Recent progress in open-shell organic conjugated materials and their aggregated states

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In the last few decades, open-shell organic materials have attracted great attention from scientists due to their new chemical and physical properties, as well as their possible applications in new-generation organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs), organic spintronics and photonics, and so on. In this review, we summarize the recent progress in the design and synthesis of open-shell organic conjugated materials. First, we give a general summary of synthetic strategies towards these stable open-shell species, such as kinetic steric protections, spin delocalization by large \( \pi \)-conjugated skeletons and heteroatom-assisted protections. In particular, we will focus on their aggregated states in OFETs, organic conductors, luminescent devices and photoinduced radical materials, with the aim to provide some clue for the further development of novel open-shell organic conjugated materials.

Each electron’s magnetic moment possesses a specific energy due to the Zeeman effect, and this energy could be described as the equation of \( E = m_g \mu_B H \), among which \( m_g \) is called the \( g \) factor, \( \mu_B \) is the Bohr magnetron and \( H \) is the strength of the applied magnetic field. For monoradicals, the Zeeman energy difference between the lower and upper states of two electrons is calculated to be \( \Delta E = E_S - E_T = g_\beta \mu_B H \), and the electron spin resonance (ESR) signal would appear when its frequency (\( \nu \)) is equal to the energy of \( \Delta E = h\nu \).

Diradicals are related to molecules with two unpaired electrons. There are three cases. As shown in Fig. 1b, when the distance (\( r \)) of two electrons is large enough, the electron exchange interaction (\( J \)) of two unpaired electrons could be regarded as almost negligible, and this kind of radical could be named as a biradical with two doublet monoradicals in one molecule. However, when the distance (\( r \)) of two electrons is small enough to generate spin–spin interactions, the electron exchange interaction would produce two spin states of singlet diradicals (\( S = 0 \), spin multiplicity = 1) and triplet diradicals (\( S = 1 \), spin multiplicity = 3). For singlet diradicals, the quantum number is zero and spin multiplicity is one, indicating only one energy level. Thus, singlet diradicals are ESR silent. For triplet ones, the quantum number is 1, \( 2\beta (m_s = 1), 2\beta (m_s = 0), \beta \beta \) (spin multiplicity = 3). Thus, there are three different energy levels in the presence of a strong magnetic field, and triplet diradicals are ESR-active species. Usually, singlet diradicals have small singlet–triplet band gaps (\( \Delta E_{S-T} \)) and these molecules are easy to thermally activate to their triplet states. Accordingly, temperature-dependent magnetic measurements are commonly used methods to determine singlet diradicaloids. For example, the protons of singlet
diradicals in $^1$H NMR spectra would be broadened upon heating, and the product of magnetic susceptibility and temperature would also increase as the temperature increases, which could be monitored by variable temperature ESR or superconducting quantum interfering device (SQUID) measurements.

Triradicals and above are called high-spin radicals only when $J$ not equal to zero is considered.$^{6,9}$ Taking triradicals for example (Fig. 1c), if three radicals align in a linear lattice, one of the radicals will remain unpaired due to the electron coupling of two neighbour radicals. Therefore, the linearly aligned triradical would usually have the doublet ground state of the monoradical. If three radicals align in a triangular lattice with arbitrary, and two of them have opposite spin states (Fig. 1d), the third spin could not align itself to satisfy both of them at the same time. In other words, the energies of the two systems would be the same, no matter whether the third electron is in the spin up or down state. Therefore, the two spin states of the third electron have the same probability, and this kind of triradical is called a spin-frustrated triradical.$^{27–30}$ In the solid state, due to the random frozen states of their spin states, the magnetic susceptibility is zero macroscopically, and this triradical could be called aspin glass material. However, when applying/removing the external magnetic field, the triradical would be slowly magnetized/demagnetized and exhibit hysteresis phenomena. Triangular triradicals have shown great potential applications in molecular storage and organic quantum devices, benefiting from their unique magnetic properties; however, this kind of triradical has been rarely reported.

2. Synthetic strategies towards stable organic open-shell materials

Since the discovery of persistent stable triphenylmethyl radical 1 with its dimer 2 at equilibrium in solution by Gomberg early in 1900,$^{31}$ scientists have been always developing synthetic strategies towards stable organic open-shell materials. As shown in Fig. 2, triphenyl chloromethane was dissolved in benzene, and 1 could be synthesized upon the addition of Zn powder with the appearance of orange color. The color would fade immediately once exposed to air with the formation of white peroxide, indicating the high reactivity and instability of monoradical 1.

2.1 Kinetic steric protection by bulky substituents

Steric protection is a commonly used and effective strategy towards air stable organic open-shell molecules. Taking monoradical 1 for example, the introduction of bulky substituents on the neighbour positions in the phenyl rings of 1 would sterically protect the monoradical on $\pi$-carbon and prevent its dimerization reaction. Furthermore, the steric hindrance would also compel the phenyl rings to distort to a certain angle, and reduce the possibility of spin distribution expanding to the para positions of the phenyl rings. Therefore, hexamethoxyl substituted monoradical 3 (Fig. 3) could be stable in the solid state, and react with oxygen in air very slowly.32 Multi-chlorinated organic monoradicals 4–5 are thermally stable in air, which could be stored in air for several months.33 Recently, Li, Kusamoto and Nishihara demonstrated the possible application of these monoradicals in next-generation organic light-emitting diode (OLED) materials.34–36 In 2018, Kubo et al. reported air-stable highly congested tri(9-anthryl)methyl monoradical 6a with an unpaired electron.
mainly localizing on the central carbon. However, if the 10-position of one anthracene is not protected by the mesityl group, a tail-to-tail dimer would be isolated instead, rather than the head-to-tail dimer. Further thermodynamic analysis revealed the much larger equilibrium constant of 6b and its dimer 7 with a log $K_D$ of 6.69 at 198 K, in comparison with that of 1 and its dimer 2 with a log $K_D$ of −3.48.

