric species (later identified as **4**), and some critics suggested the substance was merely an unusually reactive dimer. Gomberg correctly postulated that a stable dimer exists in equilibrium with, and serves as a reservoir of the triphenylmethyl radical,[4] and in 1910 Wilhelm Schlenk isolated tris(4-biphenylyl)methyl radical **5** exhibiting almost no dimerisation under anaerobic conditions.[5] Many variants of congested triarylmethyls (**6**, **7**)[6,7] as well as heteroatom-centred radicals such as the air-stable α,α-diphenyl-β-picrylhydrazyl (**8**)[8] were developed in the early 20th century, establishing the field of persistent neutral free radicals (Fig. 2).

The development of persistent radicals coincided with the emergence of modern theories of molecular structure and quantum mechanics, which provided theoretical insights into

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the behaviour of free radicals, and more generally, open-shell species with unpaired electrons. Pioneered by Lewis, Langmuir and Pauling, the electronic theory of chemical bonding explained how molecules with unpaired electrons could be stable.[9] Resonance structure theory in particular provided a framework to explain the relatively high stability of the triphenylmethyl radical by illustrating how the unpaired electron on the central carbon could be delocalised over multiple atoms, reducing its reactivity (Fig. 1).[10] In parallel, Uhlenbeck and Goudsmit proposed the concept of electron spin in 1925.[11] Afterwards, Heisenberg's exchange theory and Dirac's work on spin Hamiltonians provided a mathematical framework for describing electron spin interactions brought about by unpaired electrons.[12] Then, the introduction of Hund's rules and the spin selection rule clarified the importance of spin multiplicity (*vide infra*) in determining the behaviour of open-shell systems.[13]

Finally, with the development of electron spin resonance (ESR) spectroscopy by Zavoisky[14] and Bleaney[15] in the 1940s to characterise unpaired electrons, the study of persistent radicals quickly grew as a field. From biology to catalysis, and from energy to electronics, one century after Gomberg's discovery, new open-shell systems continue to emerge as functional materials, where the unique properties of unpaired electrons can be harnessed for various applications.

2 Theoretical background

An open-shell system refers to any multiatomic system with one or more unpaired electrons. Here, we provide a general theoretical framework for open-shell systems that allows us to discuss their molecular design as well as their unique properties.

2.1 Electronic structure

Molecular orbital (MO) theory posits that individual atomic orbitals $\{\varphi\}$ combine constructively or destructively to generate molecular orbitals $\{\psi\}$, which describe the spatial distribution and energy of the electrons. Electrons populate them following the Aufbau and Pauli exclusion principles, and they are classified as bonding, antibonding, or nonbonding. In a closed-shell ground state system, every MO is either doubly occupied by one α (spin-up) and one β (spin-down) electron of the same energy, up to the highest occupied molecular orbital (HOMO), or empty from the lowest unoccupied molecular orbital (LUMO). Open-shell systems possess one or more singly occupied MOs (SOMOs). The presence of the unpaired electron breaks the degeneracy between the α and β spin orbitals, and the β counterpart of the α-SOMO is often referred to as SUMO (singly unoccupied molecular orbital, Fig. 3). The SOMO–SUMO gap can be probed electrochemically, through the oxidation/reduction of the radicals. This unpaired electron occupancy results in unique chemical reactivity and strong interactions with magnetic fields.

The delocalisation of the SOMO throughout the molecule controls the spin density, which is defined as the difference between α- and β-electron densities. *Spin delocalisation* and *spin polarisation* are complementary mechanisms that shape the

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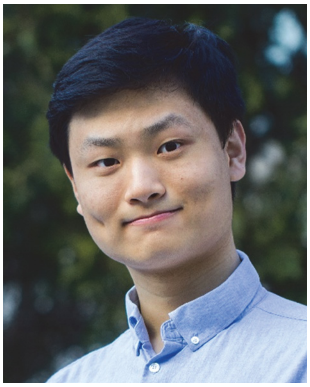

Cheng-Hao Liu

Chenghao Liu received his PhD from McGill University under the mentorship of Prof. Perepichka, while concurrently conducting research at Mila with Prof. Yoshua Bengio. He is currently a FutureHouse Postdoctoral Fellow at Caltech, working with Prof. Frances Arnold. Chenghao's research lies at the intersection of chemistry and machine learning, where he explores how uncharted electronic and catalytic properties emerge from molecular structures, and their design from the infinite chemical space.

Dmytro F. Perepichka

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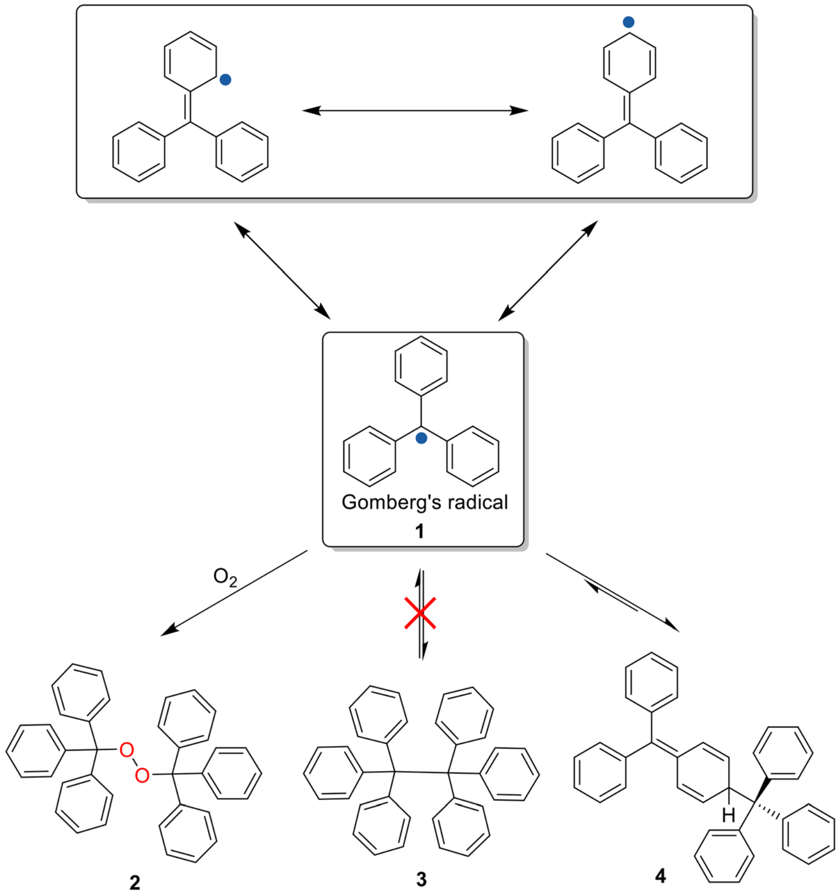

Fig. 1 The triphenylmethyl radical **1** represented by three resonance forms, and its quenching pathways *via* reaction with oxygen and dimerisation. While Gomberg initially favoured the correct quinoidal structure of this triphenylmethyl dimer (**4**), an alternative hexaphenylethane structure of the dimer (**3**) was later proposed by Bernard Flürscheim and for a long time accepted by the community. The correct structure **4** was only proven in 1968 with NMR spectroscopy.[2]

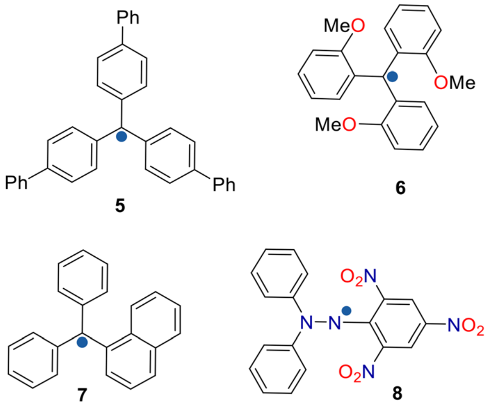

Fig. 2 Examples of early studies of persistent radicals.

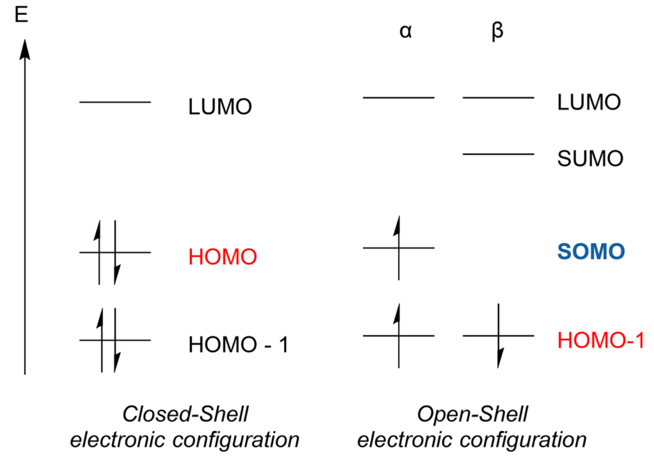

Fig. 3 Frontier orbitals and electronic configuration of a closed-shell (left) and an open-shell (right) system.

spin density. Spin delocalisation arises from direct orbital overlap, which delocalises the unpaired electron over atoms with nonzero SOMO amplitude, which is only significant in π-conjugated systems. Spin polarisation, in contrast, is a through-bond electron-correlation effect in which the *unpaired* electron perturbs nearby *paired* electrons, even on atoms with little or no SOMO amplitude, which leads to alternating opposite-sign spin densities along the bonding framework.

An electron possesses an intrinsic, quantised angular momentum characterised by the spin quantum number $s = 1/2$.

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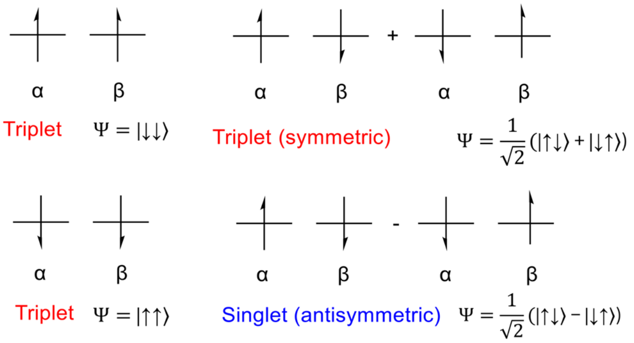

Fig. 4 Schematic representation of the electronic configurations of triplet and singlet states.

When placed in an external magnetic field, the projection of the spin can take two values, m_s = +1/2 (spin-up) or −1/2 (spin down). In a system with multiple electrons, individual spins sum up to produce a total spin angular momentum, S. The spin multiplicity $M = 2S + 1$ indicates the number of possible projections of the total spin (M_S). The common spin states are defined as follows:

Singlet State ($S = 0$, $M = 1$): all spins are paired, resulting in a net zero spin. This occurs in closed-shell molecules, or open-shell molecules with an even number of unpaired electrons (*e.g.*, diradicals) whose spins are antiparallel.

Doublet State ($S = 1/2$, $M = 2$): one unpaired electron, leading to two possible spin states. This is observed in free monoradicals.

Triplet State ($S = 1$, $M = 3$): two unpaired electrons with parallel spins, leading to three possible spin orientations with symmetric configurations (Fig. 4). This is common in diradicals and excited states of molecules.

Quartet State ($S = 3/2$, $M = 4$): Three unpaired electrons, with a total of four possible spin states. This can be observed in triradical systems[16] and some transition metal complexes.

Macroscopically, the spin multiplicity manifests as a magnetic moment **M**:

$$\mathbf{M} = -g_s \mu_B S \tag{1}$$

where $g_s \approx 2.0023$ is the electron spin g-factor and μ_B is the Bohr magneton.

2.2 Spin coupling

When multiple unpaired electrons exist, the question of how their spins couple – parallel or antiparallel – determines the ground-state multiplicity and many physical properties. The origin of the spin coupling is the Pauli exclusion principle, which dictates that no two electrons can occupy the same quantum state, forcing them to have opposite spins if they share an orbital. This antisymmetry introduces the exchange energy E_{exchange} in electron–electron interaction. The exchange interaction between two electrons can be described using the Heisenberg–Dirac–van Vleck exchange Hamiltonian:

$$\hat{H}_{\text{exchange}} = -2J \cdot \mathbf{S}_1 \cdot \mathbf{S}_2, \tag{2}$$

where J is the exchange coupling constant and $\mathbf{S}_1$ and $\mathbf{S}_2$ are the spin operators for the two electrons. A positive J indicates a preference for parallel spin alignment (ferromagnetic coupling), while a negative J favours antiparallel alignment (antiferromagnetic coupling). For systems with more than two spins, the Hamiltonian generalises to a pairwise sum. In a system with an even number of electrons, E_{exchange} is represented as the singlet–triplet gap ΔE_{ST}:

$$E_{\text{exchange}} = \Delta E_{\text{ST}} = E_{\text{triplet}} - E_{\text{singlet}} = -2J, \tag{3}$$

A positive ΔE_{ST} indicates a preference for a singlet ground state while a negative ΔE_{ST} indicates triplet. Experimentally, ΔE_{ST} can be determined by variable-temperature ESR spectroscopy or other magnetic measurements.

Let us now show how to predict the sign and magnitude of J. In diradicals, two unpaired electrons occupy non-bonding or weakly-interacting MOs. These orbitals are separate in space and nearly degenerate in energy. The interaction between these two electrons is manifested *via* a weak one-electron overlap integral over the volume,

$$S_{1,2} = \int \phi_1(1)\phi_2(1) d^3 r_1, \tag{4}$$

and a two-electron exchange integral:

$$K_{1,2} = \int \phi_1(1)\phi_2(2) \frac{1}{r_{1,2}} \phi_1(2)\phi_2(1) \mathrm{d}r_1 \mathrm{d}r_2, \tag{5}$$

where r_i and ϕ_i are the distance from electron i and the wavefunction of electron i, respectively, and $r_{1,2}$ is the distance between electrons 1 and 2. A two-electron Coulombic interaction also exists between the electrons, but it is independent of spin configuration and does not affect the spin multiplicity. The competition between $S_{1,2}$ and $K_{1,2}$ determines the exchange coupling constant J and hence the ground-state multiplicity. Generally, a large $K_{1,2}$ indicates the electrons are exchangeable, which favours the triplet state, while a larger $S_{1,2}$ favours the singlet, because bond formation requires antiparallel spins. For more details, see ref. 17.

In systems with two unpaired electrons, this interplay between $S_{1,2}$ and $K_{1,2}$ can result in three distinct scenarios:[18]

(1) *Biradicals*. In the limit where $r_{1,2} \to \infty$, the $S_{1,2}$ and $K_{1,2} \to 0$, the exchange coupling constant $J \to 0$ (Fig. 5a). Here, two radical centres are spatially separate and can be represented by two independent doublets. This situation can be theoretically examined by considering H_2 with a large interatomic distance. Note that there is a weak preference for the "singlet" state due to a faster decrease of the exchange integral. An early experimental example of such biradical system is the bisnitroxide biradical with a terephthalic linker (Fig. 5b) for which the ESR spectrum reveals non-interacting doublets.[19]

(2) *Localised diradicals* with $S_{1,2} \sim 0$, but $K_{1,2} > 0$ and the unpaired electrons are localised on different atoms. The triplet state is favoured when orbitals are degenerate and (nearly) non-bonding, *i.e.* $K_{1,2}/S_{1,2} \gg 1$. Increasing orbital overlap diminishes this ratio, eventually leading to the singlet state. A simple example of localised diradicals can be seen in twisted ethylene (Fig. 5c). In planar ethylene, the large orbital overlap $S_{1,2}$ between the two electrons across the π-bond results in the

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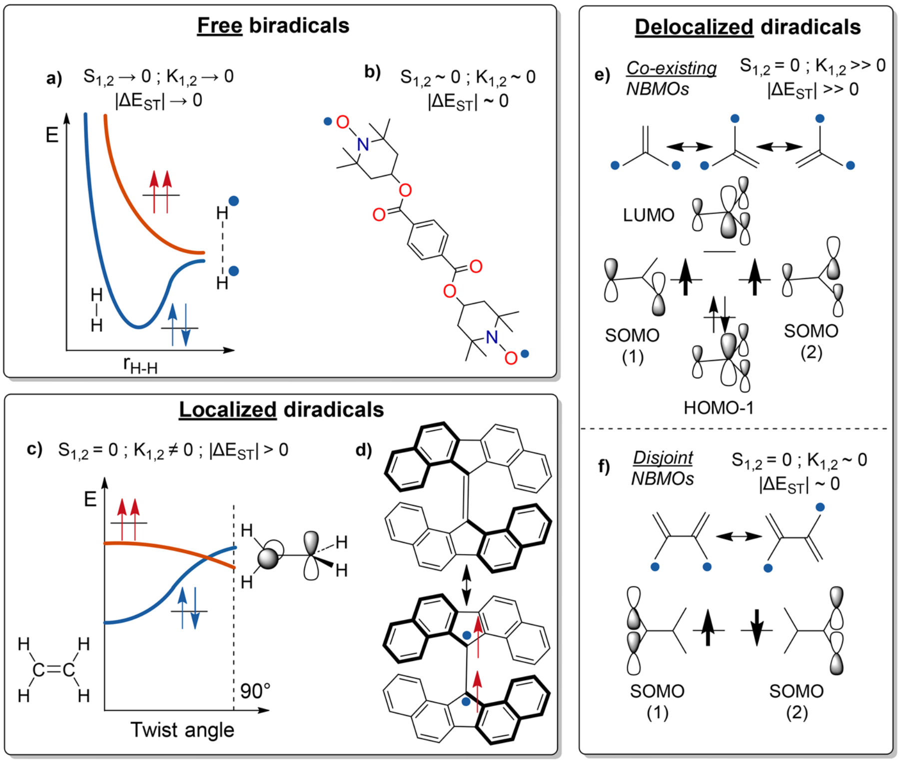

Fig. 5 (a)–(f) Classification of diradicals in terms of spin-coupling. (a) and (b) Feature free biradicals. (c) and (d) Feature localised diradicals. (e) and (f) Highlight delocalised diradicals either with co-existing NBMOs (*e.g.* TMM) or disjoint NBMOs (*e.g.* TME).

singlet state being significantly stabilised with respect to the triplet. In twisted ethylene at 90°, there is no orbital overlap as the p-orbitals are orthogonal to each other, and the remaining exchange term $K_{1,2}$ now leads to a triplet ground state. While realising such large twist in the ground state can be challenging in olefins, an equilibrium with an open-shell triplet can be observed in sterically congested environments, such as benzannulated bisfluorenylidene (Fig. 5d) at elevated temperatures (>100 °C).[20]

(3) *Delocalised diradicals* with $S_{1,2} = 0$, but $K_{1,2} > 0$ and the unpaired electrons are delocalised across the π-system in two nonbonding MOs (NBMOs). Due to their non-bonding character, the overlap integral $S_{1,2}$ is null so the exchange integral $K_{1,2}$ alone determines their spin state, and its magnitude depends on whether the two NBMOs coexist in the same spatial region. Co-existing (non-disjoint) NBMOs are delocalised and spatially close, which yields a large $K_{1,2}$, hence a triplet ground state, as is the case for trimethylenemethane (TMM, Fig. 5e).[21] On the other hand, disjoint NBMOs have very low interaction with each other leading to a low $K_{1,2}$, and hence a low ΔE_{ST} and nearly degenerate singlet/triplet states. This can be seen in tetramethyleneethane (TME, Fig. 5f), which has a singlet ground state with a small ΔE_{ST}.[22]

Several heuristic rules can qualitatively predict ground-state multiplicity. From a valence bond perspective, delocalised diradicals are often classified as Kekulé and non-Kekulé molecules.[23] Kekulé molecules possess direct conjugation, where the single/double bond alternation allows for at least one closed-shell resonance structure; consequently, they typically prefer a singlet ground state due to strong orbital overlap (*e.g.* *p*-xylylene[24]). Non-Kekulé molecules feature cross-conjugation instead, in which no intramolecular spin pairing is possible. A more granular framework assigns the molecular moieties connecting two radical centres as ferromagnetic or antiferromagnetic coupling units (FCU/ACU), where through-bond spin polarisation can cause the individual spins to either align or cancel each other, respectively (Fig. 6). The Ovchinnikov parity rule formalizes this assignment and predicts the ground spin state of a diradical by simply alternating the spin labels along the shortest conjugation pathway from one radical to another – identical labels at both termini predict a triplet, while opposite labels predict a singlet. This heuristic accounts for the contrasting behaviour of non-Kekulé TMM (ferromagnetic coupling, triplet) and TME (antiferromagnetic coupling, singlet), as well as the existence of triplet Kekulé diradicals[25,26] bearing an FCU connectivity. Note that the FCU/ACU model only predicts the sign, not the magnitude of J, which requires a more detailed analysis as outlined above.

