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Efficient light-emitting diodes from organic radicals with doublet emission

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Organic light-emitting diodes (OLEDs) with doublet-spin radical emitters have emerged as a new route to efficient display technologies. In contrast to standard organic semiconductors, radical materials have unpaired electrons. This feature results in the most well-known examples of organic radicals being where they are reactive species in chemical reactions¹. Stabilised radicals can be used in optoelectronic applications which exploit their optical and spin properties, allowing up to 100% internal quantum efficiency (IQE) for electroluminescence². Highly efficient OLEDs have been demonstrated which operate in the doublet-spin electronic state manifold with doublet emission^{2,3}. The radical-based devices present a departure from the singlet- and triplet- level considerations which impose efficiency limits in OLEDs for typical organic semiconductors (25% IQE). This Perspective focuses on radical doublet emitters for optoelectronics, outlining how the photo- and spin-physics of unpaired electron systems present new avenues for research in light-emitting applications.

I. DOUBLET EMISSION FOR OLED DEVICES

Electron and hole recombination from conduction and valence bands results in light emission for semiconductor systems. These electron-hole excited states are known as excitons. Organic semiconductors intrinsically screen the coulombic interaction of electric charges less than their inorganic counterparts, a result of the lower dielectric constant in organic molecular solids⁴. The stronger interaction of charges within organic semiconductors can give rise to Frenkel excitons, where electron-hole pairs are more tightly bound than those in the Wannier-Mott excitons found in more classical inorganic semiconductors. Frenkel excitons generally have stronger transition dipole moments for more efficient light emission in optoelectronic devices. The 'organic' approach allows more flexible manufacture of light-emitting layers than devices based on III-nitride semiconductors^{5,6}, as well as easily tuneable properties from chemical synthesis.

However, strong coulomb interactions in organic semiconductors also impose efficiency limits for light emission from charge recombination – a consequence of the quantum-mechanical spin properties of singlet (S_1) and triplet (T_1) excitons. Singlet and triplet electronic states have total spin quantum numbers, $S = 0$ and $S = 1$, respectively. Due to a singlet ground state in typical organic semiconductors, triplet excitons should be dark and non-emissive due to the rule of spin conservation in transitions for light emission. As triplet excitons are formed in 75% of charge recombination events for such organic semiconductors⁴, spin statistics would limit the electroluminescence efficiency of OLEDs to 25%. The generally larger coulomb interaction in organic semiconductors compared to inorganic systems results in a larger exchange interaction and singlet-triplet exciton energy gap; triplets act as excitonic, non-luminescent traps if their emissive properties are not enhanced because T_1 excitons are generally lower energy than S_1 excitons.

Substantial progress has been made towards real-life applications in display and lighting technologies by brightening triplet excitons directly in iridium complexes to promote phosphorescence^{7,8}, and indirectly by converting dark triplet to bright singlet excitons in delayed emission, e.g. thermally activated delayed fluorescence (TADF)⁹⁻¹¹ and triplet-triplet annihilation (TTA)¹² – see Fig. 1b. We note that triplet emission occurs on much slower timescales than spin-allowed singlet emission in these systems. Spin-forbidden phosphorescence results in emission timescales on the order of microseconds to hundreds of nanoseconds^{7,8}. Similar emission times are observed in TADF and TTA systems, where the rate-limiting steps are singlet-triplet

spin-flip processes^{13–16}. These timescales are 2–3 orders of magnitude slower than seen for spin-allowed, direct transitions between singlet exciton and ground states in standard organic semiconductor systems.

Generally, we consider that faster light emission will reduce the chance of exciton quenching processes which can limit the OLED device lifetime¹⁷ and operational efficiency¹⁸. There is therefore a commercial appetite for alternative solutions to circumvent the OLED spin statistics efficiency limit using emitters which do not contain low-abundance metals such as iridium, and have shorter light emission timescales, enabling more sustainable manufacture and improved device performance.

Radical-based organic semiconductors have unpaired electrons in non-bonding singly occupied molecular orbitals (SOMOs) which are intermediate to the highest occupied and lowest unoccupied molecular orbitals (i.e. HOMO and LUMO; valence and conduction bands). As discussed in the next section, the SOMO results in doublet-spin physics which can allow radical emitters to undergo charge recombination with unity light emission efficiency (Fig. 1a). In a sense, organic radical doublet emitters in LEDs are similar to their inorganic counterparts in not being limited by spin considerations, whilst also having the efficient emission characteristic of organic semiconductor systems.

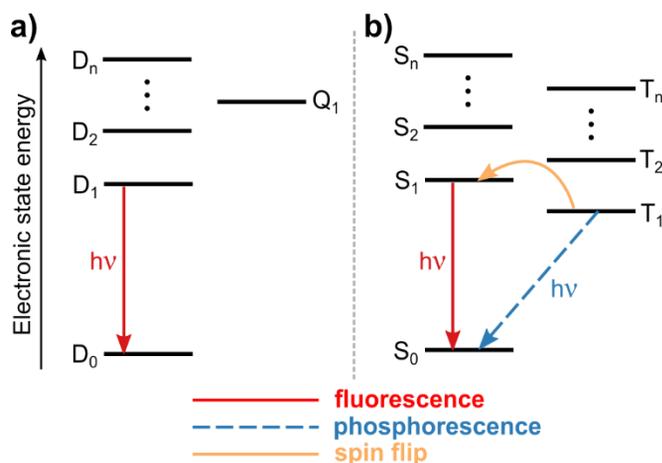


Fig. 1. Emission mechanisms for doublet- and singlet/triplet-based organic emitters

Jablonski energy diagrams of the a) doublet-quartet manifold, indicating doublet-doublet fluorescence and b) singlet-triplet manifold indicating singlet-singlet fluorescence, triplet-singlet phosphorescence and spin flip processes e.g. intersystem crossing (ISC, $T_1 \rightarrow S_1$) in TADF; triplet-triplet annihilation (TTA, $2 T_1 \rightarrow S_1 + S_0$).

These factors have allowed the development of radical based semiconductors with nanosecond emission timescales and high photoluminescence quantum efficiency (PLQE)^{19–22}. Some of the most efficient π -radical emitters have been based on derivatives of tris(2,4,6-trichlorophenyl)methyl (TTM)^{23,24},

perchlorotriphenylmethyl (PTM)^{25,26} and (3,5-dichloro-4-pyridyl)-bis(2,4,6-trichlorophenyl)methyl (PyBTM)¹⁹ radicals – see Fig. 2. Using these materials, highly efficient light-emitting devices have been shown to surpass the singlet-triplet efficiency limit that is otherwise imposed on non-radical organic semiconductors^{3,24,27}.

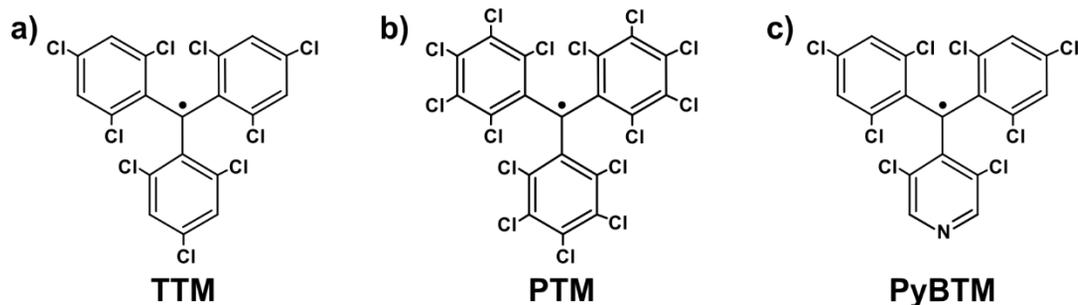


Fig. 2. Stable π -radical chemical structures

Chemical structures of a) tris(2,4,6-trichlorophenyl)methyl (TTM)²⁸, b) perchlorotriphenylmethyl (PTM)²⁹, c) (3,5-dichloro-4-pyridyl)-bis(2,4,6-trichlorophenyl)methyl (PyBTM)¹⁹ radicals.

The opportunities to use radical emitters in optoelectronics were not widely appreciated until the last decade. Organic radicals were generally thought to be dark and strong luminescence quenchers as mediators of electron exchange-induced intersystem crossing and charge transfer processes^{30–34}. The seminal work of Julia et al. in brightening the dark TTM moiety by functionalisation with carbazole to form a TTM-carbazole derivative³⁵, and subsequent advancements to produce the first generation of radical light-emitting devices^{2,3} by Li and co-workers have already been set out in a review³⁶, and is not detailed in this article.

II. DOUBLET MANIFOLD AND EMISSION MECHANISMS

In organic radicals, an odd number of valence electrons leads to the presence of an unpaired electron which does not participate in the valence and conduction bands. Consequently, a radical species has a doublet ground state which is classified as D_0 , with total spin quantum number, $S = 1/2$, and total spin projection, $M_S = +1/2, -1/2$. In Fig. 3 the D_0 state is depicted where electrons doubly-occupy levels from lower-energy orbitals up to the HOMO, with single-electron occupancy of the SOMO, and no electrons in the LUMO and higher-energy orbitals. The unpaired electron prohibits the formation of singlet and triplet excitons without the addition or removal of electrons to form even-electron systems.

By considering the requirement for spin conservation in optical excitation, transitions can occur from D_0 to higher energy $D_{x>0}$ states within the doublet-spin manifold in radicals.