Similarly, steric protections could also be used to protect diradicaloids. As shown in Fig. 4, early in 1904, diphenylmethene terminated quinoidal $p$-quinodimethane ($p$-QDM) was synthesized by Thiele, and also named Thiele's hydrocarbon, which possesses a closed-shell ground state. Its extended structure, compound 9, was synthesized by Tschitschibabin later in 1907 and therefore called Chichibabin's hydrocarbon. However, the high reactivity of 9 towards oxygen caused the impurity problem and made its ground state controversial. Until 1986, Montgomery prepared pure 9 in an inert atmosphere, and the X-ray crystallographic analysis elaborated its quinoidal structure with a significant diradical character. Recently, Wu and coworkers reported mesityl substituted Chichibabin's hydrocarbon with much improved stability, which allowed the intramolecular dynamics to be conducted. For example, variable-temperature NMR measurements revealed that the rotation energy barrier of 10-trans and 10-cis is 11.40 kcal mol$^{-1}$. The contribution of the open-shell resonance form to the ground state could be described by the biradical character index $y$. When $y = 1$, it indicates a pure diracialoid; when $y = 0$, it indicates a closed-shell structure. Conjugated extended fused quinoidal $p$-QDMs are predicted to be diradicaloids with high diradical characters. Therefore, different substitution strategies were utilized to develop stable 2,6-anthraquinodimethane ($p$-AQDM) containing compounds 11–14 (Fig. 4). Compound 11 ($y = 0.68$ at the CASSCF(2,2)/6-31G level) with four phenyl substituents developed by Kubo in 2012 could only be stable in air for a couple of days. Extended nonazethrene 12 ($y = 0.25$ at the RAS-SF/6-31G(d,p) level) with two mesityl groups and two electron-withdrawing groups developed by Wu could only show a half-life of 16 h. In contrast, compound 13 (0.381 at the UCAM-B3LYP/6-31G level), a S-atom containing acene analogue, developed by Chi and coworkers with four mesityl groups, exhibited excellent photostability with a half-life longer than one month. Extended indofluorene 14 (0.381 at the PUHF level) synthesized by Haley with trisopropylsilyl (TIPS) ethynyl substituents and two mesityl groups showed a half-life of 64 days in solution.

Recently, scientists found that steric protection strategies showed great influence on the stabilization of extremely challenging extended $[n, m]$peri-acenes. As shown in Fig. 4, Kubo et al. reported 15a and 15b with a diradical character of 0.54 and 0.91 (at the CASSCF(2,2)/6-31G level), respectively. However, these molecules could be stabilized by introducing bulky mesityl groups to the reactive zigzag edges and four tert-butyl groups. The half-life of 15a was reported to be 3 days even after being exposed to air, while the non-mesityl derivative of 15a decomposed instantly in an inert atmosphere. For zigzag-edge extended 16a, the decay curve of absorption spectra gave its half-life of 15 hours in air and under ambient light. Feng and Wu's groups independently reported the laterally extended [4, 2]peri-acene derivatives 16a (0.72 at the PUHF level) substituted by two mesityl and two 4-tert-butylphenyl groups,
and 16b (0.515 at the UCAM-B3LYP/6-31G level) protected by four 2,6-dichlorophenyl groups.49 respectively. 16a only showed persistent stability with a half-life of 3 h, while 16b had a half-life of 7 h, indicating the better protection of 2,6-dichlorophenyl groups. Very recently, Chi et al. reported the vertical extended [4, 3]peri-acene 17.50 Surprisingly, even its diradical character was calculated to be 0.948, approaching a pure diradical. However, 17 showed much better stability even than 16a and 16b with a half-life of 157 h. This could be ascribed to the bulky and electron-withdrawing 2,4,6-trichlorophenyl groups at the reactive zigzag edges, together with the additional two tert-butyl groups.

2.2 Spin-delocalization by organic π systems

Another important strategy to realize stable organic open-shell materials is to utilize the delocalization of radical electrons on organic π systems to dilute the spin density of organic open-shell molecules and consequently decrease their reactivity.

As shown in Fig. 5, 18a-c are typical pentaphenyldicyclopentadienyl radicals, and radical electrons could be delocalized on the cyclopentalienyl ring.51–53 Among them, 18c is the only air-stable monoradical due to the delocalization of TIPS ethynyl substituents.52 The fluorenyl radical could be regarded as a dibenzo fused cyclopentalienyl radical, and according to DFT calculation results, spin electrons could delocalize on the whole fluorene. Therefore, by well protecting the 3,6,9-positions with bulky substituents, Wu et al. reported air-stable fluorenyl radical 19, which could be isolated even by common column chromatography on silica gel.54,55

Phenalenyl 20a is a typical representative monoradical hydrocarbon with odd carbon numbers.56–58 Due to its high reactivity, it could not be stable in air. However, three tert-butyl substituted phenalenyl 20b could be stable and can form a π–π stacked dimer in the crystal state under low temperatures.56 Kubo et al. reported cyclopentalienyl linked two phenalenyl derivative 21, which exhibited excellent air stability with a half-life of 60 h. Interestingly, since 21 only has one n-butyl substituent, its stability obviously benefitted from the delocalization on the whole π system.59 Recently, Sun et al. reported air-stable olympicenyl radical 22 protected by the TIPS ethynyl substituent with a long half-life of 7 days. Further study indicated that 22 could form a head-to-tail dimer with a unique 20-center-2-electron structure in the solid state, and the ground state of π-dimers was found to be singlet diradicaloid.60

![Fig. 5 Representative monoradicals stabilized by spin-delocalization.](image)

2.3 Heteroatom (B and N atoms) assisted open-shell molecules

Heteroatoms could be utilized to stabilize open-shell molecules, including heteroatom-centre radicals and heteroatom-assisted open-shell molecules for their interesting electronic structures. And, we will emphasize the latter one focusing on the bridge-linking effect of heteroatoms (B and N atoms) on open-shell species through their π-orbitals.