In singlet diradicals, the open-shell contribution in the electronic structure can be quantified by the diradical character y_0 calculated from an analysis of the occupation numbers of the highest occupied and the lowest unoccupied natural orbitals using a broken-symmetry approach.[31] This parameter ranges from 0 to 1, where $y_0 = 0$ corresponds to a purely closed-shell molecule and $y_0 = 1$ to a purely open-shell molecule. Consequently, molecules exhibiting intermediate values are classified as diradicaloids.

In polyradicals, the exchange coupling between spins depends on the same factors, with the note that many different

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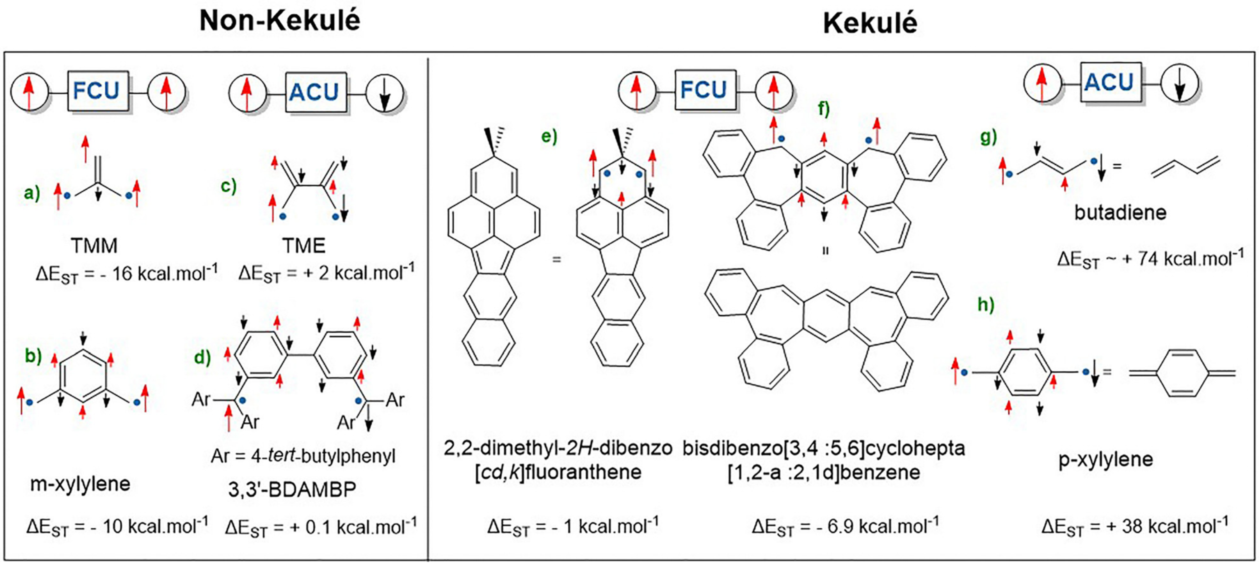

Fig. 6 Ferromagnetic and antiferromagnetic exchange coupling predicted using Ovchinnikov parity rule. Values are obtained through photoelectron spectroscopy and/or computations. Singlet–triplet energy gap are obtained from ref. 21, 22, 25, 26 and 27–30 for (a)–(h), respectively.

spin-states may coexist or even compete with one another, unless ferromagnetic or antiferromagnetic couplings are clearly preferred (when $S \gg 0$ or $S = 0$).[32,33]

2.3 Excited states

Excited states in open-shell systems were studied as early as 1944 when Lewis *et al.* described absorption and emission spectra of **1** and other triarylmethyl radicals.[34] Currently, this field is experiencing renewed interest, as open-shell systems offer unique properties for electroluminescence and quantum applications (see Sections 5.3 and 5.5).

In monoradicals with $S = 1/2$, photoexcitation promotes a transition from D_0 to D_n. In accordance with Kasha's rule, the internal conversion (IC) from D_n to the lowest doublet excited state D_1 usually occurs before the system relaxes either by fluorescence or nonradiatively to D_0. Contrary to closed-shell molecules, where the spin-forbidden but thermodynamically favourable intersystem crossing (ISC) to the triplet state T_1 is common, ISC is typically not observed in radicals. This is because the quartet excited state Q_1 requires the population of a higher orbital and, thus, is normally less stable than D_1 (Fig. 7a and b).[35]

In diradicals, the ground state can be either the singlet S_0 or triplet T_0. Singlet diradicals can fluoresce *via* S_1–S_0 transition like closed-shell molecules, while triplet diradicals exhibit spin-allowed emission (fluorescence) *via* T_1–T_0 transition (Fig. 7c and d).[36,37] A special case is presented by diradicaloids, which are molecules with a closed-shell singlet ground state but a small ΔE_{ST} comparable to the thermal energy (kT). In such cases, a thermal excitation (*via* ISC) can populate the open-shell triplet (T_1), which manifests as paramagnetic broadening in the NMR spectra and a growing ESR signal at higher temperatures.[38]

The excited states of radicals can be reshaped by their coupling with closed-shell chromophores. The nature of such excited states depends on the relative energy levels and exchange coupling between the radical and the chromophore. For example, spin coupling between a radical's doublet and a chromophore's triplet excited state can result in a quartet excited state, as further discussed in Section 5.3.

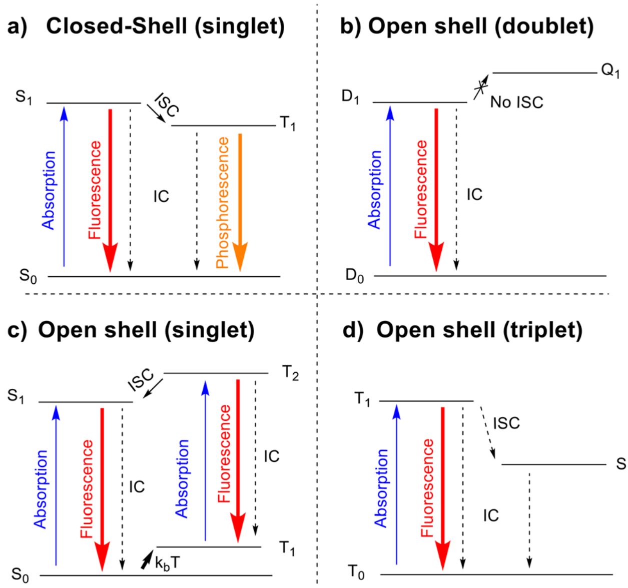

Fig. 7 Energy levels and associated photophysical processes of (a) closed-shell singlet, (b) open-shell doublet (monoradical), (c) open-shell singlet (diradical) and (d) open-shell triplet (diradical) molecules.

3 Chemistry of open-shell systems

With the above theoretical foundation, we now describe a chemist's perspective on the design of stable open-shell systems. In the literature, non-transient radicals are commonly divided into two

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categories: "persistent" radicals, which possess long half-lives (often in an inert environment), and "stable" radicals, which remain unreactive under ambient conditions and can be isolated and handled in the same manner as typical closed-shell species. Here, we focus on π-conjugated neutral radicals based on main-group elements (mostly carbon) that can be isolated and used as building blocks for functional materials. We also briefly discuss stable radical ions in Section 4.4, acknowledging these as a related but nonetheless distinct class of open-shell materials.

Neutral radicals are typically synthesised by one-electron oxidation/reduction of the corresponding anion/cation or through radical transfer (*e.g.*, hydrogen or halogen abstraction). The specific methods have recently been reviewed and will not be discussed here.[39]

3.1 Reactivity and stability of free radicals

Typical radicals, possessing freely accessible unpaired electrons, are "capable of wreaking havoc on any compound that happens to approach them".[18] To understand how to design stable radicals, one should first consider their chemical reactivity.

Radical recombination is often a barrierless reaction that forms the corresponding closed-shell species. π-Radicals can form two types of dimers: σ-dimers, such as structures **3** and **4** (Fig. 1), and π-dimers, such as the cofacial dimers of phenalenyl and olympicenyl radicals (Fig. 8).[40] The σ-dimers are connected by a classical (albeit often weak and long) σ-bond. The π-dimers are connected by a "pancake bond", a multi-electron, multi-centre bond formed by π-interactions of co-parallel molecules. Pancake bonds (typically with C···C distances of ∼2.6–3.2 Å) are much longer than σ-bonds, but still significantly shorter than van der Waals contacts.[41] σ-Dimerisation leads to closed-shell molecules, while the π-dimers can display open-shell character. Apart from homodimerisation, radicals can recombine with other radicals (the basis of radical trapping experiments) and react with other open-shell species, in particular with O_2, which is a triplet diradical in its ground state. The latter reaction was observed by Gomberg with his trityl radical **1**, which rapidly formed the peroxide **2** upon exposure to air.[1]

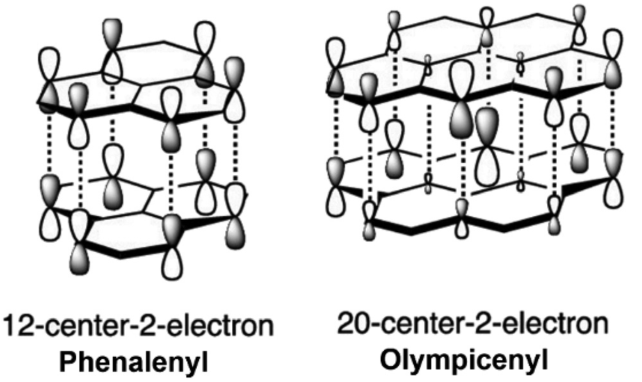

Fig. 8 Examples of structures of π-dimers of radicals. Adapted with permission from Q. Xiang, J. Guo, J. Xu, S. Ding, Z. Li, G. Li, H. Phan, Y. Gu, Y. Dang, Z. Xu, Z. Gong, W. Hu, Z. Zeng, J. Wu and Z. Sun, Stable Olympicenyl Radicals and Their π-Dimers, *J. Am. Chem. Soc.*, 2020, **142**, 11022–11031. Copyright 2020 American Chemical Society.

Persistent electron-rich radicals can react with oxidants (such as oxygen) *via* one-electron transfer, forming the corresponding closed-shell cations. This reaction limits the air stability of electron-rich radicals, such as methoxylated trityls **6**.

Generally, radical recombination *via* dimerisation or through reaction with oxygen (a triplet diradical) are the two most common types of radical reactivity, which are also the most difficult to control. The suppression of such reactivity can rely on thermodynamic stabilisation of the radical and/or destabilisation of the product (Fig. 9). Other typical radical reactions, such as hydrogen atom abstraction (HAA) and unsaturated bond addition (UBA) are generally of lower relevance for persistent radicals in the ground state. However, HAA and radical cyclisation can govern the photodegradation of otherwise highly stable chlorinated trityl radicals.[42,43]

3.2 Electronic stabilisation

Below, we summarise the strategies for the design of radicals that are stable under ambient conditions (Fig. 9).

3.2.1 Resonance effects. Delocalising the unpaired electron through resonance reduces the local spin density, which can be achieved by attaching π-conjugated units to the radical centre. Such conjugated radicals will be the focus of the following sections.

3.2.2 Inductive effects. Electron-withdrawing substituents reduce the electron density at the radical centre *via* inductive effects. The electron-withdrawing groups also lower the SOMO energy, thereby reducing the radical's tendency to undergo oxidation in air. Thus, the nonamethoxytrityl radical immediately oxidises in air to form a stable carbocation[44] while the nonachlorotrityl (TTM, **10**) is perfectly stable under air.

3.2.3 Merostabilisation. When a radical centre simultaneously interacts with both electron-donating and electron-withdrawing groups, the overall resonance stabilisation can exceed that achieved by either substituent alone. This captodative effect can be visualised with the MO diagram in Fig. 10b. The synergistic interaction of the donor and the acceptor groups with the radical leads to polarisation of the doubly-occupied HOMO−1 towards the radical centre (the point of highest SOMO amplitude). The resulting spatial proximity of the SOMO and the HOMO−1 creates a "lone-pair shielding" effect, as shown in Fig. 10a, increasing the electron–electron repulsion during radical dimerisation (one of the key factors driving instability).[45] Furthermore, simultaneous interactions with both the donor and the acceptor can provide additional stabilisation of the radical by suppressing its electrophilicity and nucleophilicity. Classical examples of captodative stabilisation in radicals are the persistent dicyano(dimethylaminophenyl)methyl and *N*-alkyl-4-carbomethoxypyridinyl radicals (Fig. 9).[46] The latter is sufficiently stable for distillation and crystallisation.[47]

3.2.4 Heteroatom effects. Heteroatoms bearing lone electron pairs, located at or adjacent to the radical centre, often enhance the stability of the radical. A special case is the stable oxygen molecule, which is a triplet diradical in its ground state. Here, the overlap of the p_y and p_z orbitals creates a pair of "two-centre, three-electron $\pi_{O\text{–}O}$-bonds" with significant resonance

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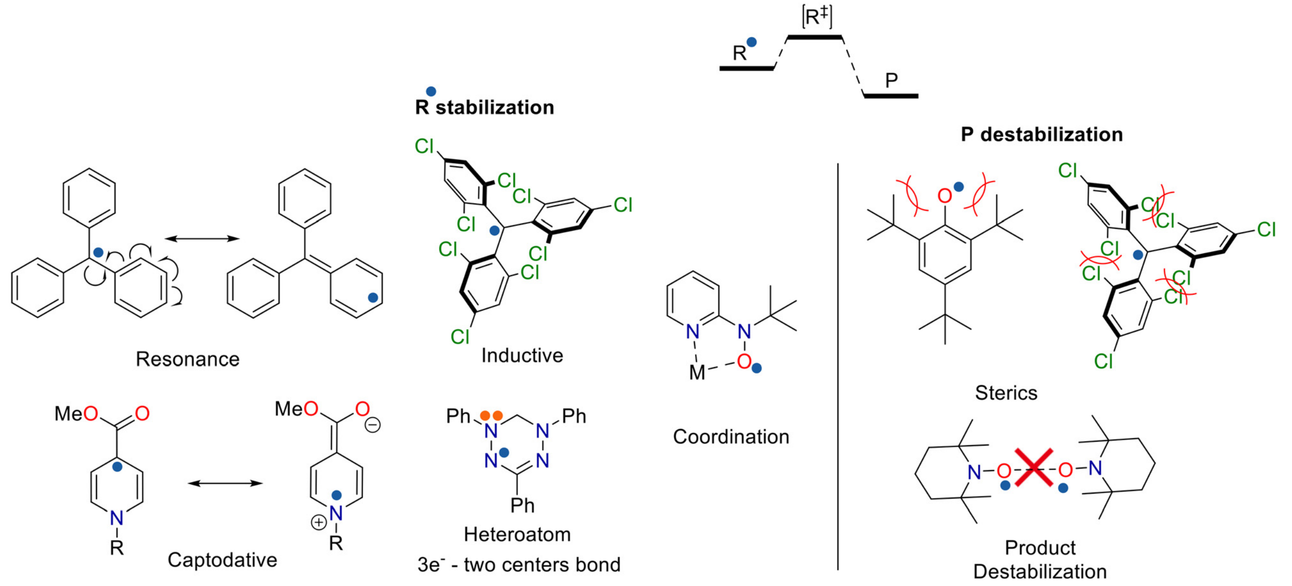

Fig. 9 General approaches to suppress the reactivity of free radicals *via* stabilisation of the radical and destabilisation of their reaction products.