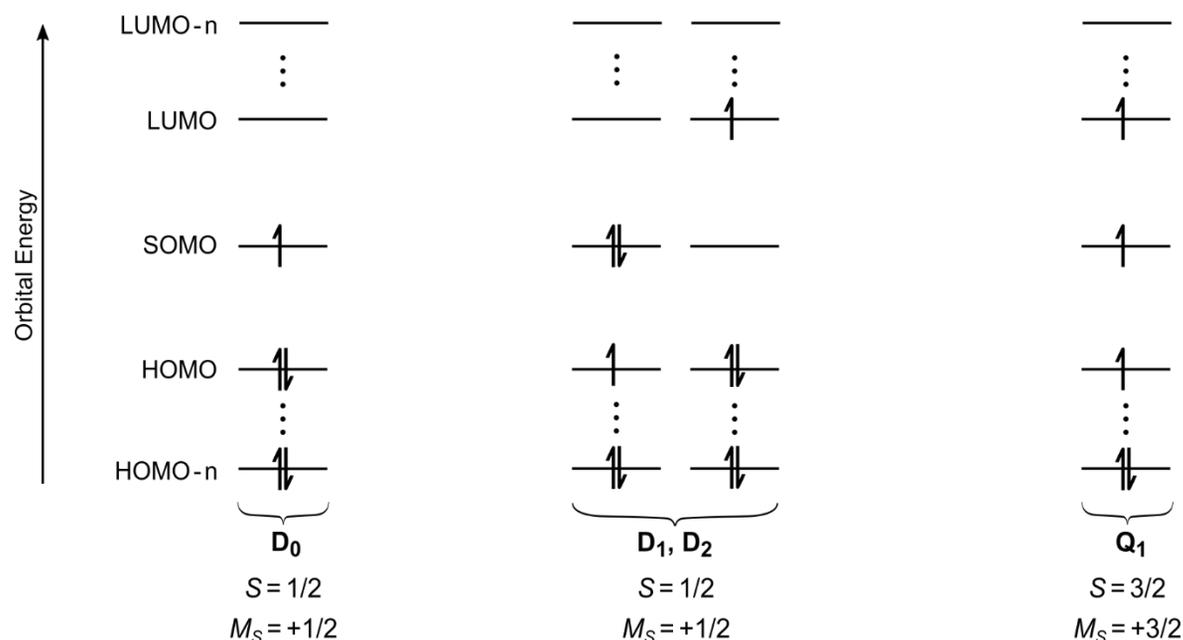


Fig. 3. Orbital occupancy of radical emitter electronic states

Molecular orbital diagrams for a doublet emitter showing electron occupancy in ground state (D_0) and excited states (D_1, D_2, Q_1). The D_1 state will be the lower in energy of the two possible configurations indicated for D_1, D_2 . Similarly, the D_2 state will be the higher in energy of the two possible configurations indicated for D_1, D_2 . Whilst not shown, an understanding of higher energy electronic states and differing spin projections will require excitations to be formed of a superposition of orbital configurations.

The D_1 lowest energy excitation can be described by HOMO to SOMO and SOMO to LUMO transitions, depending on the relative energies of these orbitals (Fig. 3). Where the HOMO-SOMO and SOMO-LUMO energy differences are non-degenerate, the D_1 and D_2 states will be the lower and higher energy transitions, respectively. Critically, the D_1 state is bright because like the ground state (D_0), it has $S = 1/2$, and can therefore radiatively decay by fluorescence to the ground state. In Fig. 3, the D_0 and D_1 states are depicted with $M_S = +1/2$ ($M_S = -1/2$ analogues of these states also exist but are not shown). Whilst odd-electron systems prohibit the formation of singlet or triplet states in any electron configuration, it is feasible that quartet states ($S = 3/2$) could be formed. In Fig. 3 the Q_1 state with $M_S = +3/2$ is shown. The quartet state is considered dark due to the spin

flip required for transitions to the doublet ground state. They are the dark triplet analogues on going from non-radical 'closed-shell' to radical 'open-shell' species.

Generally, the lowest energy excited states in non-radical ($S = 0$ ground state) and radical ($S = 1/2$ ground state) systems are dark and bright, respectively. In the singlet-triplet manifold for non-radical organic semiconductors, the dark triplet T_1 is generally lower energy than singlet S_1 . For organic radicals, the Q_1 quartet state is described by a HOMO to LUMO excitation (Fig. 3) which will be higher energy than D_1 (in the absence of substantial exchange interaction)³⁷. The quartet state derived from a HOMO-LUMO transition is not expected to play a significant role in the emission mechanism for radical-based OLEDs as electron charge trapping will have a thermodynamic tendency to the lower-energy SOMO rather than higher-energy LUMO (Fig. 4).

With the understanding that dark states can be eliminated from the functional photophysics of radical emitters as indicated in Fig. 3 and 4, we consider why π -radical systems such as TTM and PTM are not strongly emissive.

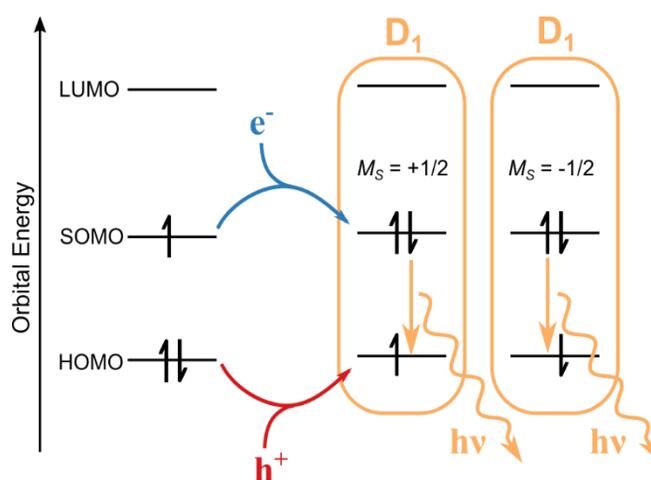


Fig. 4. Electroluminescence scheme for radical OLEDs by charge trapping

Radical-based electroluminescence scheme for charge trapping of electrons (e^-) and holes (h^+) on doublet ground state to form emissive doublet excitons, D_1 . Doublet emission-type is highlighted by emission channels for $+1/2$ and $-1/2$ total projection spin quantum numbers.

III. RADIATIVE AND NON-RADIATIVE BEHAVIOUR OF ORGANIC RADICAL EMITTERS

A. Excitation mixing of alternant symmetry systems

Alternant π -hydrocarbon systems are conjugated molecules whose π -system atoms can be divided into two sets [commonly denoted starred (*) or unstarred, Fig. 5a] such that no two atoms of the same set are adjacent. We illustrate this in Figure 5 with an example of a three-ring alternant π -system (anthracene) in Fig. 5a. Alternant systems contain even-membered rings only (Fig. 5a), whereas non-alternant hydrocarbons have odd-membered rings as shown in Fig. 5b and/or contain heteroatoms.

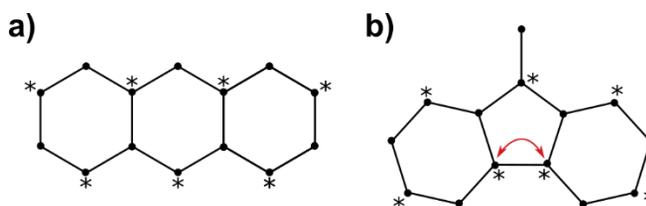


Fig. 5. Alternant and non-alternant three membered rings

Example structures of a) alternant and b) non-alternant three membered rings (π -system not shown for clarity). Alternancy symmetry allows for the atoms forming a delocalised system to be separated into two separate sets (starred and non-starred), for which no atom is adjacent to another atom of the same set. It is impossible for b) to have starred and non-starred atom assignment such that no two atoms of the same set are adjacent (see red double-headed arrow).

The Coulson-Rushbrooke theorem states that for closed shell, alternant hydrocarbons the bonding and antibonding orbitals are distributed symmetrically in energy, and that energy-adjacent orbitals (such as HOMO and LUMO, or HOMO- n and LUMO- n , where n is an integer) differ only by sign on every other carbon atom^{38,39}. Further, in alternant π -radicals such as TTM and PTM (Fig. 2) extensions to the Coulson-Rushbrooke Theorem by Longuet-Higgins lead to the splitting of anti-bonding and bonding π -orbitals with equal energy spacing about the non-bonding SOMO level⁴⁰⁻⁴², such that $E_{(\text{SOMO})} - E_{(\text{HOMO})} = E_{(\text{LUMO})} - E_{(\text{SOMO})}$, where $E_{(x)}$ is the energy of molecular orbital, x . They also state that the SOMO only has orbital amplitude on atoms which can bear a radical dot in its principle resonance structures. For the monoradicals considered in this article, this usually means that the SOMO will have orbital amplitude (and therefore electron density) on $(N+1)/2$ carbon atoms and none on the remaining $(N-1)/2$, where N is the number of conjugated carbon atoms in the molecule. This theoretical prediction is confirmed in DFT calculations of the SOMO of alternant π -radical systems^{3,43}.

Considering the orbital structure of these systems, the HOMO-SOMO and SOMO-LUMO transitions are understood to be degenerate with identical magnitude of their transition dipole moments (Fig. 6a,b)^{40,41}. One can

further show⁴¹ that these two transitions are mixed by the electronic Hamiltonian to form out-of-phase, Fig. 6b $|D_{1(TTM)}\rangle$ and in-phase, Fig. 6b $|D_{2(TTM)}\rangle$ combinations. Crucially in what follows, the out-of-phase dark transition will always be at lower energy (Fig. 6c) and the in-phase, bright transition at higher energy.