Compound 23, the quinone analogue of Chichibabin’s hydrocarbon shown in Fig. 6, possesses a closed-shell ground state. And 24, first synthesized by Galvin M. Coppinger in 1957 and also called a galvinoxyl radical, could be regarded as a methane-inserted structure of 23.61 Due to the formation of a quinoidal structure by one of the phenoxy radicals and the unpaired p electron of methane carbon, 24 shows the doublet ground state of a monoradical. Similarly, its iso-electronic structure 25 with imine nitrogen atoms was also reported to be a monoradical.62 Seki et al. reported an amine nitrogen linked two phenoxy radicals 26, and X-ray crystallographic analysis reveals the C–N bonds with multiple-bond characters, indicating the effective conjugation between two phenoxy radicals through the p-orbital of the amine N atom. Interestingly, the ground state of 26 possesses a closed-shell singlet electronic state even at 388 K.63

![Fig. 6 Representative open-shell molecules stabilized by heteroatoms.](image)

Shimizu et al. reported azoniadibenz[a]phenalenide 27 (Fig. 6) with a singlet diradical ground state.64 Further study indicates its zwitterion structure with negative charge delocalized over the periphery of the molecule and positive charge mainly localized near the nitrogen atom. Yamagushi et al. reported a B containing monoradical 28 with spin density effectively delocalized through the vacant p-orbital of the boron atom.65 Therefore, 28 is an air-stable monoradical exhibiting well balanced ambipolar carrier transport properties.

3. Aggregated open-shell organic materials in organic semiconductors

Open-shell organic conjugated materials usually exhibit special charge-transport properties, which is different from traditional
organic semiconductors due to their unique physical properties, such as unique electronic structures and aggregated structures, and temperature-dependent magnetic properties.

### 3.1 Polycyclic conjugated open-shell diradicaloids

By adjusting the substituents of indenofluorene, Haley _et al._ found that a single crystal device of compound 29 (Fig. 7) with two pentafluorophenyl groups showed a hole/electron carrier mobility of $7.0 \times 10^{-3}/3.0 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. Later in 2016, Haley reported that diradicaloid 14 (Fig. 7) also showed a balanced ambipolar carrier transport character with a hole/electron carrier mobility of $2.0 \times 10^{-3}/4.0 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. The relatively low charge transport mobility could be ascribed to the introduction of bulky substituents, which is beneficial for the stability of diradicaloids but harmful for the effective molecular π-pi packing and charge transport.

To enhance the π-π overlap of neighbour molecules, Haley _et al._ reported lateral extended indenofluorene derivatives 30–32. X-ray crystallographic analysis indicates the influence of chemical structure modifications on crystal packing. As shown in Fig. 8a, b, c, d, e and f, 30a and 30b with larger bulky substituents show disconnected 1D π-π packing, while 32 arranges in dimers and there are no π-π or C-H-π interactions between neighbour dimers. Therefore, no FET character could be detected for 30a, 30b and 32. It is claimed that both 30c and 31 crystallize in a two-dimensional (2D) π-π stacking motif, which is known for TIPS-pentacene with superior electrical properties. Therefore, OFET devices of 30c and 31 based on crystalline thin films exhibit an excellent p-type hole mobility of $1.04 \pm 0.68/4.72 \pm 1.97$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. However, the 2D crystal packing of 30c and 31 described here is not consistent with their previous results, which remain controversial.

Kubo _et al._ reported compound 33 (Fig. 7) with a singlet diradical character of 0.68 at the CASSCF(2,2)/6-31G level and a low optical band gap of 1.1 eV. Its relative high-lying highest occupied molecular orbital (HOMO) energy level and low-lying LUMO energy level make it suitable to exhibit ambipolar carrier transport character. As shown in Fig. 9a and b, 33 packs in one-dimensional (1D) column with a slipped stacking motif and an average π-π distance of 3.137 Å, which is much shorter than the common van der Vaals contact of two sp$^2$ carbon atoms, indicating its possible fast charge-transport properties.
However, the electrical conductivity of 33 has a value of $5.0 \times 10^{-5}$ S cm$^{-1}$. Furthermore, the thin-film OFET device shows its balanced hole/electron mobility of $2.6 \times 10^{-3}$/$3.2 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively.$^{69}$

Bisphenaleno-thieno[3,2-b]thiophene 34 (Fig. 7) was developed by Chi’s group.$^{70}$ X-ray crystallographic analysis reveals its typical quinoidal resonance form with an unexpected wave-shape structure due to the strong intermolecular phenalenyl-phenalenyl $\pi-\pi$ interactions in crystals. DFT calculations indicate its diradical character of 0.186 (at UCAM-B3LYP/6-31G level), which probably originated from the thermodynamic stabilizing effect of the delocalized phenalenyl moieties. In addition, its OFET devices based on solution-processed thin films exhibit hole mobilities of 0.26 cm$^2$ V$^{-1}$ s$^{-1}$, respectively.$^{71}$ X-ray crystallographic analysis reveals their dimeric structures with one molecule periodically aligned in the crystal. Although no obvious 1D or 2D $\pi-\pi$ stacking motifs were observed, top-contact bottom-gate OFETs based on single crystals of 35 and 36 give the highest hole mobilities of 0.15 cm$^2$ V$^{-1}$ s$^{-1}$ and 0.017 cm$^2$ V$^{-1}$ s$^{-1}$, respectively.

Extended acenes with a significant diradical character for OFETs are rarely reported, as limited by their poor stability.$^{72}$ Frigoli et al. reported slipped bisacene compounds 37 and 38 with a diradical character of 0.50 and 0.64 (at the UHF/6-31G(d, p) level), respectively. However, 37 and 38 showed a long half-life of 6.5 and 4.9 days, respectively. The excellent stability allows their thin-film OFET devices to be fabricated, with a mobility of up to 0.77 cm$^2$ V$^{-1}$ s$^{-1}$ and 1.4 cm$^2$ V$^{-1}$ s$^{-1}$ for 37 and 38, respectively.

3.2 Tetracyano terminated open-shell diradicaloids

Tetracyano terminated $p$-QDMs could serve as $n$-type semiconductors due to their low-lying LUMO energy levels caused by the strong electron-withdrawing effect of the terminal group and planar conjugated structures favourable for solid packing and charge-transport in organic electronics.