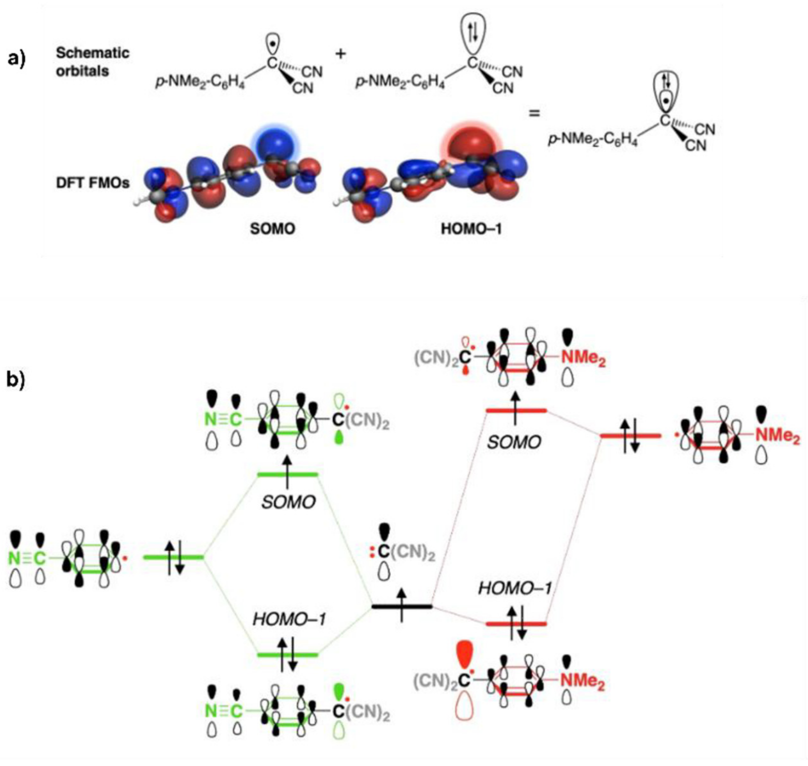

Fig. 10 (a) Schematic representation of the "lone-pair shielding" effect. (b) Schematic MO diagram showing how the HOMO−1 and the SOMO of $RPh(CN)_2C^{\bullet}$ radicals arise from the interaction of $RPh^{\bullet}$ + $C(CN)_2^{\bullet\bullet}$ for R = CN *versus* NMe_2. Adapted from E. Blokker, M. ten Brink, J. M. van der Schuur, T. A. Hamlin and F. M. Bickelhaupt, Origin of the Captodative Effect: The Lone-Pair Shielded Radical, *Chem. Eur. J.*, 2023, **1**, e202300006. © The Authors. ChemistryEurope published by Chemistry Europe and Wiley-VCH GmbH. Licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

stabilisation.[48] A similar stabilisation effect operates in aminoxyl radicals as well (Fig. 11a). The relative stability of heteroatom-centred radicals can be further explained by the destabilisation of the products of their recombination reactions (dimerisation, reaction with $^3O_2$). The bonds formed in such reactions are thermodynamically disfavoured by the repulsive interactions of non-bonding orbitals (lone pairs).[49]

3.2.5 **Coordination.** Radical centres located on heteroatoms can also be stabilised through coordination to metals,[50] rare earths[51] or other atoms such as phosphine.[52] For example,

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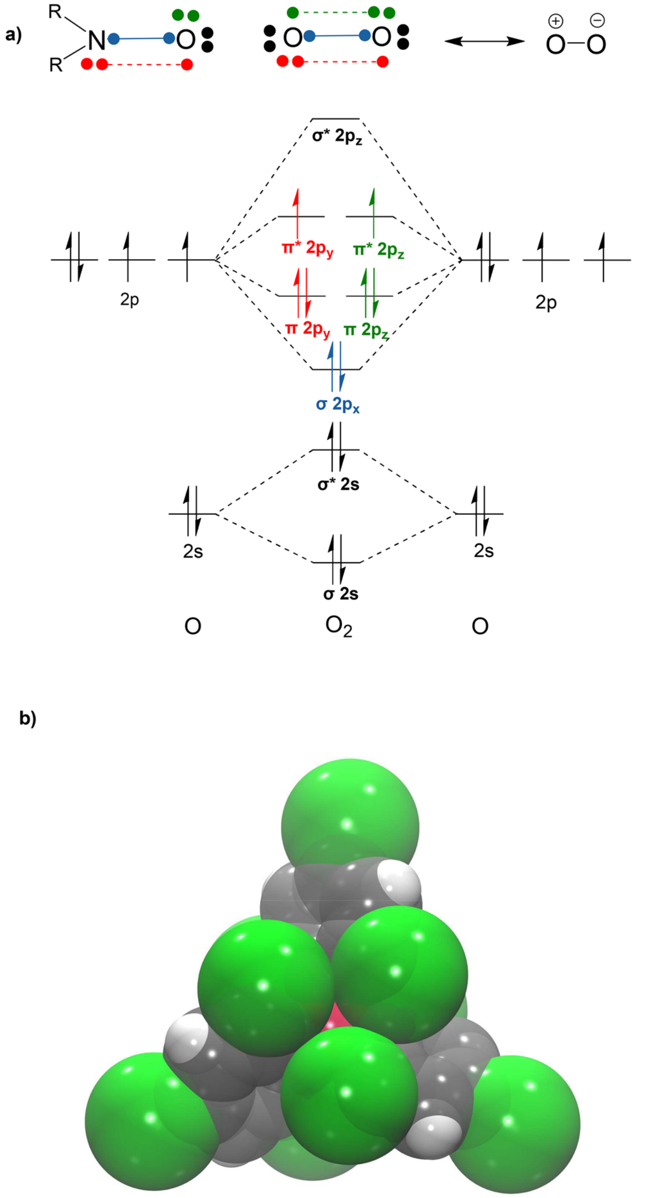

Fig. 11 (a) Two-centre three-electron π-bonds in O_2 and a nitroxide radical, and molecular orbital diagram of O_2. (b) Space filled model representation of TTM in which the central carbon is highlighted in red.

the unstable *t*-butyl-2-pyridylnitroxide (Fig. 9) can be readily isolated after coordination to Ni(II) or Cu(II).[53]

3.3 Steric protection

Placing bulky groups around the radical centre physically shields the spin density and reduces the probability of bimolecular reactions such as homocoupling. This spatial protection can render the corresponding dimers thermodynamically unfavourable. All carbon-centred and most heteroatom-centred stable neutral radicals rely on steric protection, typically in combination with electronic stabilisation. An instructive example is the well-studied tris-*t*-butylphenoxy radical, with a half-life of 7 days at 25 °C under N_2, compared with the unsubstituted phenoxy radical, which cannot be isolated.[54] Some of the most stable carbon-centred radicals are designed by introducing bulky substituents in Gomberg's trityl radical (*e.g.*, TTM **10**), which fill the space around the radical centre blocking its reactivity (Fig. 11b).

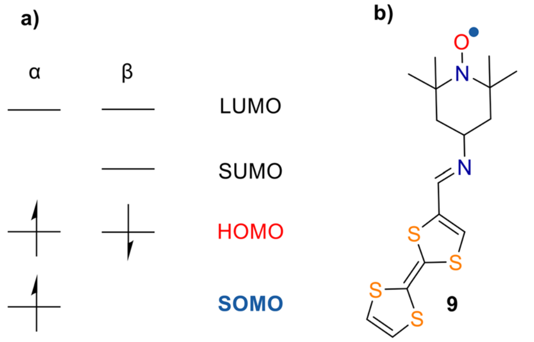

Fig. 12 (a) Molecular orbital diagram representing a radical with SOMO–HOMO inversion. (b) Example of the seminal radical with SOMO–HOMO inversion.

3.4 SOMO–HOMO inversion

An interesting and unusual feature of certain radical systems is the possibility of SOMO–HOMO inversion, where the SOMO is no longer the lowest occupied orbital in the molecule (Fig. 12a). The result of such an electronic configuration is that upon oxidation, the electron is taken from the (doubly occupied) HOMO rather than from the SOMO, leading to a diradical cation. The chemical design of such systems generally relies on attaching a strong donor moiety to the radical centre. Since the first report of SOMO–HOMO inversion in TEMPO–TTF **9** in 1993 (Fig. 12b),[55] this concept has attracted growing attention.[56,57] This phenomenon is often described as a violation of the Aufbau principle, since the SOMO lies below the HOMO, but we note that the SUMO still lies above the HOMO, hence the orbitals remain occupied in the order of their energy levels.[56] It has been suggested that such SOMO–HOMO inversion leads to increased chemical and photostability in these radicals. In our opinion, the observed stabilisation in such systems can be explained by general donor-radical interactions (*i.e.*, the captodative effect or charge-transfer in the excited state) and does not necessarily require SOMO–HOMO inversion.

4 Molecular design of stable π-radicals

Now, we turn to examine stable open-shell systems that have been experimentally studied. Chemically, they can be categorised based on the atoms bearing the unpaired electrons, their charge, their lifetimes (persistence), their number of unpaired electrons, and their structure. We start by examining neutral monoradicals, some di- and poly-radical systems, and briefly touch on radical ions.

4.1 C-centred monoradicals

We here discuss the most prevalent carbon-centred neutral π-conjugated radical building blocks highlighting the above-mentioned stabilisation strategies.

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4.1.1 Triarylmethyl radicals. The large majority of persistent C-centred radicals are derivatives of triphenylmethyl, even though the parent (unsubstituted) trityl readily dimerises in solution and reacts with oxygen (Fig. 1). Substituents introduced in the *ortho*-positions of trityl sterically stabilise the radical, and further substitution in the para-position can make it completely air-stable. Indeed, tris(2,4,6-trichlorophenyl)methyl (TTM, **10**) and perchlorotriphenylmethyl (PTM, **11**)[58,59] are some of the most stable and the most studied C-centred radicals developed by Ballester *et al.* (Barcelona group) (Fig. 13). Chlorine atoms in the *ortho*-position provide both steric protection and inductive stabilisation, making these radicals oxidatively, thermally, and chemically robust. Air-stable trityl radicals can also be made with bromine substituents,[60] but fluorine appears to be too small to provide full steric protection against oxygen.[61] Perfluorinated trityl radicals **12** with Cl/Br substituents in the *para*-position were recently isolated and characterised by X-ray crystallography but they still react with oxygen to form peroxides in a matter of days.[62] A number of TTM/PTM derivatives featuring carboxy (**13a**[63] and **14a**[64]), iodo (**13b**),[65] fluoro (**14b**),[62] acetylene (**13c**),[66] and nitro groups (**14c**),[67] have been developed through the years. Of particular importance are carbazole-substituted TTM derivatives which came into prominence since the discovery of highly efficient luminescence in radicals **15** by Julia and co-workers.[68,69] Several dozen various carbazole-TTM derivatives have been synthesised, including **16**, which brought a wide attention to the field of radical emitters by demonstrating nearly 100% internal quantum efficiency in OLEDs devices.[70] These properties will be further discussed in the following sections. Highly emissive TTM and PTM derivatives have also been developed with triarylamine (**17**)[71,72] and, recently, diphenylphosphine oxide (**18**)[73] substituents.

Beyond halogens, other substituents have been used to stabilise the central carbon in trityl radicals. Several trityl radicals with electron-donating substituents have been reported, even though they usually show a lower stability. The tris(3,5-di-*tert*-butylphenyl)-methyl radical (**19**)[74] was found to be bulky enough to prevent dimerisation but, without *ortho* substituents, it still degrades in air through the formation of peroxides. While the peroxide formation can be blocked with *ortho*-methoxy substituents, such as in tris(2,6-dimethoxyphenyl)methyl **20**,[75] the low oxidation potential of the methoxylated radical facilitates its oxidation in air, forming stable carbocations. Air-stable trityl radicals with tunable SOMO levels have been recently obtained by combining both chlorine and methoxy substituents.[44] Another notable example is the sulfanylated tris(2,3,5,6-tetrathiaaryl)methyl **21**, which is completely air stable, and its derivatives have been widely used in biological sensing.[76]

Steric stabilisation is also achieved in π-extended trityl radicals with extra fused benzene rings. Thus, trianthrylmethyl **22** was reported to be highly air-stable (no decomposition in aerated solution for at least one month), but only when the anthryl groups are capped at the 10-position by mesityl substituents.[77] We note that the steric demands on the aromatic rings control the dihedral angle between the central sp^2-carbon and the aryl substituents, which affects the orbital overlap. The latter can be significantly increased in triarylmethyl radicals by fusing of two of their aryl rings, either directly as in dibenzofluorenyl **23**,[78] or *via* heteroatom bridges as in xanthyl **24a** and its thio/seleno-analogues **24b/c**.[79] Nonetheless, achieving air stability in these radicals still requires sterically bulky (anthryl or trichlorophenyl) substituents which are oriented nearly orthogonally to the fused ring system, screening the radical centre. Fusing all three rings in triarylmethyls leads to (hetero)-triangulenes **25**, another famous family of radicals. Devoid of any steric protection, the trioxatriangulene **25a** readily forms σ-dimers and quickly reacts with oxygen.[80] However, trioxotriangulene **25b** and its derivatives are highly air-stable due to strong resonance stabilisation of the spin on the carbonyl groups, and they only show reversible π-dimerisation in solution and the solid state.[81,82] Other important examples of triangulene monoradicals include the dicyanoethylene-bridged **25c**[83] and the boron-bridged triangulene **26**.[84] Through the exploration of π-extended fused porphyrins, a serendipitous reaction spontaneously created the air-stable radical **27a**, which can be viewed as a doubly-fused triarylmethyl with one heteroaryl (porphyrin) group.[85] Extending the conjugation by benzannulation in **27b** creates a chiral (and enantiomerically stable) [6]helicene moiety which led to intriguing magnetic and chiroptical properties.[86]

Several heteroaromatic groups have been used in place of phenyl to afford stable triarylmethyl radicals. Most of these still rely on steric protection of chlorine substituents in *ortho*-positions, and one of the first reported examples was tris(2,4,5-trichloro-3-thienyl)methyl **28**.[87] The use of (di)chloropyridyl groups proved to be particularly useful as it results in strongly luminescent radicals, such as tris(2,5-dichloro-4-pyridyl)methyl (**29**) which showed a ∼10 000 fold increase in photostability compared to TTM.[88] The coordinating ability of the pyridine nitrogen adds further functionality to such molecules, and **29** was utilised to create the first doublet-emitting 2D coordination polymer.[88] Nitrogen atoms in triarylmethyl radicals can also form intramolecular hydrogen bonds, increasing the rigidity of the molecule. This effect has been explored in diaza-TTM radical **30**, which displayed highly efficient NIR emission with excellent photostability.[89] As described above for TTM, the optoelectronic properties of such aza-TTM radicals can be manipulated by coupling with amine (**31**) functional group.[90] A different type of luminescent heteroarylmethyl radicals is the chlorinated carbazolyldiphenylmethyl **32**, with carbazole's nitrogen directly attached to the radical centre. Similar to Julia's carbazolyltrityl radicals **15**, **32** showed improved photostability and luminescence efficiency compared to TTM.[91] For more details regarding trityl radicals, we refer the reader to ref. 92 and 93 and to supplementary information (SI) for an extensive list of reported trityl derivatives.

4.1.2 Dicyanoarylmethyl radicals. One or two of the aryl groups in triarylmethyls can be replaced with other resonance-stabilizing but non-aromatic groups to afford persistent, and in some cases, remarkably stable radicals. A particularly notable example is the dicyanoarylmethyl radical family whose stability is brought about by the strong resonance effect of the two cyano groups. Despite the lack of steric protection, such radicals

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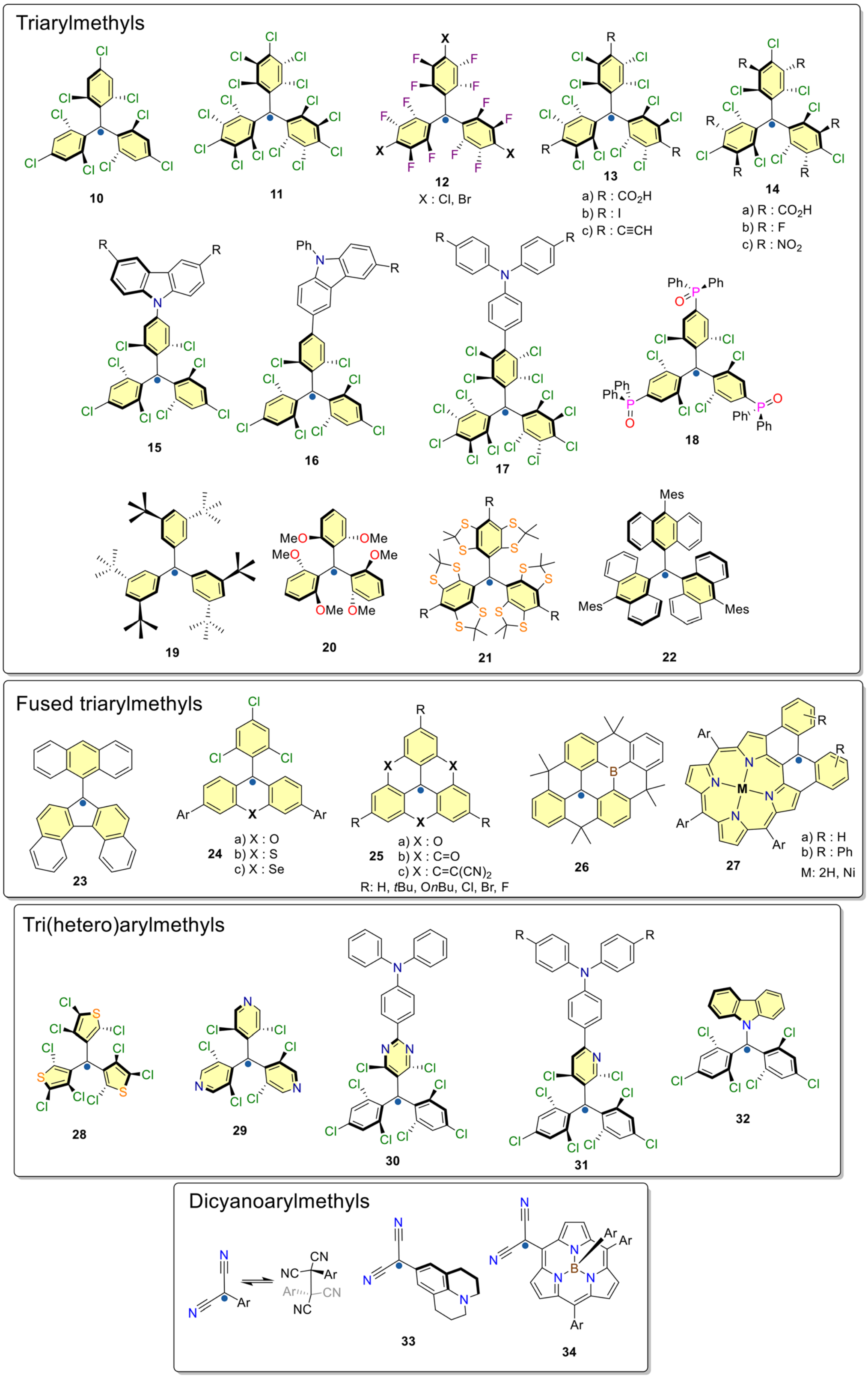

Fig. 13 Categories and examples of persistent C-centred arylmethyl radicals.

can be air-stable, although many of them undergo reversible σ-dimerisation. A further stabilisation of such radicals is achieved with electron-rich aryl groups *via* the captodative effect: the julolidinedicyanomethyl **33** preferentially forms weak π-dimers[94] while the boron(III) subporphyrinyldicyanomethyl **34** exists in its monomeric radical form in solution.[95]

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4.1.3 Highly delocalised C-radicals. While significant spin delocalisation is present in the arylmethyl radicals discussed above, in all of these, most of the spin is still concentrated on one (methyl) carbon, as depicted by their most stable resonance form. In contrast, highly delocalised radicals can be represented with several *equivalent* resonance forms leading to a very high spin delocalisation around the conjugated structure (Fig. 14).