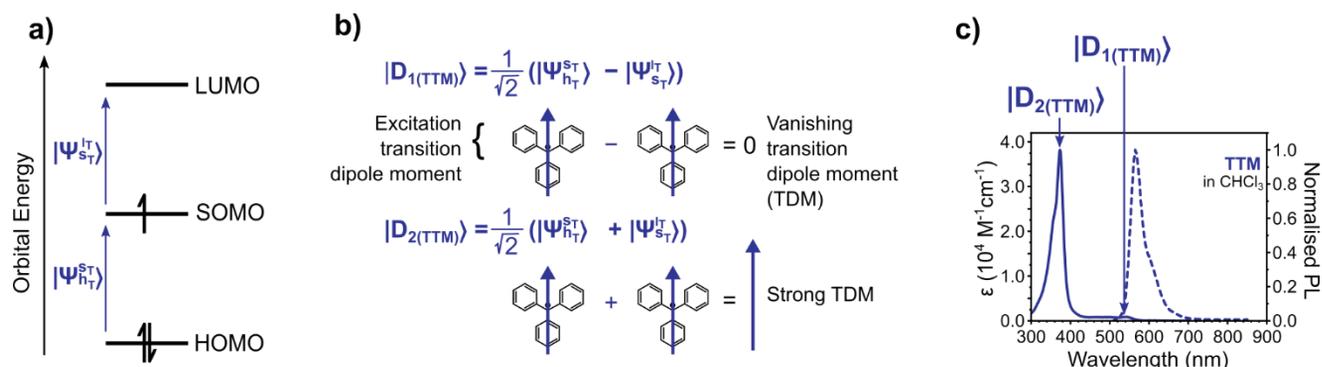


Fig. 6. Excitation mixing in alternant radical systems

a) Schematic diagram of the frontier molecular orbitals of TTM, with the HOMO-SOMO, $|\Psi_{h_T}^{s_T}\rangle$, and SOMO-LUMO, $|\Psi_{s_T}^{l_T}\rangle$, labelled. b) The mixing of the $|\Psi_{h_T}^{s_T}\rangle$ and $|\Psi_{s_T}^{l_T}\rangle$ transitions to form the dark $D_{1(TTM)}$ and bright $D_{2(TTM)}$ excitations. c) Absorption (solid) and emission (dashed) spectra of TTM in CHCl_3 with the D_1 and D_2 transitions labelled for absorption. b) and c) have been adapted with permission from Nat. Mater. 19, 1224-1229 (2020). Copyright 2020 Springer Nature.²⁷

This means that the lowest energy excited state (D_1) of an alternant organic radical will have a vanishingly small transition dipole moment; this can be seen in $< 1000 \text{ M}^{-1} \text{ cm}^{-1}$ extinction coefficients for the lowest energy absorption bands in alternant hydrocarbon radicals²⁷. As the rate of spontaneous emission is proportional to the square magnitude of the dipole moment⁴⁴, light emission from such organic radicals ($k_r \sim 10^6 \text{ s}^{-1}$) is generally outpaced by non-radiative internal conversion processes to the ground state. In theory the D_2 state should be highly emissive, but by Kasha's rule, in the event a molecule were to form this state it would rapidly undergo internal conversion to the dark D_1 state. The key result is that alternant radical hydrocarbons are likely to have very poor emission from D_1 , which is outpaced by non-radiative losses, and are therefore likely to be unsuitable for radical OLEDs²⁷.

In Fig. 7 we show a selection of bright and dark radical systems. Careful inspection shows that all dark systems are alternant radicals, and all bright systems are non-alternant, confirming the theoretical predictions. We stress that not being alternant substantially increases the likelihood of a radical being emissive, but is not in itself a sufficient criterion for a radical to be emissive; in addition to breaking the alternacy symmetry a

molecule's radiative rate will also need to outcompete non-emissive processes such as internal conversion. Conversely, there may also be cases (such as tris(2,3,5,6-tetrachloro-4-iodophenyl)methyl radical (3I-PTM)⁴⁵ discussed later) where an alternant radical has a very weak D₁ absorption (and no emission when in pure solid), but by immobilising it in a host matrix, and therefore restricting conformational changes that facilitate non-radiative decay, emission is observed.

B. Breaking the alternancy symmetry

1. Non-alternant radical structures

If the alternancy symmetry in π -radicals can be broken, either by having conjugated rings with an odd number of atoms, or heteroatoms, or both, then the HOMO-SOMO and SOMO-LUMO transitions cease to be degenerate. This can then allow the D₁ state to achieve a higher transition dipole moment and radiative rate.

Radical structures without alternant symmetry have been found in the PyBTM¹⁹ and (N-pyrido[3,4-*b*]indolyl)bis(2,4,6-trichlorophenyl)methyl (PyID-BTM)²⁰ radicals (Fig. 7), as well as the (N-carbazolyl)bis(2,4,6-trichlorophenyl)-methyl radical (CzBTM)⁴⁶ radical. In PyBTM the higher electronegativity of the nitrogen atom perturbs the alternancy symmetry of the triaryl system, whereas in PyID-BTM the five-membered central ring of the carbazole (and the nitrogen atom) breaks this symmetry in the molecule.

Some indications of higher PLQE in these materials compared to TTM (2.0% in cyclohexane²⁷) and PTM (1% in cyclohexane²⁵) were reported, namely 26% for PyBTM dispersed in a PMMA matrix¹⁹ and 19.5% for PyID-BTM dissolved in cyclohexane²⁰. Radiative rates for PyID-BTM being measured at $1.39 \times 10^7 \text{ s}^{-1}$ place them an order of magnitude faster than those for TTM at $1.22 \times 10^6 \text{ s}^{-1}$ (both in cyclohexane)²⁰.

More substantial improvement in radiative rates ($k_r > 10^6 \text{ s}^{-1}$) and PLQE is conceivable from discovery of new chemistry strategies for using non-alternant radical motifs in doublet emitters.

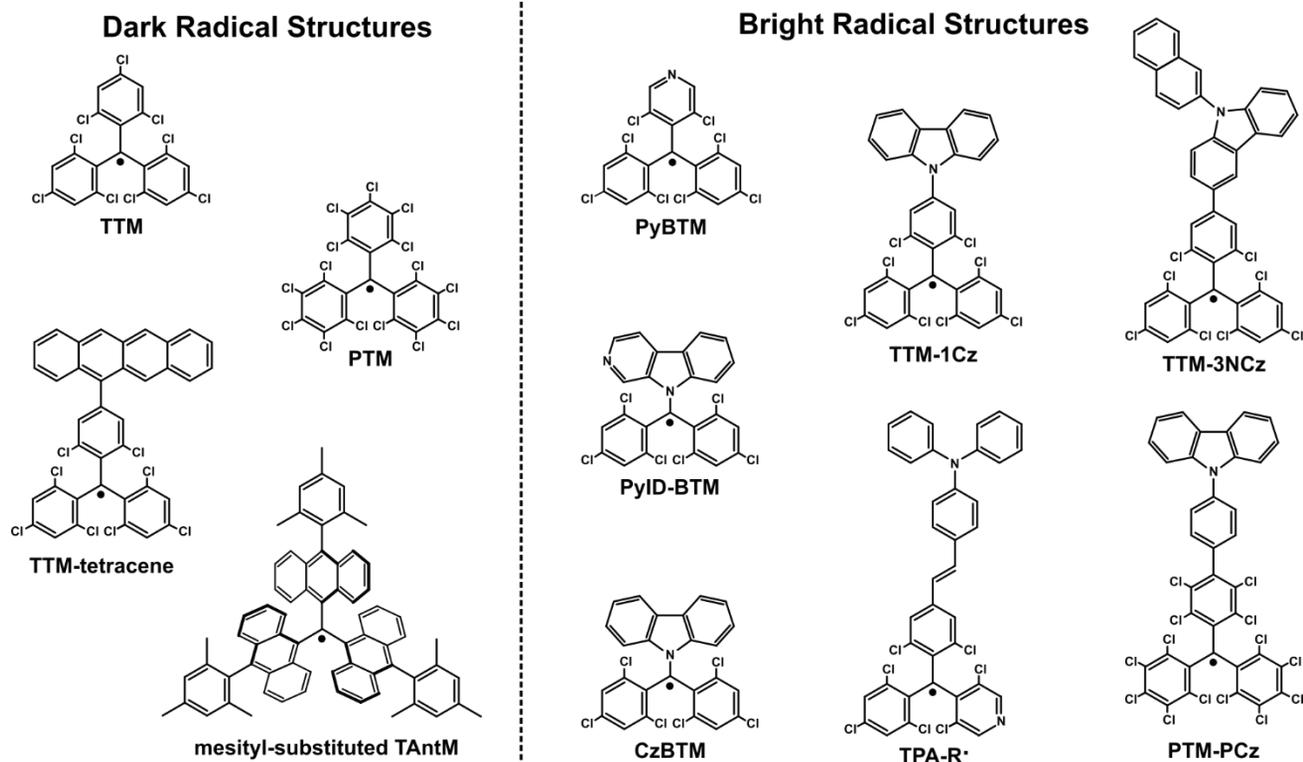


Fig. 7. Dark and bright radical structures

Chemical structures of the dark TTM²⁸, PTM⁴⁷ and TTM-tetracene²⁷ radicals, as well as the bright PyBTM¹⁹, PyID-BTM²⁰, CzBTM⁴⁶, TTM-1Cz³⁵, TTM-3NCz³, TPA-R⁴⁸ and PTM-PCz²⁵ radicals. Alternant radicals (left) are generally non-emissive, whilst non-alternant radicals (right) can have efficient light emission. We also give the structure of the unusual alternant radical mesityl-substituted tri(9-anthryl)methyl (TAntM)⁴⁹, which is similarly found to have a very weak D₁ absorption.

2. Non-alternant donor-acceptor radical systems

Organic radicals with overall non-alternant hydrocarbon properties can be designed from alternant radical moieties if functionalised with non-alternant chemical groups. This has proven to be the most successful strategy to date, where non-alternant electron donor groups attached to TTM and PTM have led to an order of magnitude increase in the radiative rates of their derivatives^{24,25,50,51}.

The rationale for this is shown by comparing Figs. 6 and 8. In Fig. 6, the HOMO-SOMO and SOMO-LUMO excitations are degenerate, leading to a D₁ state which is a dark, out-of-phase combination of these excitations as discussed earlier. If, however, the radical is bonded to an electron-rich, non-alternant molecule with a high HOMO (such as carbazole), as shown in Fig. 8a, then the lowest-energy excited state becomes the charge-transfer excitation from the electron donor-HOMO to radical SOMO, and there is no corresponding SOMO-LUMO

excitation of the same energy for this to destructively interfere with. Alternatively the radical can be bonded to an electron-acceptor molecule as shown in Fig. 8b, where D_1 is now the charge-transfer excitation from the radical-SOMO to acceptor-LUMO, and there is no degenerate HOMO-SOMO excitation for this to interfere with.