Tetracyano terminated $\pi$-extended quinoidal structures would also show an increased diradical character.$^{15}$ As shown in Fig. 10, in 2005, Otsubo et al. reported compounds 39a-f with up to six quinoidal thiophene rings by fusing the $\beta$-positions of each thiophene ring with bis(butoxymethyl)cyclopentane substituents. Further experimental and DFT calculated results reveal that molecules longer than 39c ($n = 3$) show a gradually increased open-shell singlet diradical ground state accompanied by the extension of quinoidal oligothiophenes.$^{73}$ In 2007, by reducing two bulky substituents, Takimiya et al. reported the $n$-type charge transport properties of 40 with a mobility of 0.16 cm$^2$ V$^{-1}$ s$^{-1}$, revealing their potentials in $n$-type semiconductors.$^{74}$

Tetracyano terminated cyclic fused compound 41 reported by Li and coworkers displayed $n$-type FET behaviour with an electron mobility of up to 0.9 cm$^2$ V$^{-1}$ s$^{-1}$ under ambient conditions, which is beneficial for its low-lying LUMO energy level ($\approx$-4.3 eV).$^{75}$ In 2014, Takimiya et al. reported the synthesis and characterization of two regioisomers 42 and 43 with moderate electron mobilities of $3.2 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ and $1.4 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively.$^{76}$ It is worth noting that the low-lying LUMO energy levels around $-4.6$ eV enable their stable operation in $n$-channel OFETs under ambient conditions. Later, they further synthesized another regioisomer 44a,$^{77}$ which showed significantly red-shifted absorption for its up-shifted
Electronic Frontier Energy Values compared to that of 42. Furthermore, 44a showed a moderately high electron mobility of 0.1 cm² V⁻¹ s⁻¹. However, all these compounds were studied as semiconductors, and their ground states were not well investigated.

By changing capping groups, in 2016, Takimiya and Casado reported the (alkyloxy)carbonyl)cyanomethylene groups capped quinoidal naphthodithiophene 45, which could undergo reversible diradical σ-dimerization/σ-polimerization triggered by mild stimuli such as solution concentration, temperature and pressure. The reaction reversibility was caused by the quinoidal molecule 45, which could change its structure to aromatic species by forming weak and long intermolecular C-C single bonds (Fig. 11a and c). The two opposite but complementary quinoidal and aromatic tautomers provided two Janus faces of the reactants and products, which caused the huge chromic effect of about 2.5 eV. However, no such changes were detected for the quinoidal naphthodithiophene 44b with dicyanomethylene terminal groups, since it can only form π-dimers (Fig. 11b). The reversible reactions of 45 reveal an unusual mechanism of weak covalent supramolecular bonding, which provides a typical model to understand the fundamental properties of the diverse aggregated modes of π-conjugated diradicaloids.

4. Aggregated open-shell organic materials in one-component organic conductors

Organic conductors have been studied for more than 60 years. To realize the organic metallic state with good conductivity, it usually requires three basic conditions: (1) the existence of unpaired electrons; (2) a solid structure with charge transport channel and effective delocalization of unpaired electrons in a metallic band; (3) weak electron-electron Coulomb repulsive interactions.

Early in 1973, the charge-transfer complex TTF-TCNQ (Fig. 12) was obtained as a metallic molecular crystal with a conductivity of 10⁻² S cm⁻¹. The formation of a radical cation and radical anion by charge transfer and the corresponding partially filled band structure generated from the mixed valence state contribute to the conducting behaviour of TTF-TCNQ salts.

4.1 Open-shell organic diradicaloids for conductors

One component diradicaloids usually have semiconductor characteristics as described above. Recent studies demonstrated that dicyanomethylene capped π-extended quinoidal structures could exhibit self-doping behaviour and consequent intrinsic conducting properties.

1,2,4-Benzotriazinyl radicals (46, Fig. 13), which could also be called Blatter radicals, have attracted scientists’ attention due to their interesting magnetic and electronic properties, and especially their exceptional air and moisture stability. In 2015, Wudl’s group synthesized benzotriazinyl diradicaloids 47a with a small optical energy gap of around 1.20 eV. The sharper and new extra peaks observed upon cooling in VT¹ H NMR spectra indicated its singlet diradical ground state. However, further ESR studies on the polycrystalline solid demonstrated an intermolecular quintet state at room temperature. The followed work by cooperation of Wudl and Nguyen revealed the unprecedented self-doping behaviour of 47a and 47b, involving a radical anion–radical cation pair. Moreover, the number of radical anion–radical cation pairs of 47a and 47b was found to be temperature dependant and reversible, indicating that the phenomenon was not originated from oxygen doping. To further confirm the enhanced doping strength with the increasing temperature, OFET devices were fabricated by doping 47a/47b with the strong electron acceptor 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ). It was found that transfer curves were insensitive to the F₄TCNQ concentration, with Iₒ all exhibiting a flat response to Vₒ. Interestingly, the transfer curve of pristine 47a at 370 K in a high Vₒ region almost

Fig. 12 (a) Chemical structures of TTF and TCNQ; (b) quasi-1D chain like segregated stacking motifs in TTF and TCNQ. Copyright 2008, Springer Nature.

Fig. 13 Chemical structures of a Blatter radical and derivatives.
overlapped with that of the F4TCNQ doped OFET at 300 K, which helped to confirm the temperature-enhanced self-doping and electrical conductivity in both systems. To our knowledge, this is the first example for diradicaloids exhibiting self-doping phenomena, regardless of the low conductivity of 1.06 × 10⁻⁴ S cm⁻¹.