An early example of extreme radical stability achieved *via* multiple resonance delocalisation is 1,3-bisdiphenylene-2-phenylallyl **35**, which was reported to be shelf-stable for > 20 years[96] (although recent studies[97] suggest slow degradation of solid **35** when exposed to air). Interestingly, Frederick Koelsch prepared this compound in 1932, but the editors of *J. Am. Chem. Soc.* rejected the paper due to its lack of reactivity with air which was thought to be incompatible with a radical. 25 years later, Koelsch measured the ESR spectrum, confirming its radical nature. The paper was resubmitted to *J. Am. Chem. Soc.* and accepted without changes.[96]

Another large and important family of stable radicals in this category is represented by phenalenyl **36**, which can be viewed as the smallest open-shell fragment of graphene and was extensively studied in the design of conducting materials. The unpaired electron in **36** is equally delocalised among six peri-carbons represented by six resonance structures, while the seventh, high symmetry resonance structure shown in the middle, is destabilised by antiaromaticity of the 12-electron outer ring. Although the parent phenalenyl **36a** readily undergoes σ-dimerisation,[98,99] a number of substituted phenalenyl derivatives have been isolated as stable radicals, including the sterically encumbered tris-*tert*-butylphenalenyl **36b**,[100] electronically stabilised tribromophenalenyl **36c**,[101] perchlorophenalenyl **37**[102] and 1,9-dithiophenalenyl **38**.[103] The phenalenyl moiety can be found in a number of larger polycyclic hydrocarbon radicals such as **39**,[104] phenalenyl[5]-helicene **40**[105] and olympicenyl **41**.[40]

A number of highly delocalised stable radicals have been developed by connecting tri(hetero)arylmethyl groups in macrocyclic porphyrinoid-type π-frameworks (for a detailed review, see ref. 106), with prominent examples including corrole **42**[107] and cyclopentathiophene **43**.[108] Incorporating the unpaired electron within the cyclic π-conjugated structure also enable switching between the 4*n* + 2 aromatic and 4*n* antiaromatic state by reversible one-electron oxidation/reduction of such radicals.[108]

Finally, a very peculiar yet highly air-stable ("for weeks as a solid and for days in solution") radical is the pentakis(triisopropylsilylethynyl)cyclopentadienyl **44**, which, to our knowledge, is the only example of a stable C-centred radical devoid of any aromatic rings.[109] Despite spin delocalisation among the five cyclopentadienyl carbons, such open structures are prone to dimerisation and/or peroxide formation in air, which is the case for the pentaphenylcyclopentadienyl radical. The unusual stability of **44** was explained by the strong propargylic/allenic resonance stabilisation provided by the five alkyne groups.

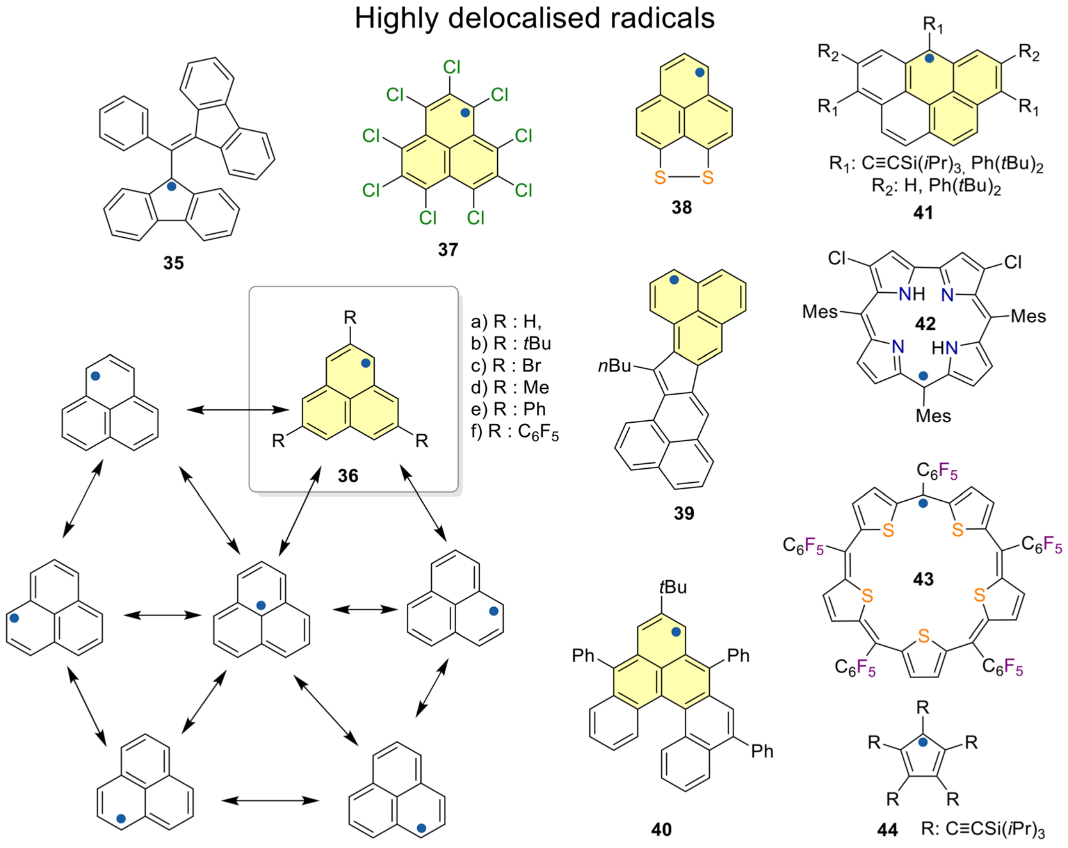

Fig. 14 Examples of highly delocalised persistent C-centred radicals.

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4.2 *N*- and *O*-centred monoradicals

Many stable heteroatom-based neutral radicals have been synthesised alongside carbon radicals. As discussed previously, the lone pair of heteroatoms can have a significant effect on the stabilisation of radicals by creating a "two-centre, three-electron π-bonds" with the unpaired electrons. Here we summarise the common nitrogen and oxygen-centred radicals (Fig. 15) and refer the reader to a dedicated review for other heteroatom-centred radicals.[110]

Oxygen-based radicals are most commonly represented by aminoxyls (nitroxide radicals). Their stability is generally defined by the moieties adjacent to the N–O$^\bullet$ group. Thus, blocking the possible dehydrogenation pathways by methylating the adjacent CH_2 moieties affords (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, **45**), one of the most stable and commonly used neutral free radicals.[111] These radicals are historically known for their high stability, versatility and redox/magnetic properties.[112]

Unlike TEMPO **45**, π-conjugated nitroxide radicals such as diphenyl nitroxide **46a** and *tert*-butyl phenyl nitroxide **47** are less stable, as the spin delocalisation to the para-position of the phenyl rings enables dimerisation and peroxide formation.[113] Their stability can be improved by blocking the reactive para-position, as shown in 4,4′-dianisyl (**46b**) and 4,4′-dinitrophenyl (**46c**) nitroxides.[113] Introducing chelating groups into π-conjugated nitroxide radicals enables the design of paramagnetic ligands, as demonstrated for bipyridinyl nitroxide **48**, an air-stable radical which forms ferromagnetically coupled complexes with copper and nickel *via* tridentate (*N*,*N*,*O*) coordination.[114]

A very strong stabilisation effect can be achieved by conjugating a C═N bond to the nitroxide which creates a dinitrogen allylic-like structure. This strategy is implemented in imino nitroxides **49**[115] and nitronyl nitroxides **50**,[116] which have also been extensively studied for their coordination properties.[117] The stability of nitronyl nitroxide radicals is maintained upon replacing the blocking methyl groups with a fused benzene ring, which allows for stronger intermolecular contacts without σ-dimerisation. Accordingly, a number of derivatives of radical **51** have been studied in pursuit of organic magnets.[118]

The importance of the stabilizing effect of the adjacent nitrogen's lone pair can be assessed by examining the behavior of other O-radicals lacking such a structure. While simple phenoxyl radicals have been observed in solutions of diaryl peroxides as early as in 1922,[119] they are too reactive and, in most cases, could not be isolated. The first persistent phenoxy radical, 2,4,6-tri-*tert*-butylphenoxyl **52**, was synthesised in 1953.[120] The first air-stable phenoxy radical **53**, named galvinoxyl after its inventor Galvin Coopinger, was discovered in 1956, and its stability is owed to an extensive delocalisation and large steric protection.[121] Several other air-stable phenoxy radicals have been developed by combining the steric protection of an *ortho*-*tert*-Bu group with electronic delocalisation, *e.g.* **54**[122] and **55**.[123] For more details about phenoxyl radicals, interested readers should refer to the dedicated review.[54]

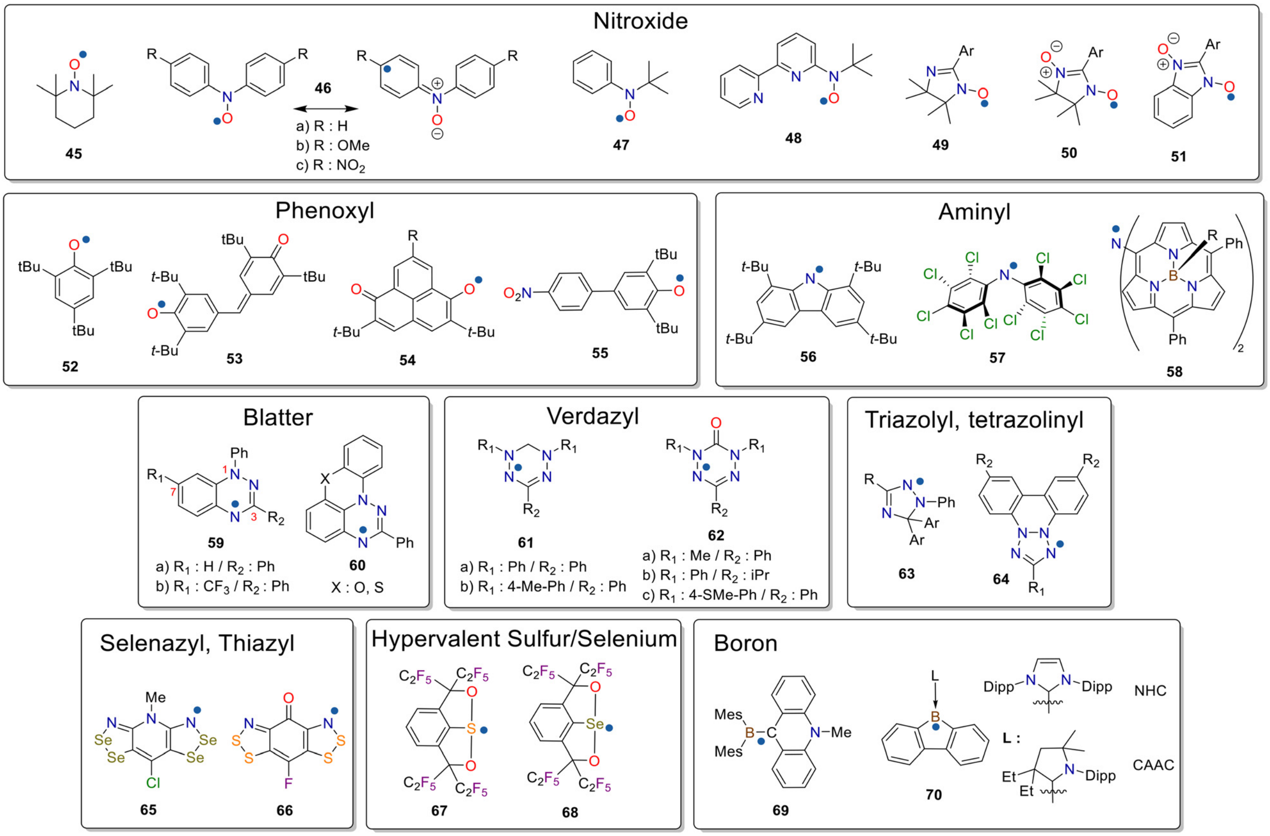

Fig. 15 Categories and examples of persistent heteroatom-centred radicals.

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The discovery of nitrogen-centred radicals traces back to Wieland's 1911 work on the decomposition of tetraphenylhydrazine leading to the meta-stable diphenylaminyl.[124] However, it was not until the early 1970s that air-stable aminyl radicals such as tetra-*tert*-butylcarbazyl **56**[125] and perchlorodiphenylaminyl **57**[126] emerged. The latter can be seen as an analogue of PTM **11**, highlighting that N-centred radicals require lesser steric protection compared to C-centred radicals. More recently, the family of stable aminyl radicals has been extended to involve boron subporphyrins **58**.[127]

Similar to nitroxide radicals, the adjacent nitrogen atoms enable "two-centre, three-electron π-bonds", which greatly enhances the stability of hydrazyl radicals. A classic example is α,α-diphenyl-β-picrylhydrazyl radical **8**,[8] one of the common ESR standards, commonly known as *dpph*.

From these early insights, several families of N-heterocyclic radicals have been developed. Among the most prominent are the 1,2,4-triazine-based Blatter radicals, with the parent compound **59a** reported in 1968.[128] Blatter radicals are notable for their high stability and configurability *via* three different substitution sites that enable tuning of their properties.[129] Notably, a trifluoromethyl group at the 7-position (**59b**) confers high thermal stability ($T_{\text{dec}} \sim$ 288 °C) and resistance to oxidative stress (MnO_2, $KMnO_4$) to these radicals.[130] Beyond simple substitution, peri-annulation can be used to planarise and enhance π-conjugation in Blatter radicals, as in near-IR absorbing radical **60**.[131]

In parallel, 1,2,4,5-tetrazine-based verdazyl radicals **61** were introduced by Kuhn and Trischmann in 1964 (**61a**), with stability and versatility comparable to Blatter radicals.[132] Unlike many other persistent radicals, verdazyls and oxo-verdazyls (**62a**[133]) do not require bulky substituents for stabilisation. Their tunability and exceptional stability make them particularly attractive for electrochemical applications, with recent demonstrations in redox flow batteries (**61b**, **62b**),[134,135] and single-molecule junctions (**62c**).[136]

Five-membered-ring nitrogen-centred radical families such as triazolyl (**63**)[137,138] and tetrazolinyl (**64**)[139] have received less attention, but some of them can also display very high air and thermal stability.[140] We refer the readers to other reviews for a more detailed overview of N-centred stable radicals.[129,141–143]

Chalcogen atoms such as sulphur and selenium have also been widely used to stabilise π-radicals by forming "two-centre, three-electron π-bonds", as discussed above. A number of thiazyl and related radicals have been developed as molecular conductors and magnets.[144,145] While these species are generally stable in air, they readily dimerise, which is detrimental for their conducting properties. Circumventing this problem by increasing π-delocalisation was extensively explored by Oakley's group, exemplified by diselenazyl **65**[146] and oxodithiazoyl **66**.[147] While σ-dimerisation is completely arrested in these radicals, a weak π-dimerisation is still observed in their crystals, and is the main obstacle for achieving metallic conductivity in ambient conditions.[147] In contrast, no dimerisation was observed neither in solution nor in the solid state for hypervalent sulphur **67** and selenium **68** π -radicals, which have been characterised by XRD and ESR.[148]

Boron-centred radicals have attracted considerable recent interest as a means of expanding radical chemistry, mostly fuelled by the main-group synthetic chemistry community. The first persistent boron radical, dimesitylacridylboron **69**, was reported in 2007 by Gabbaï and co-workers.[149] Its persistence could be explained by a boron-carbon "two-centre, three-electron π-bonds", as well as the captodative effect with the boron as acceptor and the *N*-methylacridine as donor. A significant recent breakthrough in the field was the use of strongly σ-donating and π-accepting N-heterocyclic carbene (NHC) or cyclic (alkyl)(amino)carbene (CAAC) ligands. Their coordination effectively stabilises the formally divalent boron radical centre, as demonstrated by Gilliard and co-workers for borafluorene radicals **70**.[150] We note, however, that these boron-centred radicals are very electron-rich and are only stable under an inert atmosphere.

4.3 Diradicals and polyradicals

The liberty of organic chemistry enables the assembly of neutral monoradical building blocks into complex architectures with full structural control. A large number of persistent diradicals, triradicals, and polyradical systems have been prepared over the years.

As with monoradicals, the stability of polyradicals is largely determined by the extent of the delocalisation of spin density, as well as other electronic/steric effects. Steric protection is commonly executed by attaching bulky mesityl groups which were used, *e.g.*, to stabilise the otherwise highly reactive triplet triangulene diradical (**98**).[151] Currently, the two major design strategies for diradicals are: (1) connecting two stable radicals *via* an aromatic bridge; (2) controlling topology in polycyclic aromatic hydrocarbons.

4.3.1 Connecting two stable radicals by π-conjugated bridges. The simplest strategy to create a stable diradical with controlled magnetic interaction between the spins is to connect two stable monoradical building blocks with aromatic bridges (Fig. 16). The first examples of this strategy are represented by Thiele's hydrocarbon **71**,[152] and its π-extended derivative Chichibabin's hydrocarbon **72**.[153] Both **71** and **72** are diamagnetic at room temperature, and their ground states are best described by the quinoidal, closed-shell resonance structure. Such molecules are now referred to as diradicaloids, to acknowledge the partial diradical character manifested in their reactivity and low-lying triplet state.[154] Such spin-pairing in quinodimethane-type diradicals is accompanied by the loss of aromatic stabilisation of the bridges; thus, increasing the number of aromatic rings should destabilise the closed-shell structure. This was indeed observed for Müller's hydrocarbons **73** and **74**, both of which were proven to be open-shell molecules by magnetic measurements.[155] Notably, such spin-pairing is impossible with meta-connected bridges, as was already realised more than a century ago in Schlenk's hydrocarbons **75**[156] and **76**,[157] which represent the first reported non-Kekulé persistent diradicals.