This has been demonstrated in practice by functionalisation of the dark TTM radical moiety with a carbazole group which produces the bright TTM-1Cz doublet emitter. The radiative rate increases roughly tenfold from 10^6 to 10^7 s⁻¹ and the PLQE increases from 3% to 53% in cyclohexane³⁵. For TTM-1Cz, an emission band is observed at 603 nm in cyclohexane, which is lower energy than both TTM (537 nm) and carbazole (331 nm) only photoluminescence³⁵. Further, the protonated (non-radical) precursor, α H-TTM-1Cz, displays distinctly higher energy emission (335 nm) than TTM-1Cz in cyclohexane³⁵. The lower energy emission feature in TTM-1Cz is derived from a carbazole-HOMO to TTM-SOMO charge transfer-type (CT) transition (Fig. 8a); such lower energy features emerge in all electron donor-acceptor hydrocarbon radicals. Using non-alternant groups functionalised to TTM moieties, PLQE values in excess of 80% has been observed, and can be translated to devices with external quantum efficiencies as high as 27%³.

We also expect good emission properties in systems where the radical is paired with a non-alternant electron acceptor, but such systems have not been demonstrated to date, likely due to the difficulty in finding acceptor groups with sufficiently low LUMO levels to have energetic matching with the radicals' low energy orbitals.

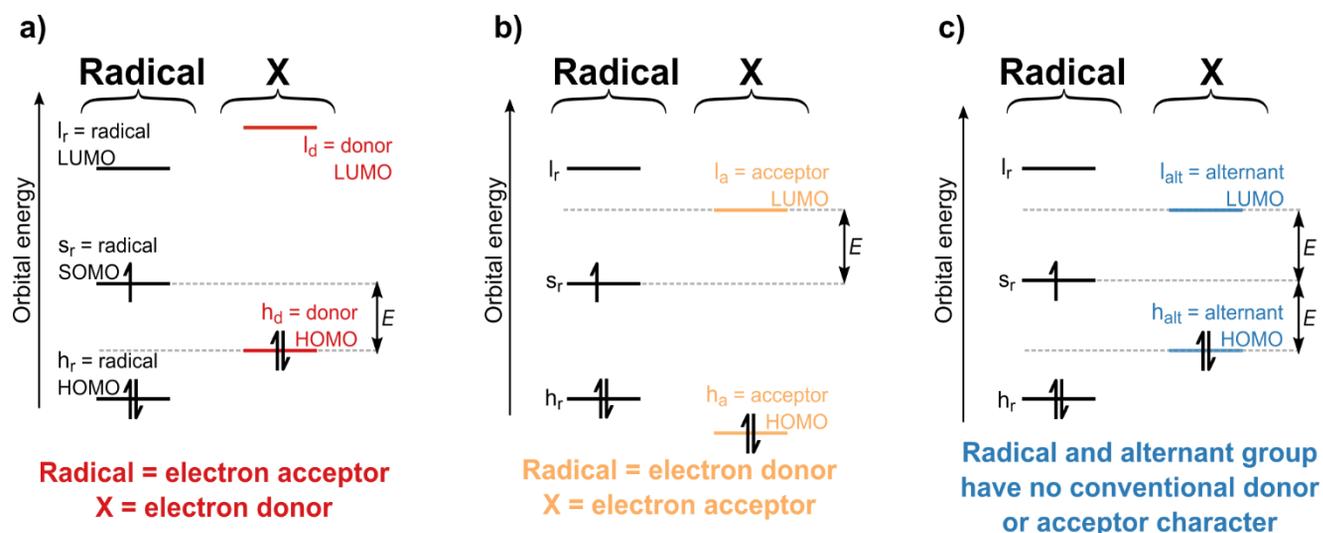


Fig. 8. Charge-transfer radical excitations

Schematic molecular orbital diagrams for a radical moiety and functional group for a) a radical acceptor-electron donor configuration, b) a radical donor-electron-acceptor configuration and c) a radical functionalised to an alternant group. E indicates the lowest energy excitation ignoring two electron (Coulomb and exchange) effects. This figure has been adapted with permission from Nat. Mater. 19, 1224-1229 (2020). Copyright 2020 Springer Nature.²⁷

Conversely, in the case that a donor-acceptor radical is obtained from an alternant hydrocarbon functional group (Fig. 8c), the overall radical will still have alternancy symmetry. Alternant donor-acceptor radical systems also follow the Coulson-Rushbrooke theorem and have degenerate transitions derived from the functional group-HOMO to radical-SOMO and radical-SOMO to functional group-LUMO. Slow radiative rates from weak D_1 transition dipole moments hinder the emission properties of these CT systems, even where orbital transitions occur between distinct parts of the molecule²⁷. The dipole-cancelling effect from the out-of-phase combination of HOMO-SOMO and SOMO-LUMO excitations is still seen. This effect is observed in TTM-Tetracene where the lowest energy D_1 absorption band at 630 nm has an extinction coefficient value of $1174 \text{ M}^{-1}\text{cm}^{-1}$, and no light emission was reported²⁷. This is also observed for the alternant mesityl-substituted tri(9-anthryl)methyl (TAntM) radical⁴⁹, where the lowest energy D_1 absorption band at 1020 nm has an extinction coefficient value of $\sim 250 \text{ M}^{-1}\text{cm}^{-1}$.

C. Brightening of dark charge transfer states

The D_1 excitation being primarily of intramolecular charge-transfer character is a common feature in the leading, highly emissive radical systems reported to date^{3,35,52}. We note that charge transfer states are usually dark because, by construction, the orbital from which the electron is excited, and the orbital to which it is excited,

are spatially separated and non-overlapping, leading to a vanishing transition dipole moment⁵³. Radical systems whose lowest energy excited state (D_1) is mainly charge-transfer (CT) in character will therefore need to acquire locally-excited (LE) state character in order to be emissive, such as by mixing with bright electronic transitions centred on the radical moiety.

Several groups have provided theoretical examinations for the brightening of the D_1 state in radical doublet emitters^{27,54} using frameworks of intensity borrowing or hybridisation between states. We emphasise that the following discussions for brightening CT states are similar to discussions for TADF materials. However, whilst luminescent donor-acceptor radicals generally require non-alternant hydrocarbon electronic symmetry²⁷ as outlined in the previous sections (whereas TADF emitters in general do not), radical emitters do not have to navigate the trade-off in low and high excited-state CT character for good oscillator strength and efficient reverse intersystem crossing that is seen in TADF⁵⁵⁻⁵⁷.

In our previous work, we suggest that the D_1 state in TTM-1Cz can be described as a dark CT excitation from the donor (carbazole) HOMO to acceptor (TTM) SOMO mixing with, and therefore borrowing intensity^{53,58} from, transition of TTM²⁷. This is evidenced by the intense near-UV absorption peak of TTM (ca. 375 nm) decreasing in intensity on going from TTM to TTM-1Cz, accompanied by a bright D_1 absorption for TTM-1Cz. In this analysis of TTM-1Cz radicals, the TTM and carbazole groups are first treated as separate moieties. We defined LE states to be those involving orbitals localised solely on the TTM moiety (or solely on carbazole) and CT states to involve electronic transitions from an orbital entirely on the donor (carbazole) to entirely the acceptor (radical)*. The true D_1 electronic state was suggested to be composed of the CT excitation from the carbazole HOMO to TTM SOMO with a contribution from the bright TTM LE state seen experimentally around 370 nm. The mixing of LE character arises from the consideration of the TTM and carbazole moieties and the resulting electronic interactions of bringing these groups together from separation⁵⁸. Mixing of CT-LE states can then be explained by intensity borrowing perturbation theory^{53,58}, having a cosine dependence on the dihedral angle linking the TTM and carbazole moieties²⁷, and leads to a non-zero transition dipole moment between the ground state $\left|D_{0(\text{TTM-1Cz})}^{(0)}\right\rangle$ and (perturbed) first excited state $\left|D_{1(\text{TTM-1Cz})}^{(1)}\right\rangle$, i.e. $\left\langle D_{0(\text{TTM-1Cz})}^{(0)} \left| \hat{\mu} \right| D_{1(\text{TTM-1Cz})}^{(1)} \right\rangle \neq 0$ where $\hat{\mu}$ is the transition dipole moment operator.

On the other hand, Cho et al. in their analysis of PTM-TPA systems take the alternative approach of calculating the electronic structure for the entire radical molecule rather than starting their consideration with

separate moieties⁵⁴. They find⁵⁴, similar to our study²⁷, that the lowest energy D_1 state is principally composed of a charge-transfer excitation and is emissive**. Unlike us, however, they denote this adiabatic D_1 state CT, such that this state has oscillator strength with the ground state. They then consider the hybridisation of their CT state (our D_1) with the ground state and LE states, and compute and explain the radiative and nonradiative decay rates⁵⁴.

These studies^{27,54} echo the result that lowest energy excitations in bright donor-acceptor radical systems contain predominantly charge-transfer character but are brightened by mixing of LE character, and can be considered as part of general design rules for obtaining luminescent emitters.

D. Energy ordering of HOMO, LUMO, SOMO towards alternative doublet emission

Cornil, Robvira, Veciana et al. have described the emission properties of PTM derivatives using hybridisation of the ground state orbitals⁴³. In these studies the extent of thiophene substitution onto PTM cores was investigated, showing the importance of energy level alignment between thiophene and PTM moieties in HOMO delocalisation for good oscillator strength properties.

The hybridisation of the ground state orbitals was also used to rationalize organic radicals with non-Aufbau inversion of their electron orbital occupancy⁵⁹. In non-Aufbau radicals, the highest energy occupied orbital is not the SOMO^{26,48}, but rather the double-electron occupied HOMO of the donor group attached to the radical moiety. On going from TTM-3NCz to PTM-3NCz, the electronic structure of these systems were observed to switch from Aufbau to non-Aufbau configurations²⁶. The difference occurs because of the extra Cl bulk in PTM-3NCz, leading to the PTM and 3NCz moieties being almost orthogonal and resulting in less hybridisation than in equivalent groups in TTM-3NCz. Photostability improvements of up to 2-3 orders of magnitude were observed in donor-acceptor non-Aufbau materials compared to parent radicals, and was partly attributed to the energetically higher lying HOMO preventing chemical reactions with the SOMO.