In 2018, Zhu et al. reported 48a and 48b with dicyanomethylene capped two-dimensional extended quinoidal oligothiophene structures. Electrochemical measurements revealed their surprisingly narrow band gaps of 0.67 and 0.65 eV for 48a and 48b, respectively. DFT calculations (at the UCAM-B3LYP/6-31G level) revealed their diradical character of 0.49 and 0.52, respectively. The singlet and triplet band gaps were calculated to be −3.73 kcal mol⁻¹ (0.16 eV) and −3.56 kcal mol⁻¹ (0.15 eV) for 48a and 48b, respectively, which allowed them to generate thermal activated triplet species. It was clear that the special energy levels of two diradicaloids enabled the possible promotion of free carriers by thermal activation. And, the electrical conductivities of 48a and 48b were further measured to be 0.0080 and 0.29 S cm⁻¹, respectively. Later, Zhu et al. reported a series of quinoidal molecules 49a–49d. From dimer to pentamer, DFT calculations showed their increased diradical character of 0.00 (49a), 0.02 (49b), 0.22 (49c) and 0.46 (49d), revealing that the ground state changed gradually from closed-shell states to open-shell states. Single component electrical measurements demonstrated that 49a and 49b showed a typical semiconductor character, and in contrast, 49a and 49b exhibited conductor behaviour with conductivities of 1.5 × 10⁻⁴ S cm⁻¹ and 3.0 × 10⁻⁴ S cm⁻¹, respectively. The formation of free carriers here could also be explained by thermal activation through the narrow bandgaps of extended quinoidal diradicaloids. Interestingly, from 49a and 49d, the gradually changed aggregation mode was also observed by AFM and GIWAXS characterization. As shown in Fig. 14b, 49b had a slipped π-π stacking. However, 49c (Fig. 14c) showed a cholesteric-like π-π arrangement with a 3.7 Å of inter-molecular distance and a 30° average rotating angle between neighbour molecules. For 49d, the possible σ-polymerization in the solid state with the formation of C–C bonds between neighbour terminal methylene carbons was predicted to be formed due to the relative high diradical character of 49d.

Guo et al. reported the two dicyanomethylene capped imide-bridged fused quinoidal oligothiophene 50 and 51. The incorporation of a strong electron-withdrawing imide group into the tetracyano-capped oligothiophene backbones ensured their deep LUMO levels (~4.58 to ~4.69 eV 50 and 51, respectively), and the remarkable ambient stabilities of the diradicaloids with half-lives longer than two months. DFT calculations (oB97X-D/6-31G**) indicated that the diradical characters of 50 and 51 were 0.37 and 0.67, respectively. Furthermore, 51 exhibited a cross-conjugation assisted self-doping in the film state (Fig. 15b), which could be confirmed by XPS and Raman studies. Accordingly, 51 exhibited a high electrical conductivity of 0.34 S cm⁻¹, which is among the highest values in single-component organic radical-based conductive materials.

### 4.2 One-component organic monoradicals for conductors

In principle, one-component neutral monoradicals are ideal building blocks for organic conductors and spintronics. In practice, however, monoradicals usually show poor conductivities even if 1D π-π stacking charge transport channel could be formed. This should be ascribed to the conduction barrier limited by the on-site neighbour Coulomb repulsion (U, Mott insulator) of relative localized monoradicals. The electronic structure of monoradicals in solid states could be depicted as a half-filled band Mott–Hubbard model. To generate conductivity, the key issue is to realize the equation of W > U, where W = 4β, W is the electronic bandwidth, and β is the intermolecular

![Fig. 14](https://example.com/fig14.png)

**Fig. 14** (a) Chemical structures of dicyanomethylene capped quinoidal oligothiophenes and the possible aggregation modes of (b) 49b, (c) 49c and (d) 49d in the solid state. Copyright 2019, Elsevier.

![Fig. 15](https://example.com/fig15.png)

**Fig. 15** (a) Chemical structures of 50 and 51, and (b) proposed self-doping mechanism of 51 through the formation of intermolecular charge transfer species, the fundamental species of the organic conductive compounds. Adapted with permission from ref. 87, copyright 2020, American Chemical Society.
X-ray crystallographic analysis indicated the absence of bulky substituents 20b with three steric tert-butyl groups could form a π-dimer in the crystal; however, bulky substituents prevented the effective interactions between neighboring dimer pairs.56 20d with the pentfluorophenyl substituents could form 1D π–π stacking columns with an interplanar distance of 3.503 Å; however, the measured conductivity of compressed pellets was only \(1 \times 10^{-10}\) S cm\(^{-1}\), revealing its intrinsic insulator character. Haddon et al. reported a series of spiro-biphenalenyl radicals exhibiting remarkable conductivity by substituent engineering. As shown in Fig. 17, in 1999, Haddon et al. reported the first spiro-biphenalenyl monoradical 52e without bulky substituents, which could be regarded as an intramolecular zwiterionic structure.59 X-ray crystallographic analysis indicated the absence of σ-dimer and π-dimer (Fig. 18a and b), and instead, only C–H⋅⋅⋅π interactions could be observed. Even though, a room-temperature conductivity of 0.05 S cm\(^{-1}\) could be achieved. As shown in Fig. 18e, it was speculated that the delocalized electronic conduction band (0.5 eV) should be responsible for the transport properties of 52e. However, it was separated from the ground state of 52e, or a degenerate Mott–Hubbard insulator, by an energy gap corresponding to the on-site Coulomb repulsion energy (\(U = 0.4\) eV), which allowed the thermal population of electrons to conduction bands possible.

Later, by adjusting hexyl groups to ethyl and butyl ones, compound 52a and 52e were synthesized, with the change from C–H⋅⋅⋅π interactions to π-dimers as observed in the crystal structures (Fig. 18d).90 Interestingly, 52a and 52e exhibited bistability in electrical, optical and magnetic aspects. For example, the distance of the π-dimer was about 3.3 Å at a high temperature (\(T > 350\) K); however, when \(T\) decreased below 320 K, the distance shortened to about 3.2 Å. As shown in Fig. 18e, at high temperatures, the two radicals were located in the two outer phenalenyl moieties of the π-dimer with paramagnetic properties, whereas at low temperatures, the two radicals moved to the inner phenalenyl units and behaved as π-dimers with a diamagnetic character. Correspondingly, the conductivity sharply increased by two orders of magnitude in the diamagnetic state.91

By further changing the substituents to cyclohexyl groups, 52h showed a spiro-conjugated 2D-like structure with effective π–π overlaps of neighboring molecules (Fig. 19). Therefore, the room-temperature conductivity was 0.3 S cm\(^{-1}\), which could be ascribed to the quarter-filled energy band and the significant reduction of on-site Coulomb repulsion energy band \(U\).92 However, the introduction of more alkyl chains was harmful for charge transport. For example, by changing two O atoms to methylamine groups, the conductivity decreased to \(4 \times 10^{-2}\) and \(1 \times 10^{-3}\) S cm\(^{-1}\) for 53a and 53b, respectively.93 The attempt by reducing the substituents of changing alkylamine groups to O atoms produced 54a and 54b. Single crystal analysis revealed their continuous array of π–π stacking structures with very short intermolecular C–C contacts. Thus, 54a and 54b exhibited the conductivities of 0.1 and 0.3 S cm\(^{-1}\), respectively.93

4,8,12-Trioxotriangulene (Fig. 20a) radicals represented another kind of stable monoradical even without steric protection due to the delocalization of spin density on the whole backbone with 25π electrons (Fig. 20b).94 Similar to phenalenyl radicals, X-ray crystallographic analysis of 55a revealed the formation of a π-dimer with a shortest C–C distance of 2.987 Å, much shorter than the sum of van der Waals radii of two sp\(^2\) carbons (3.40 Å).95 The dimers stacked together to construct a 1D column with a much larger intradimer distance of 3.684 Å (Fig. 20c).