All of the above parent (unsubstituted) diradicals and diradicaloids are not very stable and react with oxygen, but their synthesis provided the foundation for the currently booming field of diradicals.[33,158] Many examples of stable diradicals inspired by these parent molecules have been synthesised since

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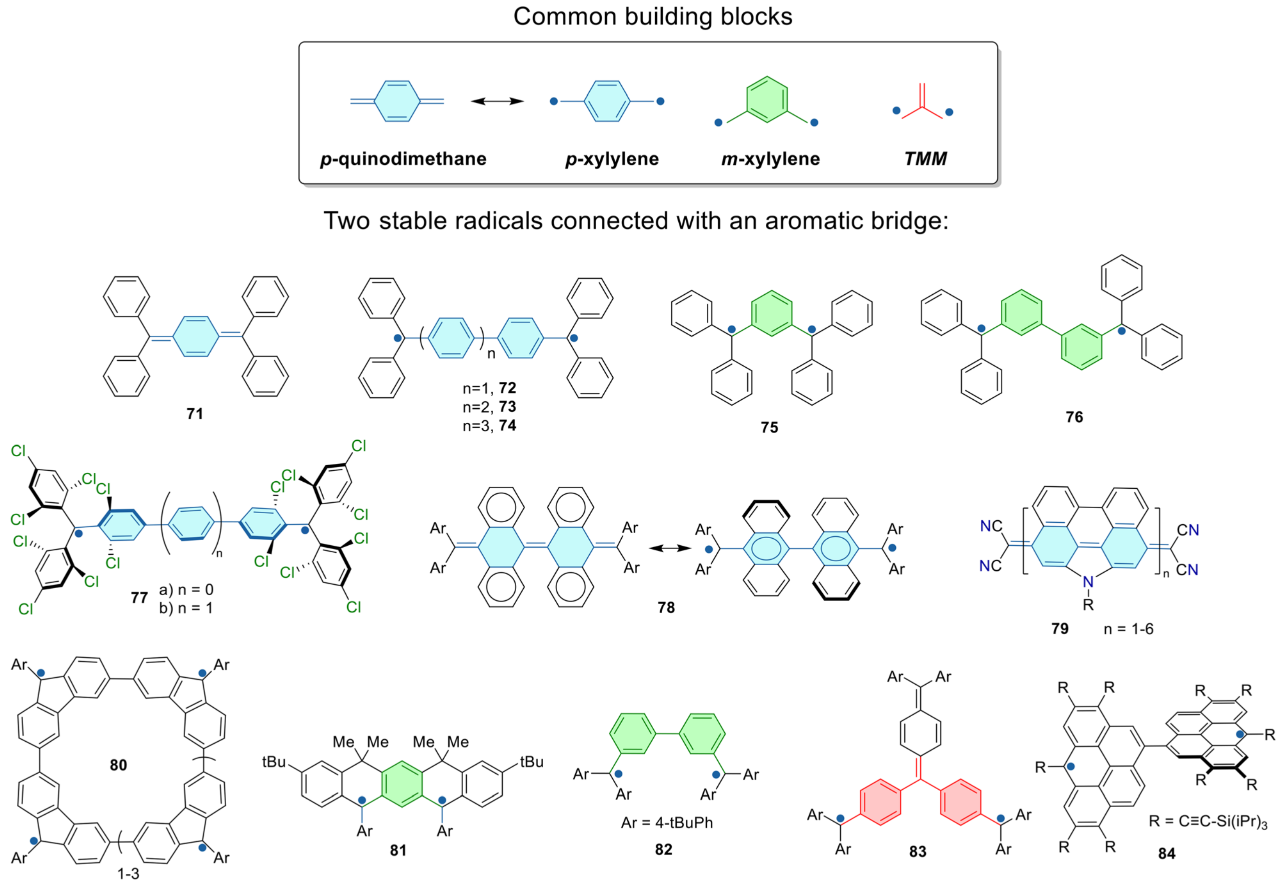

Fig. 16 Examples of persistent C-centred diradicals and polyradicals connected with an aromatic bridge.

then, such as the chlorinated Chichibabin diradical **77a**[159] and Müller diradical **77b**.[160] Another illustration of tunable diradical character in *p*-quinodimethane derivatives is provided by compounds **78**[161] and **79**.[162] In both cases, the benzannulation of the linker stabilises the closed-shell quinoidal form according to Clar's sextet rule,[163] while the sterically induced twist between the anthracene (in **78**) and perylene (in **79**) linkers favours the open-shell diradical form. Through an interplay of these two factors, the ground state structure dianthracene-bridged **78** can be either closed shell or open shell triplet depending on the terminal Ar groups, and the ground structure of **79** evolves from a closed-shell quinoid (n = 1) to a diradicaloid (n = 2–4) and ultimately to a *bi*radical (two weakly interacting doublets) for n = 5–6. An interesting implementation of the Chichibabin diradical motif is the macrocyclic cyclo[*n*]fluorenyl **80**. The even-membered macrocycles **80** are diradicaloids with a small singlet–triplet gap which decreases with the growing size of the ring (ΔE_{ST} = 2.8 kcal mol^{-1} for n = 4; 1.7 kcal mol^{-1} for n = 6). The odd-membered macrocycle (n = 5) is formally a monoradical, but with a similarly small doublet–quartet gap (1.7 kcal mol^{-1}).[164]

Rajca and co-workers investigated stable *m*-xylylene (Schlenk-type) diradicals **81**[165] and **82**,[28] both of which are non-Kekulé systems with no possible closed-shell structure, but their spin state varies with the molecular structure. Consistent with Ovchinnikov parity rule (Fig. 6), the planar Schlenk-type diradical **81** exhibits a triplet ground state,[165] whereas its biphenyl analogue **82** adopts a singlet ground state, albeit with a very small singlet/triplet gap.[28]

Another common design of non-Kekulé triplet diradicals is based on the trimethylenemethane (TMM) motif. A variant of this design has been implemented in stable (in the absence of air) diradical **83** which showed strong ferromagnetic coupling in a triplet ground state.[166] Finally, a notable recent example of non-Kekulé diradicals is biolympicenyl **84** which was reported to have a remarkably high stability (half-life >3 years in solution in air).[167] The disjoint NBMOs in this diradical (as discussed in Section 2.2) lead to a singlet ground state.

4.3.2 Polycyclic aromatic hydrocarbon (PAH) diradicals.

Another general approach of diradical design is based on controlling the topology of planar conjugated polycyclic systems. Compared to most π-bridged diradicals discussed above, the rigid coplanar structure of polycyclic systems leads to a stronger interaction between the unpaired electrons. The open-shell electronic structure can be enforced by the topology of the ring connectivity (in non-Kékulé diradicals), and the aromatic stabilisation gain in the diradical resonance form following Clar's sextet rule (in Kekulé diradicals). The latter principle is exemplified in longer acenes (**85**): calculations predict a singlet diradical ground state starting from heptacene,[168] which explains their chemical instability (in the absence of sterically

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protecting substituents). Several highly stable diradicals with a singlet ground state have been obtained by fusing multiple acene moieties and blocking reactive sites, such as perihexacene **86**[169] and rylene nanoribbons **87**[170] (Fig. 17).

Common π-diradical motifs discussed in the previous section such as TMM and *p*-, *m*-, *o*-xylylene units have been widely incorporated into PAH diradical(oid)s (*cf.* **88–94**). One of the earliest examples of PAHs with significant diradical character are zethrenes **88** ($n = 0$), originally developed by Clar.[171] As with other *p*-xylylene/*p*-quinodimethane-type diradicals, increasing the size of the aromatic bridge favours the open-shell state, as was demonstrated for substituted octazethrene ($n = 2$).[172] The singlet open-shell character in Kekulé PAHs can often be enforced by introducing antiaromaticity, which inherently favours the diradical structure.[173] This approach has been demonstrated with many pentalene (**89**),[174] bisphenalenyl (**90**)[175] and indenofluorene (**91**,[176,177] **92**,[178] **93**[179]) derivatives. Importantly, the complex connectivity in PAH diradicals can give rise to spin interactions distinct from those described in the previous section. Thus, *m*-xylylene- and TMM-motifs produce non-Kekulé structures with triplet ground state in linearly connected diradicals (*e.g.*, **81**, **83**), but embedding these units in PAH diradicals **89**, **93**, **94**[180] leads to Kekulé diradicals with a singlet ground state.

As mentioned above, the spin recombination in Kekulé PAH diradicals can be suppressed by aromatic stabilisation of the open-shell diradical form and antiaromatic destabilisation of the closed-shell quinoidal form. Nonetheless, achieving the triplet ground state in such systems is generally difficult. In principle, the inclusion of ferromagnetic coupling units such as *m*-xylylene can enhance electron exchange interactions, favouring the triplet state. In practice, only a few examples of Kekulé PAH diradicals with triplet ground states have been reported, and accurately predicting their ground states remains a challenge. Thus, the recently synthesised diradicals **95**[26] and **96**[181]

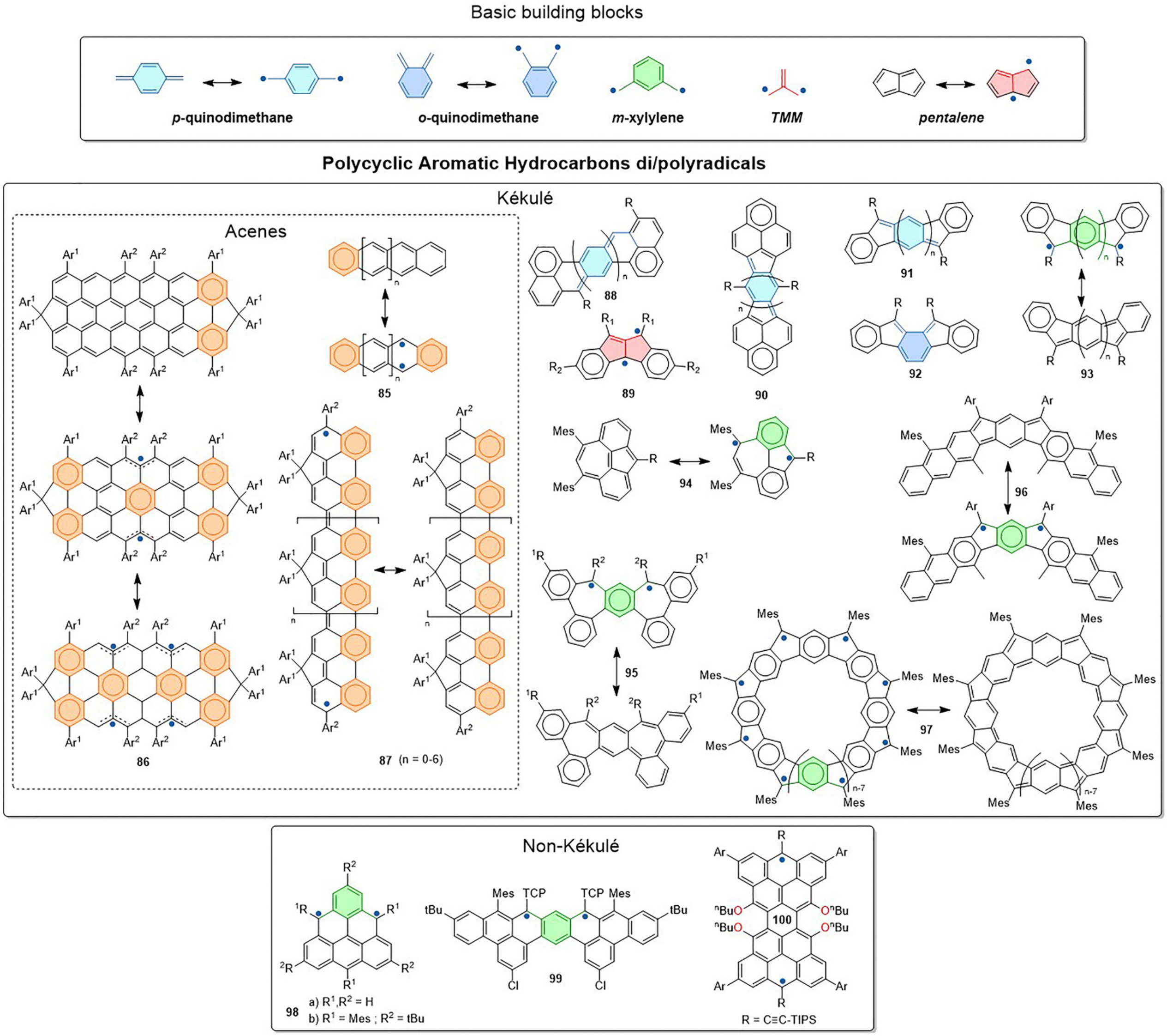

Fig. 17 Examples of persistent polycyclic aromatic hydrocarbon diradicals and polyradicals.

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have an experimentally confirmed triplet ground state, while the structurally similar **93**[179] is a singlet diradical. An interesting example of triplet-ground state Kekulé diradicals is the series of annulenes **97** developed by Jishan Wu and co-workers.[182] Their ground state is controlled by the interplay between the aromaticity/antiaromaticity of the inner and outer rings, leading to either a singlet or a triplet ground state depending on the size of the molecule.

Among non-Kekulé PAHs, arguably the most famous example is Clar's triangulene **98**.[183] While the unsubstituted **98a** is extremely unstable in ambient conditions, its on-surface synthesis on Au(111) under ultra-high vacuum has been demonstrated using non-contact atomic force microscopy (AFM).[184] When protected with sterically bulky substituents, it can also be synthesised under inert conditions in solution, and the crystal structure of **98b** was recently reported.[151] The *m*-xylylene motif in non-Kekulé PAHs, including the triangulene **98** and dibenzoheptacene **99**[185] reliably predicts a triplet ground state in these diradicals. Conversely, achieving a singlet ground-state in non-Kekulé PAH diradicals is challenging, and one of the few known examples is the fused Clar's goblet **100**, which displays similar properties to its non-fused analogue bisolympicenyl **84**.[186]

4.3.3 Nitrogen-centred polyradicals. Several heteroatom-centred diradicals have been developed by leveraging the same design strategies as discussed for carbon-centred diradicals in Section 4.3.2. Some of the earliest examples are the *m*-benzenediaminyl **101**[187] and tetraaminyl **102**[188] inspired by *m*-xylylene (Fig. 18). As expected, their non-Kekulé topology favours the high spin (triplet and quintet, respectively) ground state, but both compounds were, unfortunately, quite unstable. Extending π-conjugation through porphyrin units enabled the aminyl triradical **103** with a quartet ground state to achieve exceptional stability, with a lifetime exceeding one year.[189]

Highly chemically robust N-centred polyradicals have been developed based on Blatter radical motif, including triplet diradical **104**,[190] and non-conjugated triptycene-linked diradical **105**[191] and triradical **106**.[192] The latter two display thermal equilibrium between low-spin (singlet and doublet, respectively) and high-spin (triplet and quartet, respectively) states due to a small ΔE_{ST} controlled by through-space orbital interactions.

4.3.4 Radical-containing polymers. Since the first theoretical proposal by Mataga,[193] the incorporation of radicals into macromolecular (polymeric) systems has been explored as a strategy to achieve macroscopic magnetic properties through intramolecular spin–spin interactions.[32] Experimental realisation of ferromagnetic polymers proved to be challenging, not only because of the chemical instability of many of the explored polyradicals, but also because the magnetic ordering in such materials is also affected by *inter*molecular interactions and conformational flexibility of the polymer chain. Some of the most significant work in the area was performed by the Rajca group using the *m*-xylylene ferromagnetic coupling unit. A notable example is the cross-linked polymer **107**[194] exhibiting a magnetic moment of $S \approx 5000$ at 3.5 K (Fig. 19).

In parallel, Nishide and co-workers aimed to develop high-spin polymers by attaching the stable 2,6-di-*tert*-butylphenoxyl radical to the backbone of conjugated polymers including polythiophene **108**[195] and poly(phenylenevinylene) **109**.[196] Although the temperature-dependent magnetisation studies suggest that a weak long-range ferromagnetic coupling could be realised in such systems, the conformational flexibility of these polymers certainly complicates the control of their magnetic properties. Beyond the design of ferromagnetic materials, radical-containing polymers are of interest for their (opto)electronic properties. A notable example is the BDPA polymer **110** developed by Swager and co-workers with the radical moiety in the

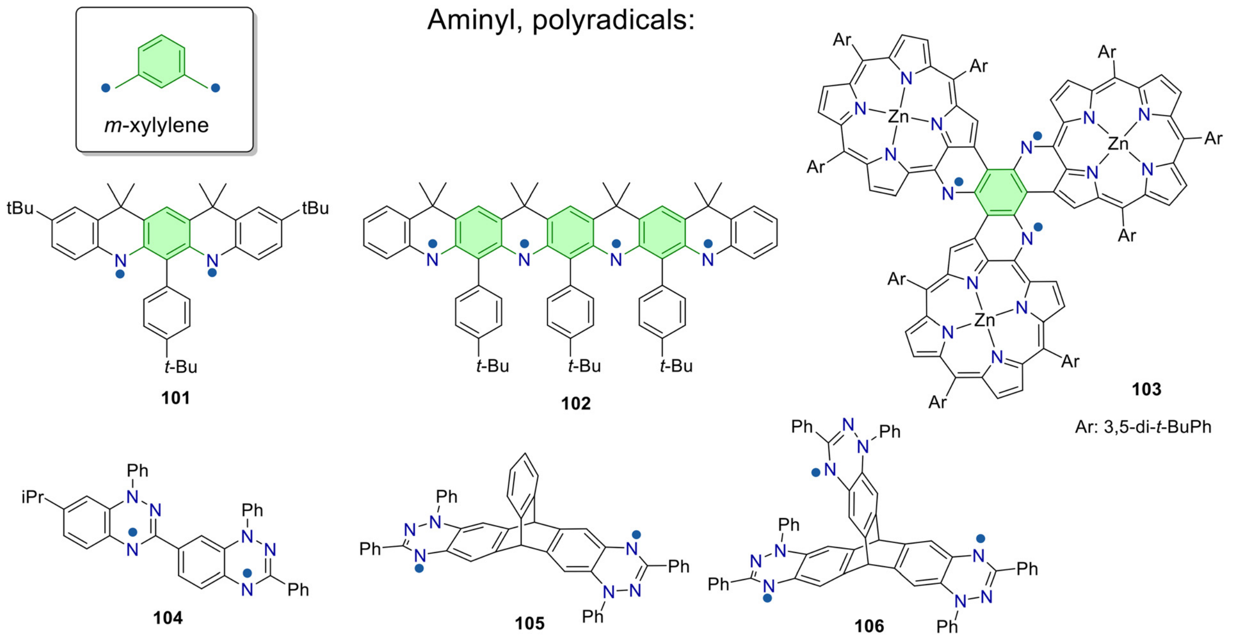

Fig. 18 Examples of persistent N-centred diradicals and polyradicals.