It is noteworthy that doublet emitters have also been designed in materials where radicals are appended to chromophores and do not participate in electronic transitions for the lowest energy exciton states. Beldjoudi et al. have demonstrated that pairing of pyrene (Py) with the dithiadiazolyl (DTDA) radical moiety does not produce luminescence at a new wavelength, with respect to emission from its constituent radical and non-radical components⁶⁰. The radical centre imparts its doublet-spin property on the singlet and triplet-spin excited states

of pyrene to yield overall doublet states for efficient light emission (PLQE = 50%, Py-DTDA in MeCN). The presence of the radical leads to moderate reduction in efficiency compared to Py only which has PLQE = 98% (Py is pyrene without radical present). This is attributed to energy mismatch between the Py HOMO, LUMO and DTDA SOMO orbitals to minimize electron-exchange mediated exciton quenching. Using this material, radical-based OLEDs with up to 1.4% EQE were reported with sky-blue emission (EL maximum at 492 nm). The design of new emitters of this type will require careful tuning of the energetic order of frontier orbitals: HOMO, LUMO and SOMO from radical and non-radical constituents, as well as intramolecular spin interactions. We expect substantial gains in efficiency for spectator-type OLEDs with non-radical-centred excited states in future. For the remainder of this Perspective we will keep a focus on doublet emitters with radical-centred excitons.

E. Non-radiative relaxation of the doublet manifold

The doublet manifold intrinsically contains fewer non-radiative pathways, a result of intersystem crossing being unable to populate 'dark' states below the emissive D_1 excitation. The main emission quenching mechanism of D_1 is internal conversion to the D_0 ground state.

Internal conversion results from the non-adiabatic coupling of the lowest vibrational mode of the D_1 state to the excited D_0 vibrational modes. Analogous to closed shell systems, an 'energy gap law' dependence is seen for emission as a result of Franck-Condon factors for transition, with decreased non-radiative rates for systems with increased HOMO-SOMO splitting. Variation of the ortho- halogens of the pyridyl group in PyBTM from Br to Cl to F successively increased the HOMO-SOMO splitting from 2.51 eV to 2.55 eV to 2.61 eV respectively. The increased energy gap was accompanied by decreased non-radiative rates of $1.68 \times 10^8 \text{ s}^{-1}$, $1.28 \times 10^8 \text{ s}^{-1}$ and $5.2 \times 10^7 \text{ s}^{-1}$ (in chloroform) for the Br-, Cl- and F-substituted PyBTM molecules respectively⁶¹.

Order of magnitude reductions in non-radiative rates are seen from charge-transfer systems, with the spatial separation of the electron density of the ground and excited states leading to reduced vibronic coupling and internal conversion. The functionalisation of PTM with differently substituted phenyl-carbazolyl groups (-Pz and -3Pz) as well as triphenylamine (TPA) reducing the non-radiative rate by up to an order of magnitude from $1.62 \times 10^8 \text{ s}^{-1}$ for PTM to $4.85 \times 10^7 \text{ s}^{-1}$, $2.11 \times 10^7 \text{ s}^{-1}$ and $1.65 \times 10^7 \text{ s}^{-1}$ for PTM-TPA, PTM-PCz and PTM-3PCz respectively (all in cyclohexane). Similarly, TTM functionalisation with carbazolyl (Cz), bi-carbazolyl (BiCz) and tri-carbazolyl (TCz) groups reduces the non-radiative rate from $1.56 \times 10^8 \text{ s}^{-1}$ to $1.13 \times 10^7 \text{ s}^{-1}$ for TTM and

TTM-1Cz in dichloromethane²⁷ and from $1.52 \times 10^8 \text{ s}^{-1}$ to $8.42 \times 10^7 \text{ s}^{-1}$ and $4.3 \times 10^7 \text{ s}^{-1}$ for TTM, TTM-1BiCz and TTM-TCz in cyclohexane respectively⁵⁰.

Furthermore, reductions in internal conversion are seen for rigid and immobilised molecular systems, due to the intrinsic dependence of non-adiabatic coupling on the thermally-induced fluctuations of vibrational modes. The immobilisation of radical emitters in a rigid matrix restricts vibrational and rotational modes seen in solution, with PLQE efficiencies for PyBTM being boosted from 3% when in chloroform solution to 26% for when PyBTM was immobilised in a rigid polymethyl methacrylate (PMMA) matrix¹⁹. Similarly, the lower population of thermally-induced modes leads to enhanced radical emission at lower temperatures, with PyBTM showing PLQE values of 81% when embedded in an EPA matrix (diethylether:isopropanol:ethanol) at 77 K¹⁹.

Theoretically calculated values for radical non-radiative rates, calculated from the sum of non-adiabatic vibrational coupling constants, have given insights into the intrinsic non-radiative mechanisms for organic radical excited states^{62,63}. As well as consideration of excited state-ground state hybridisation in non-radiative decay⁵⁴, Bredas and co-workers have taken steps to better understanding of in-device behaviour for radical emitters in a combined molecular dynamics and DFT approach, advancing the theoretical modelling of these systems to include host-emitter interactions³⁷. Further, vibrational couplings for TTM-3NCz were found to be reduced by up to 30% when embedded in a CBP host (1% dilution of radical emitter in host). This reduction comes with a modest penalty of static disorder; minimising static disorder reduces its detrimental effect on charge mobility, leading to increased OLED efficiency and reduced turn-on voltages³⁷.

Approaching the design of radical emitters with the aim to reduce internal conversion as well as increasing transition dipole moments will enable systems with more efficient light emission.

We note that the non-luminescent nature of the majority of stable radical systems is generally attributed to the rapid internal conversion resulting from small D_1 - D_0 splittings, however, radical systems with energy gaps comparable to that of singlet emitters remain dark. In some circumstances this can be alternatively explained by the radical emitter being an alternant hydrocarbon, or very nearly alternant, such that the D_1 state has a low transition-dipole moment, leading to a low radiative rate which is outcompeted by decay processes²⁷. Nevertheless, greater research is required to elucidate which properties of bright radicals allow them to avoid ultrafast non-radiative relaxation.

IV. CHALLENGES FOR RADICAL-BASED EMITTERS

A. Device efficiency roll-off and the underlying mechanisms

Despite radical semiconductors having nanosecond emission timescales and high PLQE, the exploitation of these properties to improve on the state of the art in organic optoelectronics has not been fully realised. Given that radical emission is orders of magnitude faster than microsecond phosphorescent^{7,8}, TTA¹² and TADF⁹⁻¹¹ emitters, radical OLEDs should be able to improve on the device characteristics and performance of these more established OLED technologies. As we have already mentioned, faster light emission should reduce the probability of exciton quenching processes which can lead to device and efficiency breakdown.

OLEDs based on radical semiconductors have been shown with high peak external quantum efficiency, but generally all devices suffer substantial reductions in efficiency above current densities of $1\text{mA}/\text{cm}^2$ (i.e. 'roll-off', see Fig. 9a)³. This is a critical limitation for the commercialisation of light-emitting devices based on organic radicals.

Optical spectroscopy on working radical OLEDs has been used to study efficiency roll-off mechanisms⁶⁴. In such experiments for radical OLEDs, devices were electrically biased from 0 to 12 V in pulsed mode, and a secondary laser pulse was used to achieve a small population perturbation for which the decay lifetime was recorded²⁷. The transient decay lifetime was unchanged for different voltages (and consequently exciton density, charge density and electric field conditions), suggesting that excited state quenching of doublet excitons by self-annihilation, charges and electric fields could be ruled out from the cause of the efficiency roll-off. This is in agreement with roll-off mechanisms studied in non-radical organic emitters with nanosecond lifetimes. In such systems excited state quenching of nanosecond emitters is not generally expected until $100\text{mA}/\text{cm}^2$ and higher current densities¹⁸. When these results are considered together with the high redox- and photo-stability of organic radical emitters such as TTM-xPyID, TTM-3NCz and others^{3,27,65}, it is likely that current roll-off effects and device limitations originate from the device physics rather than photophysics of radical OLEDs.

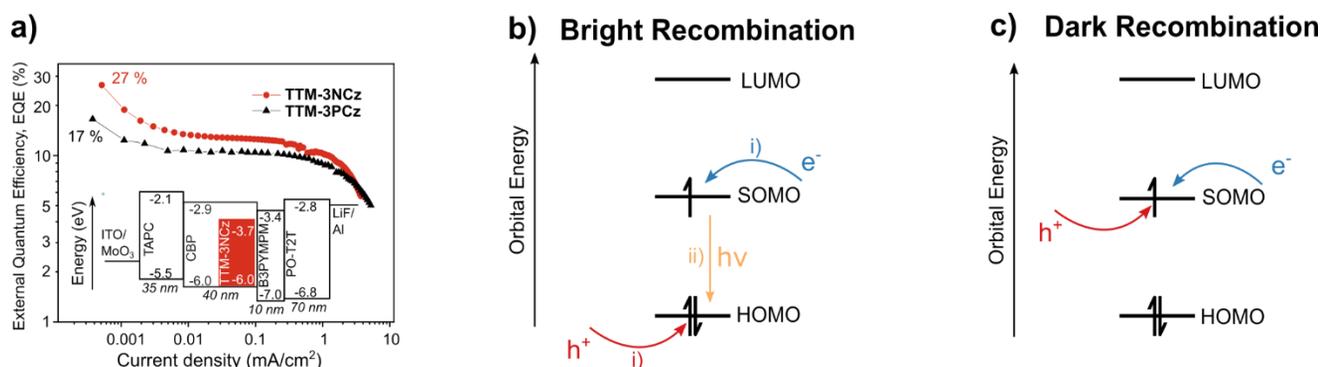


Fig. 9. Efficiency roll-off and charge balance in radical devices

a) EQE-current density curves for TTM-3NCz (red) and TTM-3PCz (black) LEDs. The inset shows the TTM-3NCz device layout; the labels give the energy levels in electronvolts and the thickness of layers in nanometres. a) has been reproduced with permission from Nature 563, 536-540 (2018). Copyright 2018 Springer Nature.³ b) Schematic molecular orbital diagram indicating i) the stepwise process of separate electron transfer into the radical SOMO and hole transfer to the radical HOMO before ii) light emission following recombination. c) shows dark recombination which results in no light emission following electron and hole transfer to the SOMO.