By introducing different substituents, 55b–f showed a similar 1D column but with different intradimer distances.96 Therefore, DFT calculations revealed their different intermolecular overlap integrals of singly occupied molecular orbital (SOMO) of intra- and inter-dimers, for example, 55b showed about 15 times larger intermolecular overlap integrals (\(s_a\)) than that of interdimer one (\(s_d\)). However, 55f formed a uniform 1D slipped π-stacking column with a π–π distance of 3.43 Å, and the overlap integral was around \(2 \times 10^{-3}\). As mentioned above, the conduction barrier in the 1D array was defined as \(U-4\beta\), and obviously, a strong orbital...
overlap was essential for the generation of high conductivity. The different inerdimer and intradimer interactions in turn resulted in the corresponding electron conductivities of $10^{-4}$, $1.2 \times 10^{-5}$, $8.1 \times 10^{-5}$ and $1.8 \times 10^{-3}$ S cm$^{-1}$ for 55b, 55c, 55d and 55f, respectively.

In principle, high pressure would compress the crystallographic lattice and increase the intermolecular overlap integrals, which in consequence, probably generate monoradical conductors. In 2016, Veciana et al. reported a TTF linked polychlorotriphenylmethyl radical 56. In the crystallographic structure (Fig. 21a), 56 formed a 1D herringbone structure with head-to-tail TTF units packing together and a S-S distance of 3.9 Å, which provided a possible charge transport channel.
values from nonpolar cyclohexane to polar chloroform solvent, indicating its high dipole moment in the excited state. It is worth noting that although the absorbance coefficient of the maximum of 57a (3740 Lmol⁻¹ cm⁻¹ at 597 nm) is higher than that of 4b (840 Lmol⁻¹ cm⁻¹ at 542 nm), it still remained at a relatively low level. Therefore, how to improve the absorbance coefficient of these monoradicals is a critical factor to realize high-efficiency OLEDs.

Furthermore, the OLED performance of 57a (Fig. 22) has never been reported, probably due to its aggregation-caused quenching behaviour in the thin-film state. Excitedly, Li et al., for the first time, fabricated OLED devices of 57a by doping the monoradical into a matrix of 4,4’-bis(carbazol-9-yl)biphenyl. The optimized maximum external quantum efficiency (EQE) (\(\eta_{\text{EQE}}\)) of 4b was up to 2.4% with electroluminescence at 692 nm. Later, by introducing 3-phenyl-9H-carbazole and 3-substituted-9-(naphthalene-2-yl)-9H-carbazole into 4b, 58a and 58b were prepared, and the performance of OLEDs could be improved to 17% and 27% with a deep-red emission at 703 nm and 710 nm, respectively. The high luminescence efficiency could be ascribed to the charge-transfer state, which could break the alternative symmetry of molecular structures and lift the degeneracy of the lowest energy orbital excitations. By further finely tuning the N position of pyridoindolyl groups, Li et al. also synthesized 57b–d, and the photoluminescence quantum yields could be as high as 91%, 89%, 32% and 99% with pure-red emissions at 620 nm, 635 nm, 612 nm and 643 nm, respectively. Finally, highly efficient OLEDs with the maximum EQE of 9.6%, 12.2%, 2.9% and 9.5% for 57b–d, respectively, could be realized. Compared to the relative low performance of 57a in OLED devices, 57b–d are much better doublet emitters. This could be ascribed to the non-alternant structures of these pyridine containing 57b–d, which would lift the degeneracy of the lowest energy orbital excitations and the intensity borrowing from an intense high-lying transition by the low energy excitation could enhance the oscillator strength of these monoradicals.

Recently, they reported that compound 59 (Fig. 22) violated the Aufbau principle with its SOMO lying below the HOMO and HOMO-1 (Fig. 23), and the special electronic structure would enhance the stability of the monoradical. Therefore, the half-
lives could reach up to several months even under UV light radiation. Furthermore, OLED-based 59 showed a deep-red emission (700 nm) with a maximal EQE of 5.3%.102

Li et al. also synthesized a new luminescent biphenylmethyl radical 60 (Fig. 22) with N atoms in the carbazole ring directly linked to the carbon radical centre.103 EPR spectroscopy results (Fig. 24b) confirmed the existence of the unpaired electron with $g = 2.0035$. X-ray single crystal analysis showed that (Fig. 24a) radicals C13, N1, C14, and C20 lied in the same plane. The molecule was propeller shaped, and the adjacent molecules were linked together by multiple C–H · · · π hydrogen bonds. The 60 in cyclohexane solution emitted at 697 nm with an absolute fluorescence quantum yield (PLQY) of 2.0%. And, OLED devices showed its maximal EQE of 0.66%.