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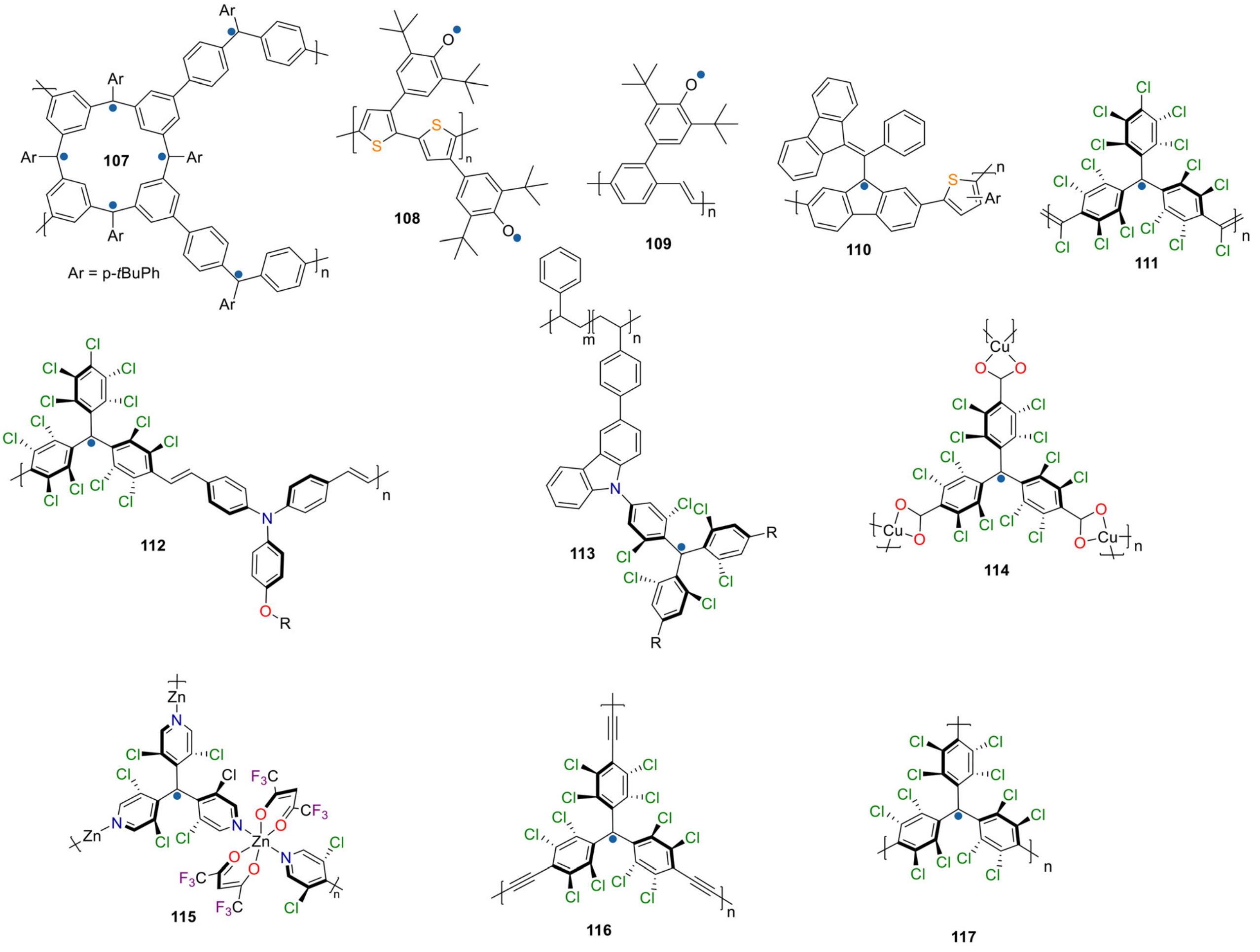

Fig. 19 Examples of persistent polymeric π-radicals.

conjugated backbone,[197] which has been studied for its magneto-optic behavior.

A number of 1D and 2D macromolecular systems have been developed based on PTM (**11**) and TTM (**10**), two of the most stable and most studied π-radicals. The first study, reported by the Barcelona group, described the dichlorovinylene-linked conjugated PTM polymer **111**, which displayed strong antiferromagnetic coupling, as expected based on the Ovchinnikov parity rule.[198] A related triphenylamine-PTM copolymer **112** was prepared by Lambert and coworkers *via* Wittig–Hoerner polymerisation, and used as a semiconductor for organic field-effect transistors (OFET). The donor–acceptor structure of this polymer creates charge-transfer interactions, manifested in NIR absorption (up to 1000 nm) and balanced ambipolar charge transport with hole and electron mobilities of $\sim 3 \times 10^{-5}$ cm^2 V^{-1} s^{-1}.[199] Grafting carbazole-TTM moieties as pendant groups on polystyrene allows for combining the luminescent properties of this chromophore with the processability of non-conjugated polymers. The low density of TTM groups in polystyrene **113** prevents the chromophore–chromophore quenching, resulting in highly luminescent radical polymer films.[200]

There is also a significant interest in incorporating PTM/TTM building blocks (and radicals in general) in 2D systems. The first implementation of this approach, also reported by the Barcelona group, was the metal–organic frameworks (MOF) based on PTM-tricarboxylate **114**.[63] The interactions between Cu metal and PTM radicals lead to a long-range magnetic ordering at low temperature, but unfortunately, the limited structural stability of this MOF did not allow for open porosity (crystallinity is lost upon solvent removal). More recently, magnetically responsive luminescent 1D coordination polymers and 2D MOFs (**115**) have been developed by coordination of pyridine-containing TTM analogues with Zn.[201]

Two examples of C–C linked 2D conjugated polymers with PTM nodes, **116**[66] and **117**[202] were synthesised by interfacial Glazer coupling of ethynyl-terminated monomer and pyrolysis of iodine-terminated PTM, respectively. Unfortunately, the crystallinity of the closed-shell (hydrogenated) precursor of polymer **116** is lost upon hydrogen abstraction. Nonetheless, the resulting material shows the expected antiferromagnetic coupling (J = 375 cm^{-1}, ~1.1 kcal mol^{-1}) in 30–300 K range.[66] In contrast, polymer **117** was found to be paramagnetic down to 1.9 K, which could be explained by poor orbital overlap between the orthogonally linked tetrachlorophenyl moieties, as well as disorder.[202] Creating highly ordered macromolecular systems with radical building blocks remains an unsolved challenge. Nevertheless, theory predicts a number of interesting electronic/magnetic phenomena including the circular dichroism Hall effect in

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ordered 2D arrangements of radical building blocks,[203] and we anticipate further efforts in this direction.

4.4 Radical ion salts

While somewhat beyond the scope of this review, we note that an open-shell (radical) structure can be created in many closed-shell molecules by one-electron oxidation/reduction. The electrostatic repulsion between such molecular ions typically makes them more resistant to recombination compared to neutral radicals. Indeed, a large number of radical-cations and radical-anions (*e.g.* **118–123**, Fig. 20) have been prepared as stable salts with various counter-ions.[204] For example, the triphenylamine radical-cation is isoelectronic to Gomberg's radical **1**, but it does not suffer from dimerisation or reaction with oxygen as long as the para position is blocked. The first known examples, salts of the tri(*p*-tolyl)amine **118** radical-cation with different halides, were isolated in 1907 by Wieland as strongly coloured solids.[205] Since then, various triphenylamine derivatives have been isolated as stable radical-cations,[93] including Magic Blue **119**,[206] a commercially available product commonly used as an oxidant or a dopant. Another important example of radical cations is represented by the viologen series (**120**).[207] Their very high chemical stability, multi-step redox behaviour and electrochemically controllable π-complexation properties have been paramount in multiple applications, *e.g.* in batteries,[208] electrochromic systems,[209] and supramolecular chemistry.[210] The most widely studied and probably the most significant class of radical cation materials is based on tetrathiafulvalene (TTF, **121**). Their special properties are defined by aromatic stabilisation of the radical cation state as well as strong intermolecular interactions (*via* S···S contacts) in the solid state. After the initial report in 1970 by Wudl *et al.* of $[\mathrm{TTF}^{+}]\mathrm{Cl}^{-}$ as an organic conductor,[211] the TTF family has rapidly grown to thousands of derivatives and congeners (with Se and Te heteroatoms), resulting in the discovery of organic superconductors (Bechgaard salts).[212,213]

In comparison, radical anions are generally less air-stable, prone to oxidation by oxygen and protonation by water (followed by various decomposition pathways). Nevertheless, stable radical anions have been prepared with several strong π-electron acceptors. Some of the earliest examples are metal salts of tetracyanoquinodimethane (TCNQ, **122**), which have been studied since the 1960s for their electrical conductivity and magnetic properties.[214] Beyond various TCNQ derivatives and homologues, which draw their stability from gaining aromaticity in the radical anion form, stable radical anions can also be created with electron-deficient aromatic molecules, such as the recently reported for tetracyanonaphthalenediimide **123**.[215]

5 Radical-based functional materials

Having explored the various designs of open-shell species, we will now cover their applications, focusing on the properties arising form unpaired electrons (rather than those common to all π-conjugated materials).

While this review focuses on the electronic and magnetic properties of π-radicals, other fields such as catalysis, spin-labelling and biology have benefited greatly from radical chemistry.[216,217] We note that most of these applications have so far been dominated by non-conjugated radicals, such as TEMPO and other nitroxide radicals. A notable exception is persulfanylated trityl radicals **124**, a.k.a, Finland trityls (Fig. 21), which are widely used as spin probes for distance measurements[218] and bioimaging.[219] Compared to nitroxide radicals, which can be reduced in biological media, Finland trityls are much more biologically inert.

5.1 Electrical conductors

Organic materials can conduct electricity through several mechanisms, often grouped into two broad categories: band transport and hopping transport. In band transport, electrons

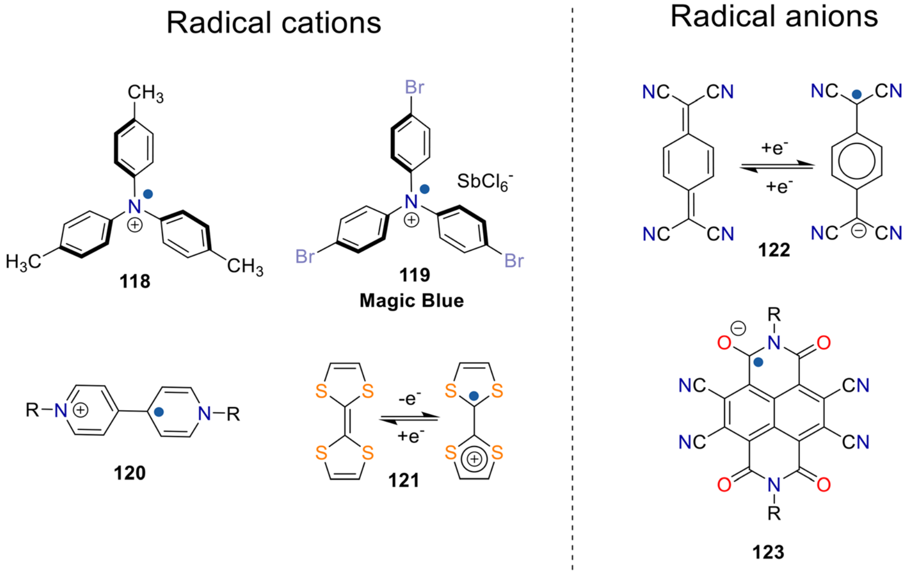

Fig. 20 Examples of persistent radical cations and radical anions.

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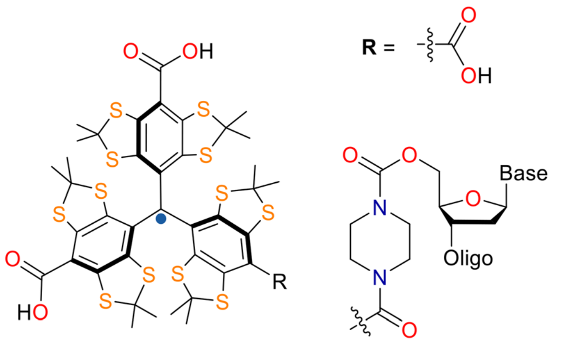

124

Fig. 21 Persulfanyltrityl radicals used for imaging and biology applications.

(or holes) move freely through partially filled conduction or valence bands, much like they do in metals. In hopping transport, electrons (or holes) move by jumping between localised sites, and this process can be assisted by thermal energy or by tunnelling.

The first organic conductor was the radical-ion salt perylene-Br$_2$ reported in 1954 ($\sigma \approx 10^{-3}$ S cm^{-1}),[220] followed by the metallic TTF-TCNQ reported in 1973 ($\sigma \approx 400$ S cm^{-1}),[221] the organic superconductors TMTSF$_2$-PF$_6$ salt in 1980 ($T_c = 0.9$ K at 12 kbar)[213] and RbCs$_2$C$_{60}$ in 1991 ($T_c = 33$ K).[222] In all these examples, charge carriers are created by removing electrons from the valence band or adding electrons to the conduction band. At a molecular level, this process is equivalent to the formation of radical-ions, and charge-balancing requires the presence of a second component (counter-ion).

In principle, neutral radicals could achieve metallic conductivity in single-component systems. The interaction of the HOMOs and LUMOs of closed-shell molecules in the solid-state results in the formation of a fully filled valence band and empty conduction band, respectively, and such materials behave as insulators or large band-gap semiconductors (Fig. 22). The propagation of charge (electrical conductivity) in such materials thus requires injection of an electron in the conduction band or a vacancy (hole) in the valence band. In contrast, the interaction of SOMOs of open-shell systems can lead to the formation of a half-filled band giving rise to metallic conductivity. In most cases, two distinct mechanisms suppress metallic conductivity: Peierls distortion and Hubbard splitting. The former originates from electron–phonon coupling, whereby a one-dimensional system undergoes a symmetry-lowering distortion, resulting in dimerisation (in this case, weak π-dimerisation of radicals within a stack) to reduce its energy and the opening of a small band-gap (Fig. 22a). The latter arises from strong electron–electron repulsion, as described by the Hubbard model, in which carriers hopping between sites experience an on-site Coulomb interaction U, leading to a Mott insulating state when the energetic bandwidth W is not large enough (Fig. 22b).[223] Therefore, metallic conductivity has only been realised under high pressure, with $\sigma = 10^2$ S cm^{-1} at 3 GPa reported for the thiazyl radical **66** (Fig. 23).[147,224] Nevertheless, even with a non-zero band-gap, many π-radical solids behave as intrinsic conductors, *i.e.* they do not require doping for electrical transport.

Single-component radical systems have been shown to exhibit both band and hopping transport, yielding conductivities within the range of $\sigma \approx 10^{-5}$–10^2 S cm^{-1}. Examples of neutral radical conductors (Fig. 23) include phenalenyl derivatives developed in Haddon's group (**125–126**)[225,226] and the thia/selenazyl derivatives from Oakley's group (**65–66**).[146,147] A relatively high conductivity has also been achieved in the oligothiophene diradicaloid **127**.[227] Charge compensation can also be achieved in radical ions by incorporating the counter-ion within the same zwitterionic

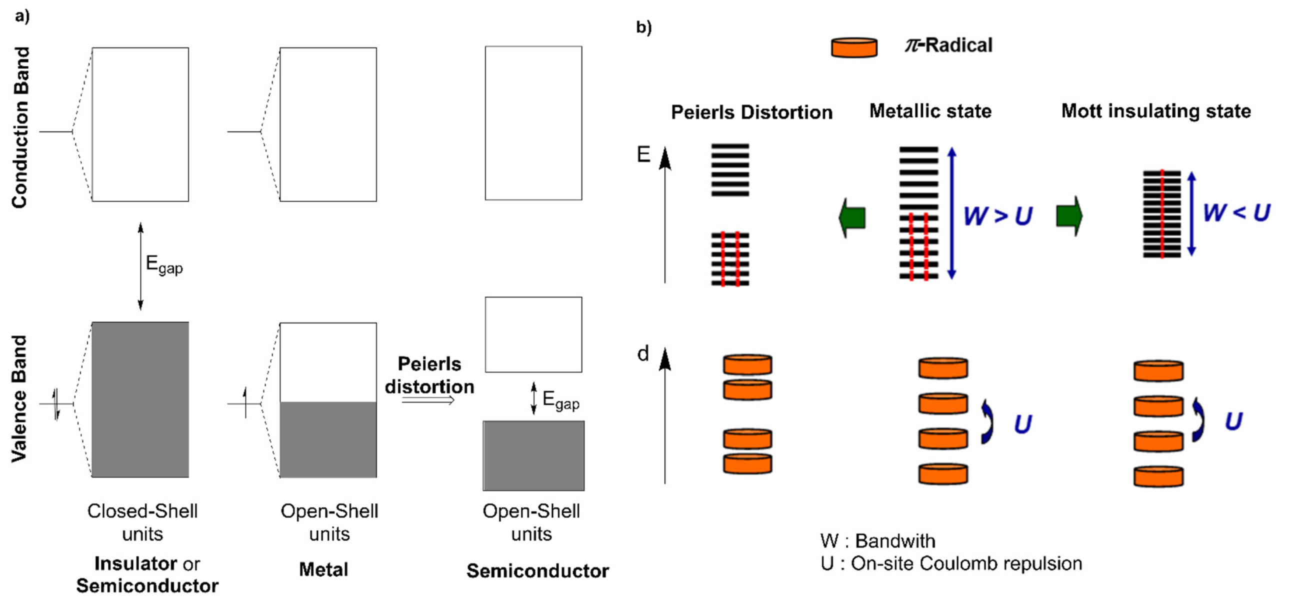

Fig. 22 (a) Comparison of the band structure of a closed-shell insulator and an open-shell conductor. (b) Schematic representation of the Peierls distortion and the Mott insulating state preventing metallisation in 1D stacks of π-radicals.

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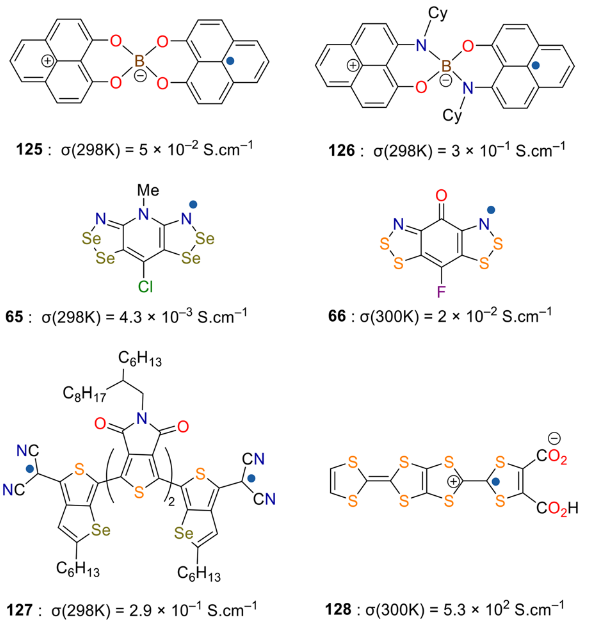


125 : σ(298K) = 5 × 10^{-2} S.cm^{-1}

126 : σ(298K) = 3 × 10^{-1} S.cm^{-1}

65 : σ(298K) = 4.3 × 10^{-3} S.cm^{-1}

66 : σ(300K) = 2 × 10^{-2} S.cm^{-1}

127 : σ(298K) = 2.9 × 10^{-1} S.cm^{-1}

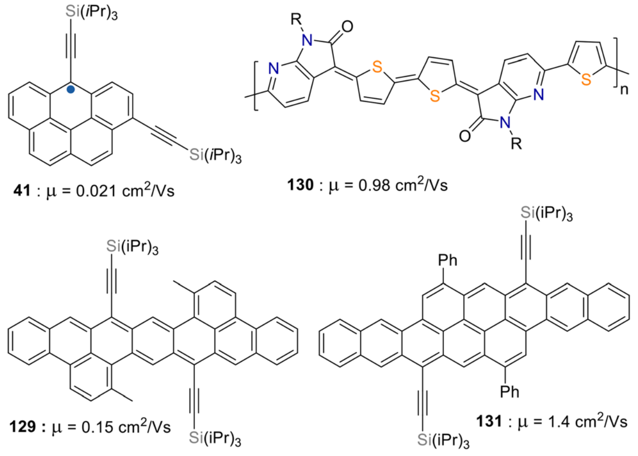
128 : σ(300K) = 5.3 × 10^{2} S.cm^{-1}

Fig. 23 Examples of single component intrinsic neutral radical conductors.

molecule. Thus, very high metallic conductivity (σ = 530 S cm^{-1}) was reported for the TTF-extended dicarboxylate **128**, which is formally a neutral radical.[228]

Besides single-component radical conductors, a few examples of conducting conjugated open-shell radical polymers have also demonstrated high conductivity.[229] For an in-depth review of neutral radical conductors, the reader is referred to ref. 230.