B. Charge balance effects

The mechanism of electrical excitation in radical OLEDs is not fully understood. One of the suggested origins for the EL efficiency roll-off beyond 1 mA/cm² in radical OLEDs is charge balance in electrical excitation²⁷. We previously considered a sequential charge trapping mechanism in which electrons and holes undergo charge transfer from host to radical in TTM-3NCz OLEDs (Fig. 9b)³. It should be emphasised that electroluminescence from radical OLEDs is surprising given the trap-like properties of the SOMO as the thermodynamically preferred site for both electron and hole occupancy. By this pathway (electron and hole insertion into the SOMO) we would not expect charge recombination on radical dopant centres to result in electroluminescence (Fig. 9c). The highest efficiency radical-based OLEDs to date use host materials (CBP) with good HOMO energy alignment to the radical (TTM-3NCz) HOMO³.

Work by Suo et al. investigated the rate of electron and hole transfer from host to radical dopants using the charge hopping model in Marcus theory⁶². The electron and hole transfer rates from CBP to TTM-1Cz radical dopants were calculated to be $5.4 \times 10^{11} \text{ s}^{-1}$ and $4.0 \times 10^9 \text{ s}^{-1}$ respectively, indicating the strong electron-trap properties of the radical in this device. A sequential electron-to-SOMO then hole-to-HOMO transfer has been put forward for a charge trapping-based electroluminescence mechanism in radical OLEDs. We speculate that

charge imbalance results in light-emitting devices where the recombination zone is pinned to the emissive and electron transport layer.

Further research is needed to explore the variation of electron and hole transport properties for improved charge balance whilst sustaining low turn-on voltages. Due to the presence of the SOMO and its ambipolar charge trapping properties, established device considerations and architectures for phosphorescent and TADF OLEDs may not directly translate to success in radical-based OLEDs.

C. Blue-shifted emission

Donor-acceptor radical systems have been demonstrated with efficient emission in the red and deep-red optical range, 600-700 nm^{2,3,24,26,27,51,66}. Lowering the emission wavelength to green and blue colours for radical OLEDs has proven challenging. The difficulty in obtaining higher energy emitters is the limited radical chemistry available, with most reports involving halogenated triaryl radical moieties.

Halogen substitutions have been extensively studied in triaryl systems, with a modest blueshift in emission on replacing Br with more electronegative Cl atoms: from 593 nm for tris(2,4,6-tribromophenyl)methyl (TBrM)⁶⁷ to 569 nm for TTM in CCl₄⁶⁸.

On the most electronegative halogen variant, synthesis of a fully fluorinated version of TTM in TTFM has not been reported. Theoretical studies have suggested that replacement of the chlorines in TTM-3NCz with fluorine could cause emission wavelength to drop from 700 nm to 610 nm⁶⁹, however this is still far from the 400-500 nm required for emitting in the blue.

For doublet emitters in the blue range, new radical moieties with intrinsically larger HOMO-LUMO gaps must be designed to enable larger HOMO-SOMO or SOMO-LUMO splitting. We note that as the D₁ energy is related to the minimum of the HOMO-SOMO excitation energy, the SOMO-LUMO excitation energy, and any linear combination of these transitions (see Fig. 6). Consequently the maximum D₁ emission energy of a radical emitter will be limited to approximately half the energy difference between the HOMO and the LUMO.

For higher energy doublet emitters, materials with less delocalised π - systems should be considered; i.e. less than the three phenyl groups in triphenylmethyl radical derivatives. Frontier HOMO and LUMO π -orbitals become higher and lower in energy respectively as a result of delocalisation⁷⁰. The larger the extent of π -delocalisation, the closer the frontier π -molecular orbitals are in energy to the non-bonding SOMO level. As

a result, higher energy doublet emission will be seen in systems with lower π -delocalisation, such as by incorporation of an sp^3 alkyl group adjacent to the trivalent radical carbon. To this end there is a chemical synthesis challenge to reduce π -delocalisation in a non-alternant hydrocarbon radical for efficient and higher energy emission.

We note that delocalisation and steric hinderance of the radical moiety are important factors in stabilising radical emitters⁷¹, and newly designed materials must also possess sufficient stability to be OLED dopants. The currently limited chemical space for radical π -system emitters is one of the biggest issues which must be developed by innovation in organic chemistry. This is key to having radical emitters across the full visible range that could compete with current display and lighting technologies.

D. Stability of radical devices

Whilst significant progress has been achieved recently to improve the intrinsic photostability of radical emitters, the operational lifetime of radical-based OLEDs must be improved beyond the minutes timescales that have been reported in order to push towards commercial viability²⁷.

The PyBTM radical and the radical-acceptor electron-donor systems show substantially longer lifetimes for maintaining intensity of PL under UV radiation than the isolated TTM and PTM moieties¹⁹. When illuminated with radiation of 370 nm within cyclohexane, the intensity of PL from PyBTM decreases with a half-life of 2.58×10^4 s, which is 115 times longer than that of TTM (224 s)¹⁹. Similarly the half-life of PTM under 355 nm radiation pulses (46.6 s) is significantly less than that of the PTM derivatives PTM-PCz (2.42×10^3 s), PTM-3PCz (8.73×10^3 s) and PTM-TPA (3.17×10^5 s) when measured in deoxygenated cyclohexane²⁵. By perturbing the alternant hydrocarbon nature of TTM and PTM radicals by aza-substitution (PyBTM) or forming donor-acceptor derivatives, the radicals appear to be less prone to cyclisation reactions which has been highlighted as one of the major degradation mechanisms^{26,72}. We note that some bonds may be weakened on going from D_0 to D_1 , leading to alternative degradation of organic radicals upon excitation. Better understanding of photostability should be supported by more detailed studies in future with quantum-chemical calculations and experiment, which could lead to the development of more stable radical emitters.

For redox stability, donor-acceptor triphenylmethyl radical derivatives have been shown to undergo reversible oxidation and reduction on the timescale of the electrochemistry experiments such as cyclic voltammetry. More long-term and solid-state redox stability has been demonstrated in molecular electronics

demonstrations⁷³⁻⁷⁶. We consider that the stability may be attributed to the non-bonding nature of the SOMO, meaning that the overall bond order of a radical material does not decrease when it is oxidized by removing an electron from the SOMO, or reduced upon addition of an electron to the SOMO. In non-radicals electron oxidation occurs to bonding-type HOMO and reduction to anti-bonding-type LUMO, leading to a reduction in bond order for the molecule in both scenarios.

If we consider high photo-, redox- and thermal stability for radical emitters such as TTM-xPyID, the short device lifetime stability cannot be explained from this²⁷. It is not understood whether this device degradation is due to intrinsic instability of the radical molecule under electrical excitation or is related to degradation of the device structure. Future efforts should focus on elucidating the degradation mechanisms to improve device lifetimes.

V. RESEARCH BEYOND DOUBLET EMISSION

A. New functionality from established radical motifs

In addition to ongoing research efforts for new radical moieties in doublet emitters, there has been important progress in the discovery of new functionalisation routes for existing π -radicals.

As discussed in the previous sections, the functionalisation of TTM, PTM and PyBTM by electron donor and acceptor groups has been explored in tuning the emissive properties of their radical derivatives, whilst also leading to improvements in thermal and photo-stability. In a sense, new radicals can be designed from old radical motifs.

Other chemical functionalisation efforts have led to well-known radical emitters such as TTM-1Cz being developed into polymers with non-conjugated backbones²¹. This has resulted in OLED with modest efficiencies of 3.0% for PS-CzTTM⁶⁶. The other related report is by An et al. who have developed a super acid-catalysed route to radical polymers with carbazole-conjugated backbones, avoiding the use of heavy metal catalysts in polymerisation, and producing 1.8% efficiency in electroluminescent devices⁷⁷. We expect further progress in the area of radical polymer devices in future. Generally, we consider that the prospect of commercially relevant radical-based optoelectronics may be accelerated by established protocols of organic semiconductors in solution-processing of polymers, as well as vacuum-deposited devices from molecular radical emitters.

In other studies, functional groups have been used to attach organic radicals between metal electrodes for studying their charge transport properties⁷³. On going from PTM to donor-acceptor-PTM derivatives, systems change from having free electrical current in both directions to acting as molecular rectifiers⁷⁴. Alkyne-functionalised PTM radicals have also been shown to form self-assembled monolayers on gold and hydrogenated silicon surfaces, enabling use as photoswitchable capacitors and multistate electronic switches^{75,76}. To this end organic radicals could lead further advancements as useful components in molecular-scale electronics. Moving forward, optical as well as current read-out from electrode-radical-electrode systems could be enabled by light-emitting radicals.

B. Electronic tuning without the usual heavy atom effect

As discussed, the quartet states in radicals are higher than the first excited doublet state, D_1 , meaning that quartets will not form by intersystem crossing on thermodynamic grounds, and do not pose the same problems as triplet states in non-radical emitters.

Consequently, heavy atoms can be incorporated in radical systems to tune emission properties without increasing non-radiative losses by intersystem crossing pathways. The result is the ability to alter the electronic structure of triaryl radical moieties through inclusion of Br and I whilst maintaining non-radiative rates to within the same order of magnitude^{45,61}. We note that the weakening of the carbon-halogen bond from the inclusion of heavier halogen atoms will also affect possible methods for device fabrication. The bond dissociation energy of C-halogen will decrease with increasing atomic number of the halogen: $C-F > C-Cl > C-Br > C-I^1$. Therefore molecules containing heavier halogens are likely to only be processable by solution-based methods such as spin-coating and not stable enough to withstand thermal evaporation. We consider that the design of new materials will be led by materials processing requirements, and consideration of the physical properties of organic radicals (e.g. temperature stability) as well as electronic and optical properties.