For open-shell species, especially monoradicals, the degradation problem under photoexcitation has always been a hindrance for the development of this area. In 2014, Nishihara et al. reported (3,5-dichloro-4-pyridyl)-bis(2,4,6-trichlorophenyl) methyl radical 5a (Fig. 3) with fluorescence quantum yields of 0.03, 0.26, and 0.81 in solution, in a PMMA film at room temperature and in an EPA matrix (diethyl ether:isopentane: ethanol) at 77 K, respectively.104 Furthermore, the photostability of 5a was 115 times higher than that of 4b, which could be ascribed to the introduction of the pyridyl group with the lowered energies of molecular orbitals. Later, by changing the halogen atoms on pyridyl from Cl atoms to Br and F atoms, Nishihara et al. synthesized 61a and 61b (Fig. 25). It was found that the halogen atoms did not affect the SOMO strongly, whereas the electronegativity of halogens showed obvious effects on their HOMOs. Therefore, as shown in Fig. 26, the absorption and emission of the three compounds exhibited bathochromically in the order of $F < Cl < Br$.104

Based on pyridine chemistry, Nishihara et al. further developed a series of luminescent open-shell radicals. By coordinating 5a with Au1, they synthesized 62a and 62b (Fig. 25).105 The Au1 complex of 62b exhibited bathochromically shifted fluorescence with a maximum peak at 653 nm compared to that of 4b ($\lambda_{em} = 585$ nm), which could be ascribed to the excitation of the transition band from the D1 state to the D0 state on the pyridyl radical centre. Another example by methylating and coordinating $B(C_6F_5)_3$ to the pyridyl imine N atom, Nishihara et al. synthesized 63 and 64 (Fig. 25).106 Further studies indicated that the chemical modification on imine N atoms showed great influence on the β-SOMO, which determined the optical and electrochemical properties. Therefore, compared to that of 5a, 63 and 64 showed red-shifted emission to the low-energy region with maximum wavelengths of 712 nm and 660 nm, respectively. They also reported CuII and ZnII complexes with two pyridyl radicals 5a as
ligands, and both 65a and 65b showed a hexacoordinated structure with an elongated octahedral geometry. However, the longer Zn–N bond length compared to the Cu–N bond length resulted in the axially coordinated Zn II complex and equatorially coordinated Cu II complex. Magnetic studies indicated that 65a displayed an efficient intramolecular ferromagnetic exchange interaction between the two radical centres and Cu II based on the orthogonality of the two spin orbitals.

In 2019, Nishihara et al. reported a 1D magnetic chain 66a (Fig. 27) consisting of Cu II and polychlorinated dipyridylphenylmethyl radical 5b. As shown in Fig. 27, a 1D –Cu II(hfac)2–5b–type zigzag chain structure formed along the a + c direction, and these 1D chains stacked together to form a layered structure. The temperature-dependent Jahn–Teller (JT) distortion was observed due to the Jahn–Teller axis rotation from the Cu–N bond direction at 298 K to the Cu–O bond direction at 93 K. Therefore, the intramolecular ferromagnetic interaction was enhanced by the reorientation of the Cu II d_x2–y2 orbital at low temperatures caused by the JT distortion.

Very recently, Nishihara et al. reported the preparation of tris(3,5-dichloro-4-pyridyl)methyl radical 5c, which exhibited much better photostability with a half-life of 2.2 × 10^4 s. And, the half-life of mono-pyridyl 5a, di-pyridyl 5b and tri-pyridyl 5c is 4, 160, 10 000 and times that of TTM 4b, respectively, which was beneficial for the introduction of more imine N atoms and gradually decreased the energy levels of frontier orbitals. Therefore, from 4b, 5a, and 5b to 5c, the maximal emission peak in solution was steadily red-shifted like the increased number of imine N atoms on the TTM skeleton with the values of 570, 585, 650 and 700 nm, respectively. In the solid state, 5c showed a blue-shifted emission peak at 665 nm. Complexation of 5c and Zn II(hfac)2 afforded 2D coordination polymers 67. As shown in Fig. 27c, 67 processed honeycomb spin-lattices with a graphene-like spin topology and exhibited luminescence at 79 K with a maximal emission peak of 695 nm, which was a rarely observed open-shell 2D structure with luminescence characteristics. Magnetic property measurements further confirmed the existence of one unpaired radical electron on each 5c unit without the loss of its radical character upon the formation of 2D polymer 67.

Nishihara et al. further reported the luminescence properties of monoradicals 5b and 5c, together with the 1D chain 66b and 2D network 67 under a magnetic field upon temperature changes. As shown in Fig. 28a and b, the emission spectra of 5b and 5c were almost unaffected by the external magnetic field. In contrast, the emission spectra of coordination polymers 66b and 67 showed significant magnetic field-dependent characters. The 1D coordination polymer 66b had almost no emission at 4.2 K and 0 T, upon increasing the applied magnetic field, emission peaks at 626 and 675 nm gradually appeared (Fig. 28c). And, the emission intensity of 67 increased by 25% when the magnetic field reached 18 T. This phenomenon could
be explained by the modulation of radical–radical ground-state interactions, and the reduction of radical–radical interactions in coordination polymers by ZnII would be the key point for the magnetoluminescence phenomena.

6. Aggregated organic photoinduced radical materials

Except for pure monoradicals, photoinduced organic radicals were found to be pivotal for the emission process of triphenylamine or triphenylphosphine-based close-shell materials upon light exposure. Recently, their possible mechanism and potential applications were preliminarily studied.

Giuseppone et al. found that tryarylamine derivatives were photoactive materials, which could generate radicals upon even white light irradiation. For example, compounds 68 and 69 (Fig. 29) in chloroform solution could form a proportion of triarylammonium cationic radical of up to 44% as a function of irradiation time with a halogen lamp. Further study indicated that the self-assembly nanostructure of 69 could display healable supramolecular properties and metallic behaviour. However, its emission phenomena have not been mentioned.

As shown in Fig. 30, Chi et al. reported 70 (Fig. 29) to be a photoinduced radical material, which unexpectedly exhibited a rapid and reversible luminescent colour change from blue to pinkish-purple in the single-crystal state by light irradiation under ambient conditions. An emission peak appeared at around 580 nm upon UV light irradiation, while the intensity significantly enhanced in response to the prolonged irradiative time. However, the phenomena could not be observed in the amorphous phase, indicating the importance of intermolecular interactions. The lifetime of this new peak at 580 nm was also measured to be 4.2 ns, revealing its fluorescence property (Fig. 30c). X-ray crystallographic analysis revealed the absence of π–π interactions, and C–H⋅⋅⋅π interactions in the crystalline state well separated the photoinduced radical cation molecules from each other, which is beneficial for the effective rapid release of its energy from the excited state to the ground state. Furthermore, this molecule could be integrated to a dual-channel photosensitive device, and showed luminescence and conducting switching upon UV light irradiation.