Open-shell semiconductors have also attracted recent attention in the development of OFETs, where charge transport through a semiconductor is modulated by an external electric field (Fig. 24). Among π-monoradicals, one of the best OFET performances was reported for the olympicenyl radical **41**, with a hole mobility of 0.021 cm^2 V^{-1} s^{-1} and a remarkably high (for open-shell semiconductors) on–off ratio of $>10^6$.[231] For instance, bottom-gate/top-contact OFETs with a hole mobility of 0.15 cm^2 V^{-1} s^{-1} have been reported for the zethrene diradicaloid **129**,[232] while azaquinoidal polythiophene **130** derivatives show electron mobilities up to 0.98 cm^2 V^{-1} s^{-1}.[233] An even higher hole mobility of up to 1.4 cm^2 V^{-1} s^{-1} (in top-gate/bottom-contact configuration) and ambipolar transport (in bottom-gate/top-contact configuration) was observed in the peripentacene singlet diradical **131**, while its closed-shell homologue, peritetracene, exhibited a charge mobility *ca.* two times slower.[234] Although these values are *ca.* one order of magnitude below the current state-of-the-art closed-shell OFET materials, they are still competitive and offer additional functionalities associated with open-shell systems.



41 : μ = 0.021 cm^2/Vs

130 : μ = 0.98 cm^2/Vs

129 : μ = 0.15 cm^2/Vs

131 : μ = 1.4 cm^2/Vs

Fig. 24 Examples of radicals and diradicaloids for OFET applications.

Electrical conductivity has also been extensively explored in open-shell MOFs[235] and covalent organic frameworks (COFs).[236] Most of the reported systems are based on radical ions generated from closed-shell materials by redox chemistry, similar to the doping of conjugated polymers or the formation of charge-transfer salts. For example, a charge mobility of 0.2 cm^2 V^{-1} s^{-1} in a MOF based on TTF-tetrabenzoic acid was reported based on time-resolved microwave conductivity (TRMC) measurements.[237] Additionally, an electrical conductivity of 0.65 S cm^{-1} was reported in a COF based on trioxaazatriangulene doped with Magic Blue (**119**).[238] By comparison, little is known about the conductive properties of framework materials based on neutral radical building blocks, as such materials are very rare. To our knowledge, the first example of conductivity measurements in neutral radical COFs was only recently reported by Souto and co-workers, based on trioxotriangulene (**25b**) building blocks (σ = 1.2 × 10^{-4} S cm^{-1}).[239]

5.2 Energy storage materials

Electrochemical reduction/oxidation of radicals produces closed-shell anions/cations, which are inherently more stable than the radical-ion redox states produced from most closed-shell molecules. This advantage has been used in applications of organic radicals in energy storage devices,[240] starting with the pioneering work of Nakahara *et al.*, which demonstrated a rechargeable lithium battery with TEMPO-functionalised polymethacrylate as the cathode.[241] The fast redox processes of radical-based electrodes allow for high charging/discharging rates, which is essential, *e.g.* in automotive applications. There is also significant interest in radical-containing polymers as anolytes/catholytes for redox-flow batteries (Fig. 25).[242] A number of organic radicals have been investigated as electrode materials over the last decade; the best examples to date are based on TEMPO, although several π-radicals such as phenoxyl[243] and trioxotriangulene[82] have also been investigated as radical materials. The amphoteric redox behaviour of π-radicals, such as verdazyls[134] and Blatter radicals[244], is of particular interest for symmetric redox-flow batteries. Using the same compound as both catholyte and anolyte mitigates the critical problem of this technology: membrane crossover. We refer the reader to a recent comprehensive review on radicals in energy storage and conversion for more information.[240]

5.3 Luminescent materials

Although there is a long-standing perception of radicals as luminescence quenchers, the fluorescence of trityl radical in a frozen matrix has already been reported in 1944,[34] and transient

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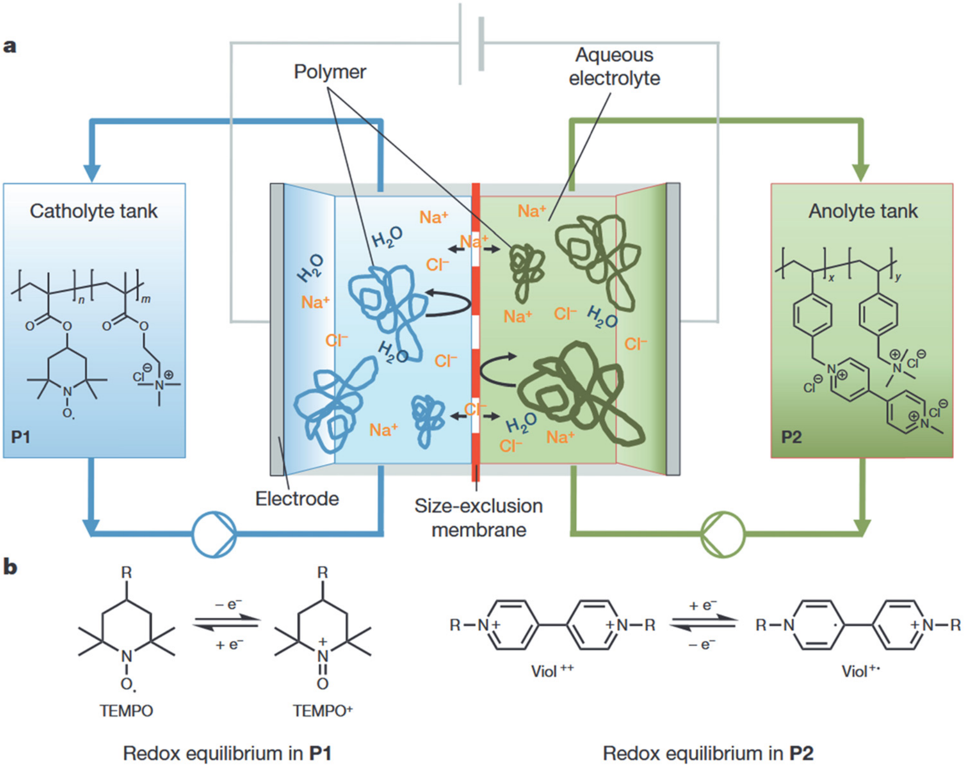

Fig. 25 (a) Schematic representation of the polymer-based redox-flow batterie. (b) Redox equilibriums happening in the catholyte and anolyte tanks. Reprinted with permission from T. Janoschka, N. Martin, U. Martin, C. Friebe, S. Morgenstern, H. Hiller, M. D. Hager and U. S. Schubert, An aqueous, polymer-based redox-flow battery using non-corrosive, safe, and low-cost materials, *Nature*, 2015, **527**, 78–81. Copyright 2015 Springer Nature.

photoluminescence has been widely used to study radical intermediates.[35] Nevertheless, among stable radicals, room-temperature luminescence remains a rare property; to our knowledge, the first reported case was PTM **11**, for which a PLQY of 1.5% was measured in solution.[42] In the early 2000s, Juliá's group found that attaching a carbazole moiety to TTM (**15**, Fig. 26a) could enhance the PLQY to over 50% while significantly improving photostability.[68,69]

These developments laid the groundwork for exploring radicals in electroluminescence. Unlike singlet emitters, which lose 75% of excitons during electroluminescence to 'dark' triplets, radical (doublet) emitters can have a 100% internal quantum efficiency, as the lowest quartet state (Q_1) is generally higher in energy than D_1 (Fig. 7). This concept was first realised in 2015 by Li and co-workers, who reported electroluminescence from carbazole-substituted TTM **15**.[245] Since then, rapid progress has been made toward device optimisation,[70] culminating in TTM-based radical derivatives achieving record efficiencies in near-infrared OLEDs (**17** in Fig. 26b).[246]

To date, most applications of luminescent radicals have been developed with TTM/PTM derivatives, as there are few (if any) air-stable alternatives with comparable PLQYs.[35] However, their major limitation is their fast photodecomposition *via* dechlorinative cyclisation, forming a non-emissive fluorenyl radical.[42] There has been significant recent interest in understanding[43] and controlling the photodegradation of luminescent trityl radicals, and 2–4 order of magnitude increase of photostability was achieved in carbazole-substituted derivatives[91] and in pyridine analogues of TTM.[88]

Major improvements in the photostability of trityl radicals have also been achieved by their immobilisation in rigid crystalline matrices. For instance, diluting triiodo-PTM **13b** in a matrix of its hydrogenated precursor increases photostability by ~5 orders of magnitude compared to in solution while achieving a near-quantitative PLQY (91%).[65] As is also the case for most closed-shell dyes, the PLQY of radical emitters drops significantly with increasing their concentration, due to the formation of less or non-emissive excimers. In some cases, these excimers display their own fluorescence, red-shifted from that of the monomeric radicals, such as is seen for PyBTM radical **132**. Notably, because the radical excimers can exist in either a singlet or triplet quantum state, their emission can be modulated by an external magnetic field (magnetoluminescence), as demonstrated by Kusamoto, Nishihara and co-workers (Fig. 27).[247] Recently, the field of luminescent radicals expanded with the very stable tribromo phenalenyl radical **36c**. Despite being in a reversible equilibrium with its π-dimer, it exhibits a high PLQY of 10.4% originated from the monomer.[101] Comprehensive reviews on the design of luminescent radicals can be found in ref. 35 and 248.

In contrast to monoradicals, the excited states of diradicals are represented by the same multiplicities (singlets and triplets) as in closed-shell molecules. However, the unique electronic configuration of diradicals imparts distinct photophysical behaviour with the possibility of spin-allowed fluorescence from both singlet and triplet excited states (Fig. 7c and d).[249] Luminescence has been reported in various halogenated

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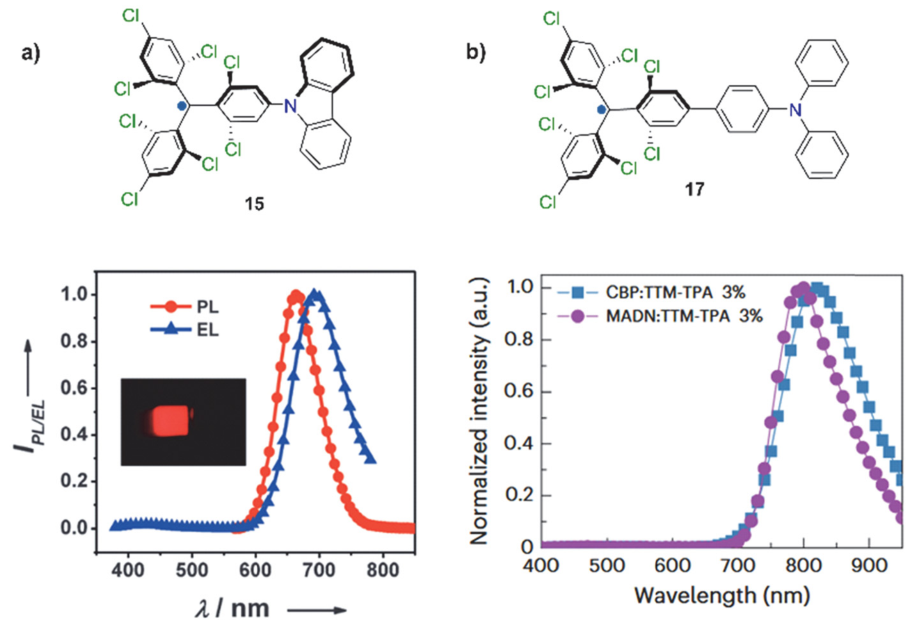

Fig. 26 (a) Structures and photo- and electroluminescence spectra of radical **15** (in a doped film). Adapted with permission from Q. Peng, A. Obolda, M. Zhang and F. Li, Organic Light-Emitting Diodes Using a Neutral π Radical as Emitter: The Emission from a Doublet, *Angew. Chem., Int. Ed.*, 2015, **127**, 7197–7201. © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Structure and NIR electroluminescence spectra of radical **17**. Adapted from H.-H. Cho, S. Gorgon, G. Londi, S. Giannini, C. Cho, P. Ghosh, C. Tonnelé, D. Casanova, Y. Olivier, T. K. Baikie, F. Li, D. Beljonne, N. C. Greenham, R. H. Friend and E. W. Evans, Efficient near-infrared organic light-emitting diodes with emission from spin doublet excitons, *Nat. Photon.*, 2024, **18**, 905–912. Licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

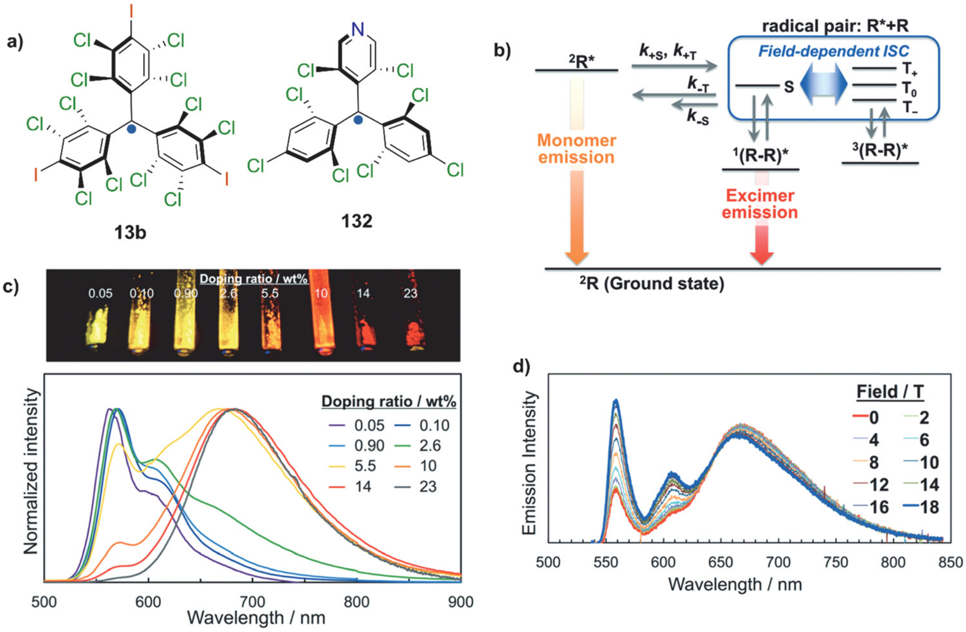

Fig. 27 (a) Structures of luminescent trityl radicals doped in their corresponding triarylmethane matrices. (b) Jablonski diagram representing the formation of the radical excimer and its field dependant states. (c) Emission spectra and photographs of **132** in α*H*-**132** matrix, at different doping ratios. (d) Magnetoluminescence spectra of **132** at 4.2 K. Adapted with permission from S. Kimura, T. Kusamoto, S. Kimura, K. Kato, Y. Teki and H. Nishihara, Magnetoluminescence in a Photostable, Brightly Luminescent Organic Radical in a Rigid Environment, *Angew. Chem., Int. Ed.*, 2018, **57**, 12711–12715. © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

quinodimethane-type diradical(oid)s, including fluorinated and chlorinated Thiele hydrocarbons **133**[250] and **134**,[251] Chichibabin hydrocarbon TTM-TTM **77a**[159] and Mueller hydrocarbons TTM-Ph-TTM **77b**[160] and **135**[252] (Fig. 28a). Thiele's hydrocarbon, with the lowest diradical character in the series ($y_0 \sim 0.3$–0.4), shows an almost quantitative PLQY from an unusual zwitterionic

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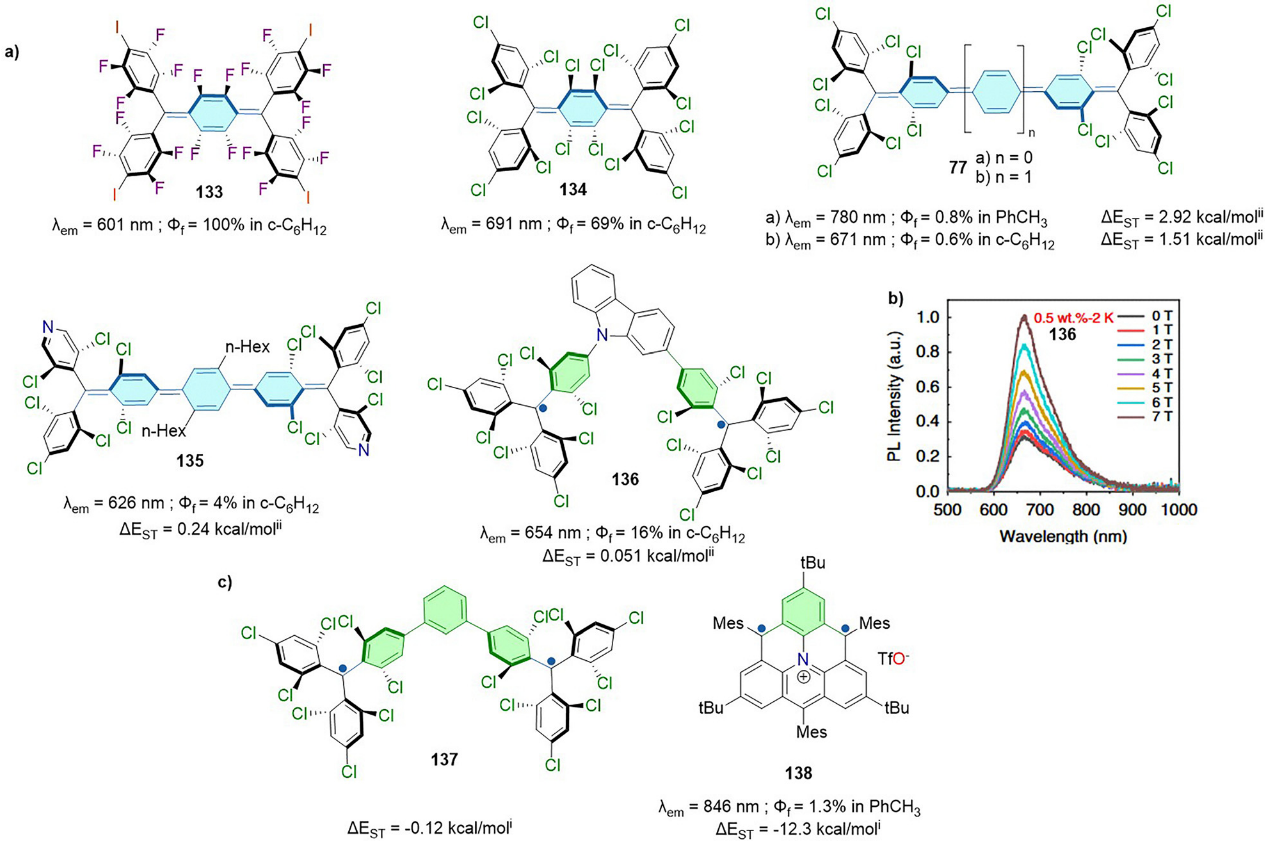

Fig. 28 (a) Examples of luminescent singlet diradicals. (b) Magnetoluminescence spectra of **136** in a 0.5 wt% film of PMMA at 2 K. Adapted from A. Abdurahman, L. Shen, J. Wang, M. Niu, P. Li, Q. Peng, J. Wang and G. Lu, A highly efficient open-shell singlet luminescent diradical with strong magnetoluminescence properties, *Light Sci. Appl.*, 2023, **12**, 272. Licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/). (c) Examples of luminescence of triplet diradicals. (i) Calculated by DFT. (ii) Experimental.

excited state (formed *via* symmetry-breaking intramolecular charge transfer).[250,251] The emission of the Chichibabin hydrocarbon **77a**, with a higher diradical character (y_0 = 0.6), is significantly red-shifted (λ_{max} ~ 800 nm), as expected, and occurs from a normal (apolar) excited state. Interestingly, the further extension of π-conjugation in Mueller hydrocarbons **77b** (y_0 ~ 0.9) results in a blue shift of emission, presumably because this molecule behaves as two weakly coupled trityl radicals. As with TTM monoradical, both **77a** and **77b** exhibit a low PLQY (<1%) and poor photostability. However, both the PLQY and photostability can be significantly improved using the same modification strategy as for the TTM monoradical, as exemplified in the pyridine-substituted Mueller diradical **135**[252] and the carbazole-linked trityl diradical **136**[253] (Fig. 28a). The very small singlet–triplet gap (ΔE_{ST} = 0.05 kcal mol^{-1}) in the latter leads to pronounced magnetoluminescence, where the emission intensity increases in a magnetic field due to increasing population of the (more emissive) triplet state (Fig. 28b). This conclusion was further supported by the luminescence quenching at very low temperatures.