The tri-iodinated radical compound, tris(2,3,5,6-tetrachloro-4-iodophenyl)methyl radical (3I-PTM)⁴⁵ mentioned earlier, is of particular interest as good emission properties are observed in a system we would otherwise understand to have alternancy symmetry, and expect to be non-emissive. This motivates further research on fundamental design rules for radical emitters beyond our current understanding of the electronic structure in these systems.

The absence of the usual heavy atom effect in triplet formation also enables fluorescent metal complexes with doublet metal-ligand emission to be designed. The nitrogen lone pair in PyBTM derivatives has been employed in ligand-complexation to Zn(II), La(III)⁷⁸ and Au(I)^{79,80} centres. Here the emission energy can be altered by substitution of the ion centre, allowing a route to tunable doublet emission from a radical centre proven to be stable, and therefore without having to develop new radical motifs⁷⁸. Furthermore, complexation of tripyrrindione to Zn(II) has shown radical emission at room-temperature (PLQE = 23% in THF) from a system not based upon the triaryl moiety⁸¹.

Coordination of radical moieties with Cu(II), Ni(II), Co(II), Fe(II) and Mn(II)⁷⁸ was observed to quench emission, and has been attributed to electron-exchange mediated mechanisms with partially filled d-orbitals.

C. Circularly polarised doublet emission

Molecular chirality can lead to chiral, circularly polarised light emission^{82,83}. One of the technology drivers for this research is to improve the light output efficiency of OLED displays⁸⁴. 'Anti-glare' circularly polarising filters are commonly used in displays to trap the reflected ambient light in order to enhance contrast. For standard OLEDs, as light is randomly polarised, this suggests that only half of the EL will leave the display. OLEDs with circularly polarised EL could double the efficiency of display technologies.

Intrinsic chirality has been recognised in the helical twist of the triaryl moiety in triphenylmethyl radicals. Bulky side-groups can lock these radicals into a particular handedness, preventing racemisation by inversion of the twist, and leading to reports of circularly polarised luminescence in TTM, PTM and related radicals^{67,68,85}. Circularly polarised PL in these demonstrations can be considered as 'local' type from the molecular site of emission⁸⁶.

Intuitively, the racemisation energy barrier was observed to increase with increasing steric bulk of the halogen groups on going from chlorine in TTM to bromine in TTBrM; see chemical structures in Fig. 10a. Circular polarised luminescence could be observed in TTBrM at room temperature with recorded polarisation values of $|g_{lum}| = 0.7 \times 10^{-3}$ (see Fig. 10b)⁶⁷, whereas TTM samples exhibited racemisation and showed polarised emission at -20°C and lower temperatures⁶⁸.

From a different physical origin, circularly polarised doublet emission has also been shown in TTM-3PCz-PMMA films as induced by a magnetic field and Zeeman splitting of the doublet-spin states⁸⁵. This report also included the demonstration of circular polarised emission in TTM-1Cz and PTM-PCz from 'non-local' chirality

origin. Light emission can be polarised by transmission through a chiral medium with dielectric anisotropy, here being chiral supramolecular and liquid crystal structures⁸⁵.

We expect that chiral radical emitters will be translated to circularly polarised OLEDs with doublet emission, where the benefits of higher internal quantum efficiency of radical-based electroluminescence can be combined with increased light-outcoupling properties.

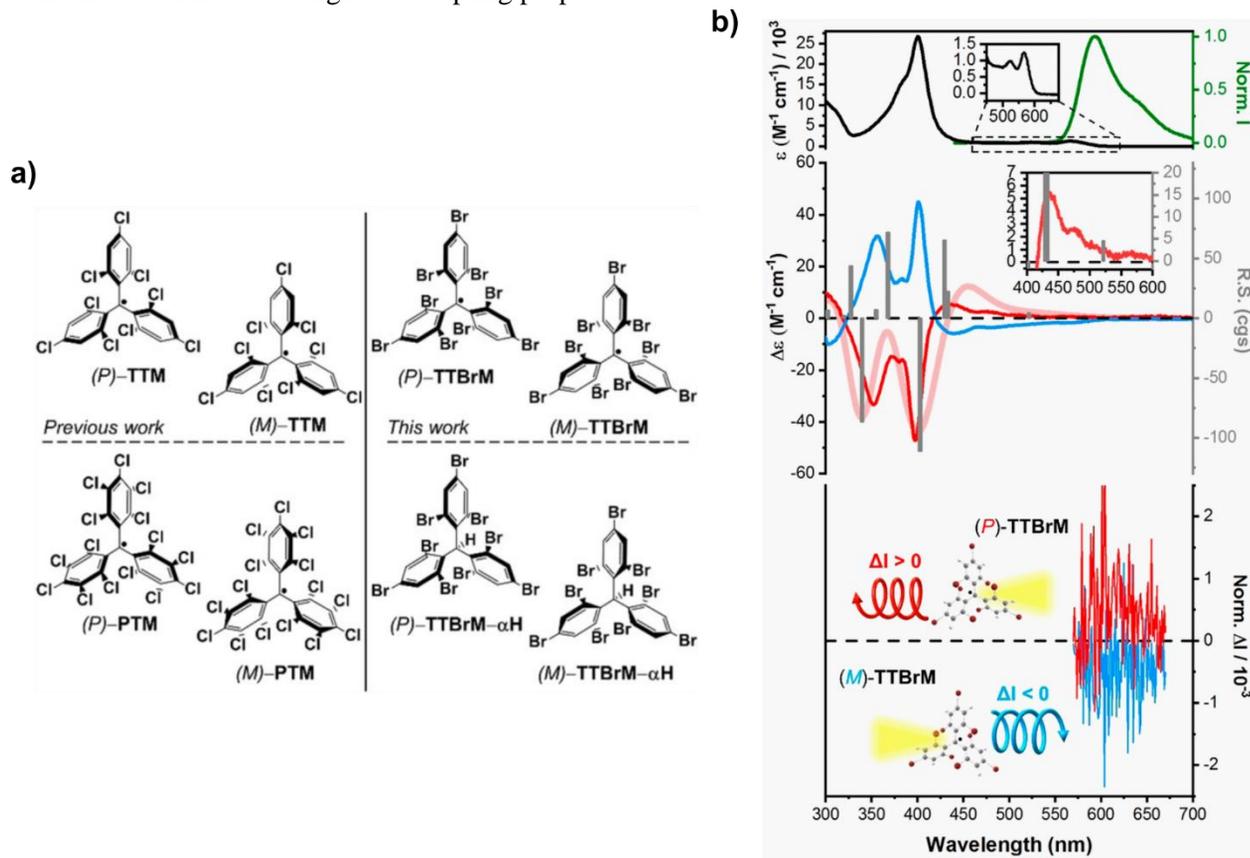


Fig. 10. Circularly polarised light emission

a) Chemical structures for TTM, PTM, TTBrM and TTBr- α H indicating right-handed, (P)-, and left-handed, (M)-, helical symmetries. b) Top: Experimental UV/Vis absorption spectra (black) of TTBrM, together with the total fluorescence spectra (green). Inset: Experimental UV/Vis absorption of lowest energy band. Central: Experimental circular dichroism spectra of (P)-TTBrM (thick light red line). The sticks (dark grey) indicate the positions and rotatory strengths of the TD-DFT calculated transitions. Inset: Experimental and theoretical circular dichroism profiles for the lowest energy band. Bottom: Circularly polarised luminescence spectra of two enantiomeric fractions of TTBrM. Additionally, a schematic representation of the CPL response (ΔI) of the two enantiomers has been included, with $\Delta I > 0$ and $\Delta I < 0$ for (P)- and (M)-enantiomers, respectively. Figure and caption has been adapted with permission from Chem. - A Eur. J. 26, 3776-3781 (2020).⁶⁷ Copyright 2020 Wiley-VCH.

D. Radical-radical interactions

Our discussion has concentrated on mono-radicals with doublet-spin-1/2 properties. However, two interacting radical groups can also form total spin-singlet-0 and spin-triplet-1 ground and excited state manifolds^{87,88}, and can occur within (intra) and between (inter) molecules.

Veciana et al. demonstrated that TTM radicals form stable and luminescent dimeric excimers with deep red excimer emission of 645-685 nm when doped in α H-TTM organic nanoparticles and \sim 734 nm when doped in a PMMA matrix⁸⁷. Given the chlorine's steric bulk in protecting the radical centre, it was surprising that substantial intermolecular π -interactions can be achieved in radical excimer formation. As well as red-shifted luminescence, radical excimer emission is substantially slower than radical monomeric emission. For excimer emission in 10.1% PyBTM/ α H-PyBTM, up to 30% contribution of emission decay was found with exponential time constant higher than 500 ns; for 0.05% PyBTM/ α H-PyBTM, the monomer emission decay was fitted to 115 ns time constant⁸⁹.

Towards better understanding these systems, the spin properties of analogous PyBTM radical excimers have been probed by Kusamoto, Teki et al.^{88,90}. PyBTM was doped (0.05% to 23%) in α H-PyBTM, and displayed decreasing monomeric emission at 563 nm and increasing excimeric emission at 680 nm with increased doping (Fig. 11a)⁸⁸. The monomer and excimer emission profiles in intermediate % doped samples (e.g. 10%) were found to be correlated, showing increasing monomer:excimer ratio with increasing field strength: for 4.2 K, \sim 0.45 at 0 T to \sim 1.3 at 18 T⁸⁸. Follow-up studies have been conducted to probe the magnetic field dependence (up to 14.5 T) on the emission decay profiles in PyBTM/ α H-PyBTM systems^{89,91}. From the field dependence on the monomer/excimer emission intensity and decay lifetime, the authors showed that these effects originated from magnetically sensitive singlet-triplet interconversion of the ground state, where the field dependence was translated to the higher-energy emission states upon photoexcitation. This is unusual because magnetic-field dependent singlet-triplet photophysics usually originates in excited state levels (e.g. radical pairs) following charge transfer⁹². Here radical-radial interactions between spin-1/2 species leads to new manifolds of singlet and triplet levels. This could be used as platforms for opto-spintronics where the relative singlet/triplet spin ratio is controlled by photoexcitation and magnetic fields.