Recently, Tang et al. reported the photoinduced generation of radicals with bright red emission (Fig. 31a), which could be ascribed to the formation of a radical cation in crystalline 71. As shown in Fig. 31b, after irradiation, 71 (i-71) showed two new absorption peaks around 496 and 520 nm. ESR measurements (Fig. 31c) demonstrated the existence of radical species in the...
crystal core. The PL emission lifetime of \( i^-71 \) with a value of 3.9 ns (Fig. 31d) revealed the fluorescence character of the emission. Similar to that of \( 70 \), the emission disappeared after grinding, indicating the importance of crystal lattice acting as a protective cage to isolate \( 71 \) from water and ambient oxygen. Notably, the radical \( 71 \) and its red emission could survive for more than seven days in the crystalline state in air. DFT calculations and single-crystal analysis further revealed the unique symmetry breaking phenomena in single crystals of \( 71 \), which in turn caused the molecular conformation change and photooxidative characteristic change. In a single crystal, the asymmetric conformation with an intermolecular \( \pi-\pi \) distance of 3.29 Å arrangement may promote the exciton separation and stabilization according to the charge hopping mechanism. The study here provided a possible way to generate in situ stable radicals upon visible light irradiation as photosensitive materials.

Very recently, our group’s work revealed the importance of cationic radicals in the photoresponsive process of a series of triarylamine compounds from \( 72 \) to \( 75 \) (Fig. 29).\(^{114}\) As shown in Fig. 32, by dispersing these triarylamine compounds into a poly(methylmethacrylate) (PMMA) matrix, \( 72@\text{PMMA} \) films showed the photoactivated phosphorescence phenomena, while \( 73@\text{PMMA} \) demonstrated only fluorescence without phosphorescence characteristics. In detail, \( 72@\text{PMMA} \) exhibited irradiation time-dependent room-temperature phosphorescence (RTP) intensity, quantum yield and lifetime, which could be ascribed to the triplet oxygen consumption after long-time UV irradiation. However, \( 74 \) and \( 75 \) had no RTP phenomena but...

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**Fig. 31**  (a) Schematic diagram of the photoinduced radical generation process. (b) UV–vis spectra, (c) EPR spectra, and (d) PL spectra of \( 71 \) crystals before and after UV light exposure for seconds at room temperature, \( \lambda_{\text{ex}} = 365 \text{ nm} \). The insets in (b) and (d) show the photographs of colour and emission changes, QY = quantum yield. (e) Time-resolved PL decay curves of \( i^-71 \) measured at \( \lambda_{\text{max}} = 620 \text{ nm} \) at room temperature, \( \lambda_{\text{ex}} = 400 \text{ nm} \). Adapted with permission from ref. 113, Chinese Chemical Society publishing.

**Fig. 32** Schematic representation of the structure of triarylamine derivatives \( 72 \) to \( 75 \) and the photoactivated phosphorescence and photochromic properties in the PMMA film. Copyright 2021, Wiley-VCH Verlag GmbH & Co.
significant change in absorption (Fig. 33b). Taking 74 for example, as shown in Fig. 33e, the 74@PMMA film showed a maximum photochromic effect upon irradiation for 30 s, and faded from green to colourless after about 15 minutes. This process could be ascribed to the formation of cationic radicals under UV light irradiation, and ESR analysis further demonstrated the existence of open-shell species through photoinduced electron transfer. Interestingly, this process could be repeated for more than 20 times. Therefore, based on these controllable phosphorescence and photochromic phenomena, information encryption and decryption, anticounterfeiting and rewritable information recording have been successfully realized.

7. Summary and perspectives

Based on traditional thoughts, open-shell organic π-conjugated compounds are considered to be unstable species, which may limit their possible applications. Actually, the combined optical, electrical and magnetic characteristics of organic open-shell materials are quite appealing in the material world. In the last few decades, the stability problem of open-shell materials has dramatically changed due to the developed novel strategies, which are universally effective towards air-stable open-shell compounds, such as kinetically steric protection, spin density delocalization and heteroatom-assisted protection. Therefore, scientists could expand their attention towards the possible applications of open-shell magnetic materials. Consequently, we summarized the recent applications of open-shell organic conjugated materials in OFETs, one-component organic conductors, luminescent areas and photosensitive devices, mainly focusing on the general progress of novel developed organic open-shell magnetic materials and the effect of solid-state aggregation on their basic electrical and optochemical characteristics.

Although great progress has been made in both open-shell material design and the exploration of their novel applications in the past, there are still quite a number of scientific problems to be further tackled. Accordingly, future research perhaps should focus on these issues:

1. The intrinsic charge transport difference between common closed-shell semiconductors and open-shell organic materials is still not clear. For example, the self-doping behaviour...
of organic semiconductors with open-shell diradical ground states is an emerging hot topic in this area. Theoretically, by reducing the temperature to a certain degree, open-shell diradicaloids should also behave as pure semiconductors rather than intrinsic conductors due to the lack of thermally activated charge carriers. Several examples of diradicaloids with remarkable conductivities reported up to now are limited to compounds with narrow band gaps and low-lying LUMO energy levels. However, their temperature-dependent measurements are rarely investigated.

(2) One of the important research areas of open-shell materials is how to design molecules with both electrical and magnetic response characteristics, like spintronic devices. However, rare examples have been reported so far.

(3) For one-component organic monoradical conductors, the main problem is the lack of new monoradicals with good stability and ease of chemical modification. Therefore, the development of novel monoradicals is always the hot topic of this area, while another challenge is how to overcome the on-site neighbour Coulomb repulsion by delicate material design or special processing techniques.

(4) For open-shell luminescent materials, the main problem is how to improve their fluorescence quantum efficiency; in other words, the low fluorescence quantum efficiencies of radical species limit the progress of this area. On the other hand, open-shell luminescent materials now available are limited to monoradial species, and the expansion of open-shell luminescent materials towards triplet diradicals or even materials with high spin states still remain quite challenging.

(5) For photosensitive materials, photoinduced radical species are important for luminescence and photochromic phenomena. However, the intrinsic mechanism remains to be further explored. Besides, seeking for more photosensitive materials is also an attracting topic.

Conflicts of interest

There are no conflicts to declare.

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Notes and references