Almost all luminescent diradicals reported so far possess singlet ground states. Some of the only examples of stable luminescent diradicals with a triplet ground state are the *meta*-phenylene-connected bis-TTM **137**,[254] which was developed as an optically addressable molecular qubit, and the azatriangulene diradical cation **138**[37] (Fig. 28c). Owing to its positive charge, the latter displays remarkable air and photostability, and its strong NIR emission (λ_{max} = 846 nm, PLQY = 1.3%) underscores a rare example of a stable luminescent (di)radicals that is not a derivative of the chlorinated trityl.

Access to higher-spin excited states, such as quartets, could be achieved by coupling three radical centres in the same molecule, or by attaching a chromophore moiety to a monoradical. Promoting the chromophore to a triplet excited state gives rise to a radical-triplet pair with a quartet multiplicity, and such systems have been studied, mostly for TEMPO derivatives, since the 1990s.[255] The formation of the chromophore triplet state can be greatly facilitated by the presence of a radical moiety, *via* radical enhanced intersystem crossing (REISC).[256] More recently, TTM-based luminescent chromophore–radical dyads and triads were shown to reach quartet and quintet excited states that are optically addressable and readable (Fig. 29).[257] Although the direct radiative emission from such quartet states is spin-forbidden, they can be observed *via* thermally-activated delayed fluorescence of the corresponding doublet state, and such materials are currently of great interest in the context of spin-optical interfaces in quantum technologies (*vide infra*).[257,258]

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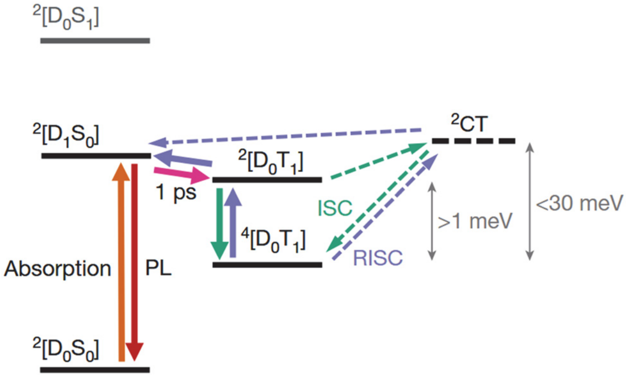

Fig. 29 Simplified energy diagrams of quartet state formation following light absorption by the radical. Adapted from S. Gorgon, K. Lv, J. Grüne, B. H. Drummond, W. K. Myers, G. Londi, G. Ricci, D. Valverde, C. Tonnelé, P. Murto, A. S. Romanov, D. Casanova, V. Dyakonov, A. Sperlich, D. Beljonne, Y. Olivier, F. Li, R. H. Friend and E. W. Evans, Reversible spin-optical interface in luminescent organic radicals, *Nature*, 2023, **620**, 538–544. Licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

5.4 Spintronics

Spintronics is a field that grew in the 1980s to exploit the electron spin, in addition to its charge, as a state variable for information processing. Organic π-radicals can be excellent candidates for spintronic applications, because they combine an intrinsic unpaired electron with the generally low spin–orbit coupling (SOC) of light-element-based organic materials. In well-designed radical molecules, this low SOC can result in slow spin relaxation and reduced spin scattering. To date, the clearest demonstrations of radical-based spintronics have been obtained in single-molecule junctions, *e.g.*, spin-valves with magnetoresistance. Here, a single open-shell molecule is connected to small ferromagnetic electrodes, and the electrical resistance of the sandwiched molecule can be manipulated depending on whether its spin is aligned with or misaligned with the electrodes' spins.[259] Thus far, conjugated molecules with aminoxyls as pendant groups and conjugated PTM molecules have been studied in single-molecular junctions and have shown large magnetoresistance at low temperatures (Fig. 30).[260,261] These studies show that even a single stable radical can act as an active spin-transport element.

However, practical applications require both ferromagnetism and conductivity in the bulk or at the single-molecule level: spin needs to be injected/manipulated, transported and detected effectively. This requirement extends beyond spin valves to spin-transistors, where the spin direction of the active material is modulated by a gate electric field and read out by non-magnetic electrodes.[262]

5.5 Quantum materials

Stable radicals are being increasingly explored as molecular quantum materials,[263] in which electronically defined spin states can be prepared, manipulated, and read out, *e.g.*, as qubits. Qubits are analogous to bits in classical computing but are capable of existing in superpositions of states (*e.g.* $\alpha\langle 0\rangle + \beta\langle 1\rangle$). This allows n qubits to represent and compute in 2^n states simultaneously, in contrast to n states with classical bits.

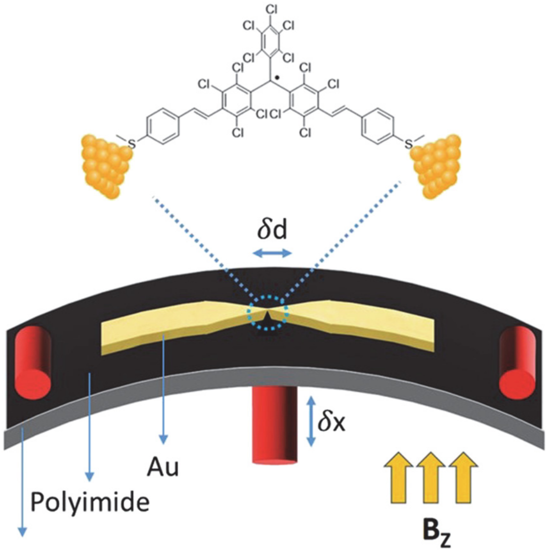

Fig. 30 Single molecule junction based on PTM derivative. Adapted with permission from G. Mitra, J. Z. Low, S. Wei, K. R. Francisco, M. Deffner, C. Herrmann, L. M. Campos and E. Scheer, Interplay between magnetoresistance and Kondo resonance in radical single-molecule junctions, *Nano Lett.*, 2022, **22**, 5773–5779. Copyright 2022 American Chemical Society.

Many groups are actively exploring photoexcited radicals as qubits, capable of maintaining superpositions on the μs to ms time scale. Compared to classical inorganic systems such as nitrogen-vacancy defects in diamond (NV defects), the synthetic chemistry of stable radicals offers, in addition to the well-defined spin manifold, fine control over spin density, spin state energy differences, and optical functionality. Recent chemical designs include the chromophore-pendant radical dyad **139**,[264] the conjugated luminescent radical-chromophore dyads **140**[257] as well as the diradicals **137**,[254] **141**[265] and **142**[266] (Fig. 31). These molecules possess either doublet (for monoradicals)/singlet (for diradicals) or quartet/triplet excited states, with the latter split into closely spaced magnetic sublevels. By applying microwave pulses, the molecules can transit between these sublevels, and the resulting state can then be "read" optically (*e.g.*, *via* optically detected magnetic resonance), enabling computational logic operations. While intrinsic molecular properties such as coherence time still needs to be improved, significant work lies ahead in isolating single molecules for functional qubit devices. For interested readers, a detailed review regarding stable radical qubits and their quantum information applications has been published recently.[267]

6 Conclusion

The discovery of triphenylmethyl by Moses Gomberg in 1900 marked the birth of the field of stable radicals, once thought to be impossible. The better part of the last century was spent on coaxing stability in such open-shell molecules. Through these efforts, we learnt how radicals die – through dimerisation, hydrogen abstraction, and oxidation – and how they can endure: by delocalising the spin, lowering the SOMO through resonance, disfavouring dimerisation thermodynamically, or shielding the

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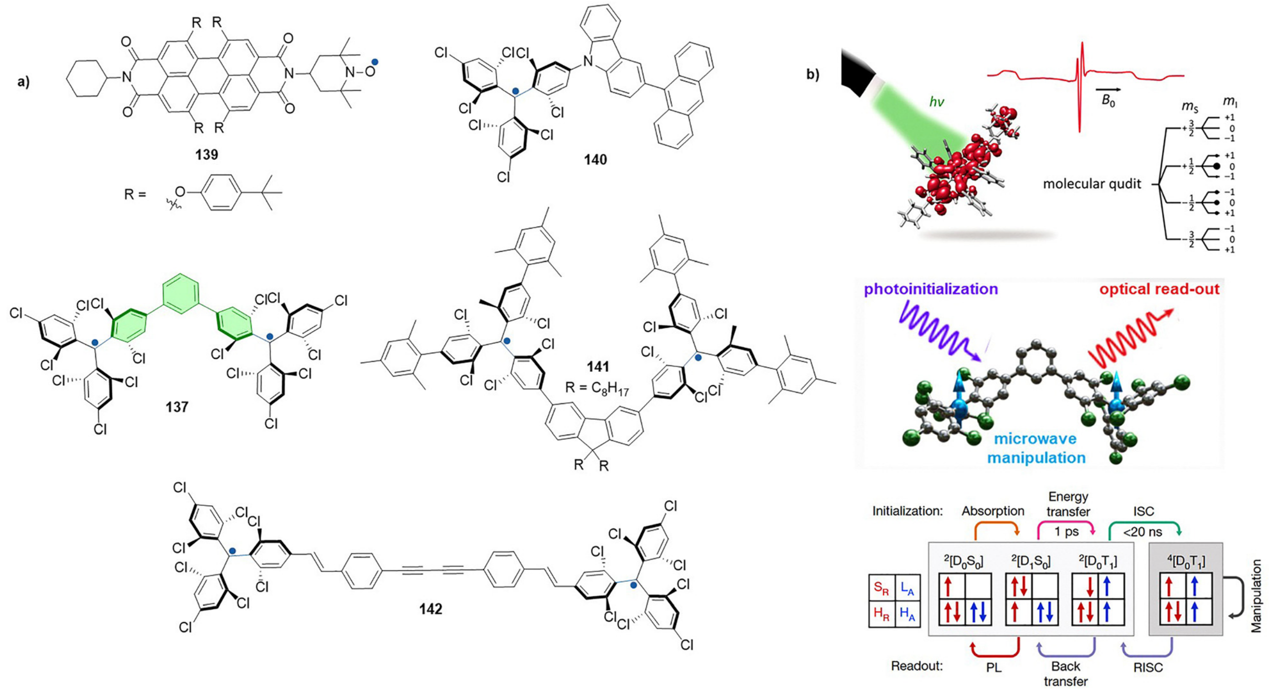

Fig. 31 (a) Examples of monoradical and diradicals qubits for quantum information applications. (b) Schemes showing the working principle of molecular qubits. (Top) Reprinted with permission from M. Maylander, S. Chen, E. R. Lorenzo, M. R. Wasielewski and S. Richert, Exploring photogenerated molecular quartet states as spin qubits and qudits, *J. Am. Chem. Soc.*, 2021, **143**, 7050–7058. Copyright 2021 American Chemical Society. (Middle) Reprinted with permission from S. M. Kopp, S. Nakamura, B. T. Phelan, Y. R. Poh, S. B. Tyndall, P. J. Brown, Y. Huang, J. Yuen-Zhou, M. D. Krzyaniak and M. R. Wasielewski, Luminescent Organic Triplet Diradicals as Optically Addressable Molecular Qubits, *J. Am. Chem. Soc.*, 2024, **146**, 27935–27945. Copyright 2024 American Chemical Society. (Bottom) Adapted from S. Gorgon, K. Lv, J. Grüne, B. H. Drummond, W. K. Myers, G. Londi, G. Ricci, D. Valverde, C. Tonnelé, P. Murto, A. S. Romanov, D. Casanova, V. Dyakonov, A. Sperlich, D. Beljonne, Y. Olivier, F. Li, R. H. Friend and E. W. Evans, Reversible spin-optical interface in luminescent organic radicals, *Nature*, 2023, **620**, 538–544. Licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

reactive sites with steric bulk. What once seemed a chemical contradiction can now, in some cases, sit indefinitely on a shelf or be implemented in electronic devices. In this tutorial review, we aimed to place the contemporary work in the field of stable π-conjugated radicals in the context of the milestone discoveries of the field over its 125-year long history. We briefly summarised the theoretical foundations of our current understanding of open-shell molecules and highlighted the general design rules for imparting chemical stability and controlling spin coupling in these materials.

The molecular space of stable radicals has grown enormously. Some of the most stable carbon-centred radicals are derived from Gomberg's triphenylmethyl, such as the halogenated TTM and hundreds of its derivatives. Through extensive π-delocalisation, high stability has been achieved in polycyclic hydrocarbon radicals such as phenalenyl derivatives, and in the cyclopentadienyl radical devoid of any aromatic ring. Heteroatom-centred radicals – nitroxides, phenoxyls, hydrazyls, verdazyls, thiazyls, *etc.* – achieve stability by different means, often engaging in three-electron-two-centre π-bonding and not requiring steric protection. Diradicals and polyradicals, built either by bridging monoradical units through conjugated linkers or by topology engineering in polycyclic aromatic frameworks, add spin–spin coupling as a tuneable parameter. Radical ions, stabilised against recombination by Coulombic repulsion, complete the picture, showcasing early applications of open-shell materials as organic conductors and superconductors.

This field has not grown in isolation. ESR spectroscopy made the unpaired electron visible and measurable. Molecular electronics uncovered the unusual physical properties of radicals, expanding the field beyond the realm of chemistry. Modern synthetic methods have opened access to increasingly complex non-Kekulé hydrocarbons, triangulenes, and nanographene-like frameworks that earlier generations could only imagine. OLED research forced a rethinking of radicals as emitters rather than quenchers. Quantum science is now asking how we can make molecular spin qubits with easily addressable spin states.

Although the basic design principles for conjugated radicals are now well established, our understanding of some of their key properties, particularly in their excited states, remains incomplete. As a result, optimising these properties primarily relies on an empirical search. On the other hand, the development of new classes of radicals and their applications is challenged not only by the intrinsic reactivity of most open-shell materials, but also by the difficulty of their characterisation. Without NMR (which is not useful for most radicals due to severe paramagnetic broadening), chemists must employ a broad range of methods, including meticulous characterisation of the radical precursors, HPLC, and X-ray crystallography, to establish the identity and purity of the newly developed radicals.

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We caution two disconnects that may well define the field's path forward. The first is between synthesis and property exploration. It is striking that, more than 60 years after Ballester's first chlorinated trityls, nearly every air- and photo-stable luminescent radical reported to date still belongs to the chlorinated triphenylmethyl family. The same observation can be made, in different guises, for the *m*-xylylene-dominated high-spin polyradicals and for the handful of phenalenyl- and thiazyl-type scaffolds that anchor the field of single-component conductors. Local search around a few proven scaffolds will eventually saturate. Meanwhile, the literature now contains many beautifully characterised, perhaps exotic-looking radicals whose excited-state dynamics, spin-relaxation behaviour, and solid-state electronic structure remain little explored. The productive question should no longer be "what new radical can I make?" or even "how do I tune property X?", but "how can we systematically discover properties that radicals can exhibit but no one has yet thought to measure?"

The second disconnect is between the molecule and the device. Radical OLEDs have reached record internal quantum efficiencies, yet their operational lifetimes are far too low for industrial adoption. Candidate molecular qubits show clean ODMR contrast in dilute frozen glasses, but the path from a 4 K solution to a single, addressable, surface-mounted spin remains unclear. We do not view device robustness and scalability as separate from molecular design, but as constraints that should enter the design phase in parallel with – not in place of – the search for new properties.

Looking back a century, the laws of chemistry consistently rewarded radical chemists who refused to take "unstable" as a final answer, and they have taught us that the exploration of open-shell matter does not only optimise known properties – it uncovers new ones. Looking forward, we conclude that a plethora of unexplored properties must exist in π-conjugated radical materials, waiting to be discovered. For synthetic chemists, designing new stable π-radicals offers an opportunity to test and challenge their chemical intuition and the fundamental theories developed from observations of closed-shell molecules. We expect the following decade to see new developments in: the design of new luminescent radicals (beyond the currently explored family of chlorinated trityl derivatives); the application of radical-based materials in semiconducting devices (*e.g.*, in circumventing the parasitic triplet state in photovoltaic devices); and the creation of well-ordered 2D polymers and covalent organic frameworks based on radical monomer units. And the most exciting discoveries, as it happens, will probably be those that cannot be predicted at this time.

Conflicts of interest

There are no conflicts to declare.

Data availability

This is a Tutorial Review manuscript. It does not report any original data.

Supplementary information (SI): a collection of reported trityl radicals with corresponding references; a list of previous reviews on stable radicals. See DOI: https://doi.org/10.1039/d4cs01126k.

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