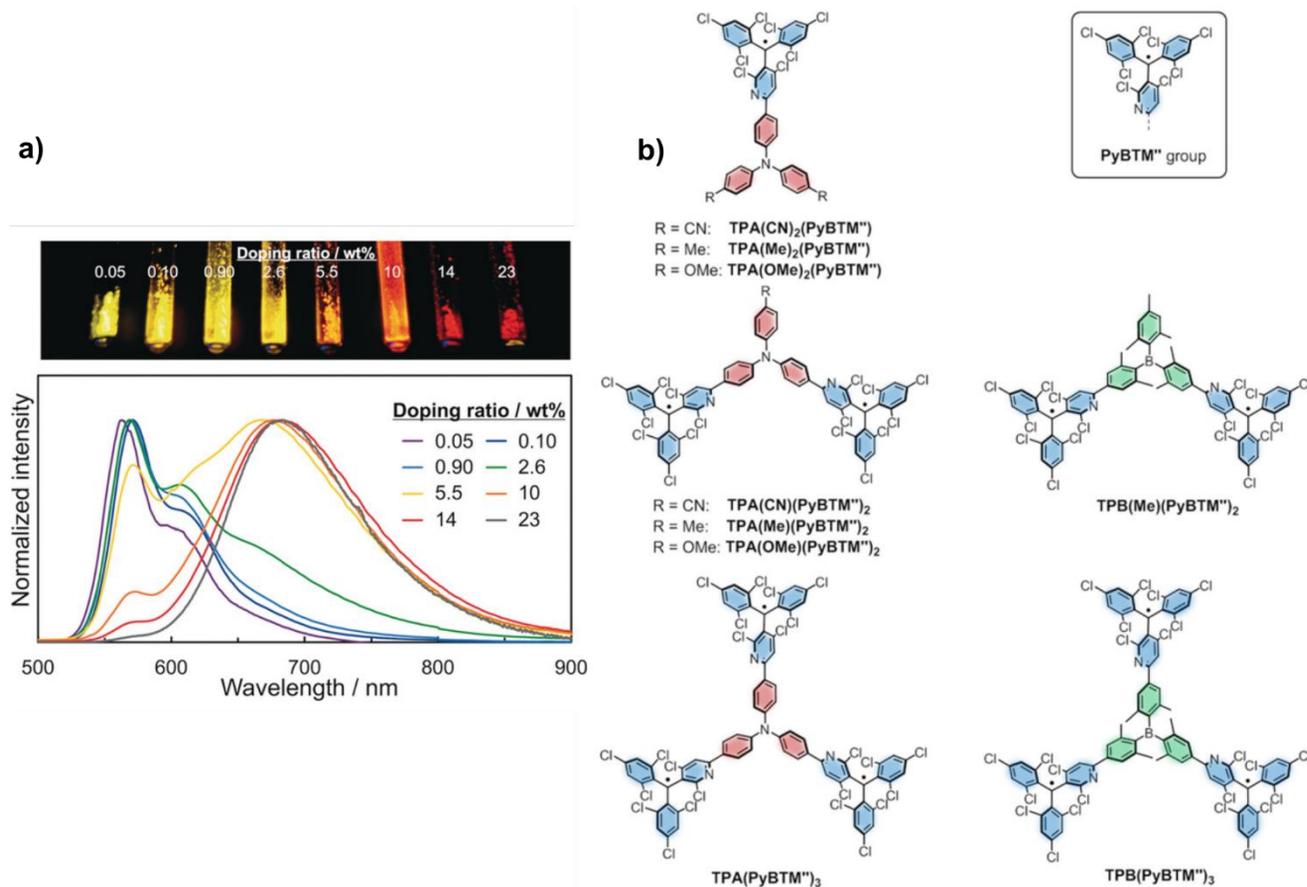


Fig. 11. Radical-radical interactions and emission properties

a) Excimer emission in PyBTM systems. Monomeric (563 nm) and excimeric (680 nm) emission can be tuned by the doping ratio of PyBTM radical within a α H-PyBTM matrix. a) has been reproduced with permission from *Angew. Chemie* 130, 12893-12897 (2018).⁸⁸ Copyright 2018 Wiley-VCH. b) Chemical structures of bi- and tri-radicals as reported by Hattori et al.⁵² b) has been reproduced from *Chem. - A Eur. J.* 25, 15463-15471 (2019).⁵² Copyright 2019 Wiley-VCH.

We note that triplet excitons can be emissive in inter- and intra-molecular biradical systems due to the presence of ground states in the triplet manifold. Synthesis of intramolecular biradicals with singlet and triplet levels, and triradicals with doublet and quartet levels, have also been shown to yield luminescent systems that can be employed in light-emitting devices⁵² – see Fig. 11b. Julia, Anglada and co-workers have also led work on cations of PTM-carbazole derivatives where conjugation can be broken due to steric bulk between electron acceptor and donor moieties, resulting in a biradical triplet ground state⁹³. Research in this area has highlighted the potential of polyradicals, in addition to monoradicals, as dopants which eliminate dark excitons for more efficient OLEDs.

VI. CONCLUSIONS

In this Perspective we have outlined the features and advancements required in radical emitters and devices which could enable them to disrupt the state of the art for organic LEDs. Organic radicals have doublet-spin properties arising from unpaired electronics, and can be designed to have rapid emission on nanosecond timescales for exploitation in OLEDs with up to 100% internal quantum efficiency. The radical emission timescales are shorter than the other leading OLED technologies based on phosphorescence and delayed fluorescence (TTA, TADF), and could lead to improved device performance due to reduction in exciton quenching processes.

For bright radical emitters, it is important to design molecules with avoided alternancy symmetry such that the HOMO-SOMO and SOMO-LUMO energy gaps are non-degenerate. Light emission must also not be outcompeted by non-radiative decay which occurs by non-adiabatic vibronic couplings for internal conversion of D_1 to the ground state D_0 .

The charge-transfer electron-donor radical-acceptor system has brought success for emissive radicals due to their non-alternant symmetry, as well as diminished vibronic coupling constants for non-radiative decay from CT excited states which can be further reduced in the solid state. We have discussed the requirement of brightening CT-based D_1 excitations by mixing local excited character.

Among many, we note there are two key challenges facing the development of radical-based OLED devices towards commercial applications:

1) Devices experience severe efficiency roll-off at higher current densities, with the insertion of the hole into the thermodynamically favourable SOMO indicated as a potential quenching mechanism. Further research is required to improved charge balance within devices, which could also enable improved operational lifetimes.

2) The available chemical space of radical-based emitters is limited. New radical systems based off π -systems with reduced delocalisation should be designed to enable more blue-shifted emission beyond 570 nm.

Current research efforts on radical systems as circularly polarised light emitters, strong intramolecular and intermolecular interactions, as well as allowing incorporation of heavy atoms without intersystem crossing-based emission quenching are also expected to present new opportunities for radical-based OLEDs.

Whilst outside of the scope of this article, the emergence of efficient devices based on doublet-doublet transitions in Ce complexes^{94,95} show how the benefits of doublet emission can extend to unpaired electrons when isolated in systems beyond p-orbitals. It is with hope that the authors look to the future of radical emitters and the possibilities offered by the doublet-spin manifold.

* Whilst CT states could also form by electron transfer from the TTM SOMO to Cz LUMO, this excitation was not considered as it is too high in energy to participate in the functional photophysics involving the lowest energy excited states.

**This agreement is perhaps surprising, since our simple model requires the CT state and TTM D₁ and D₂ states to be well-separated in energy, and this is not the case for some of the PTM-TPA radicals where the lowest two excited states are near-degenerate.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analysed in this study.

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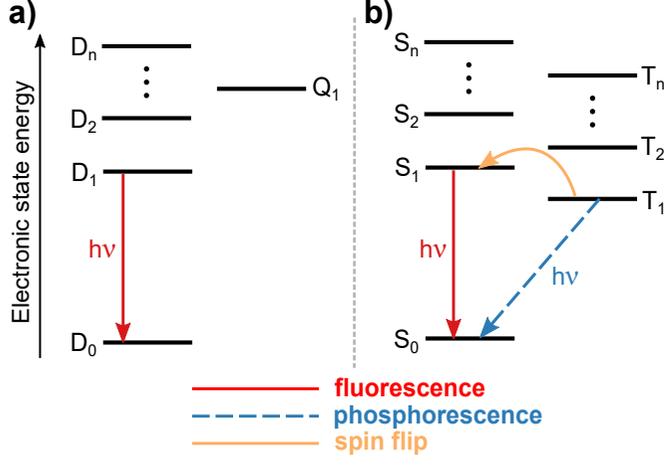
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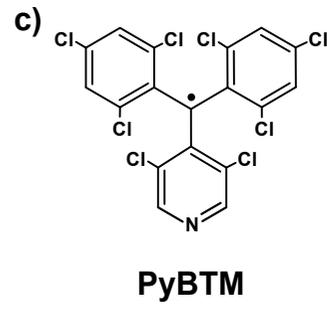
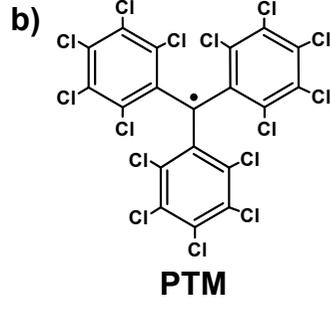
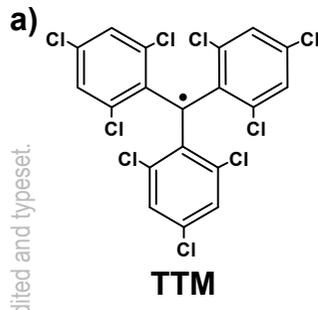
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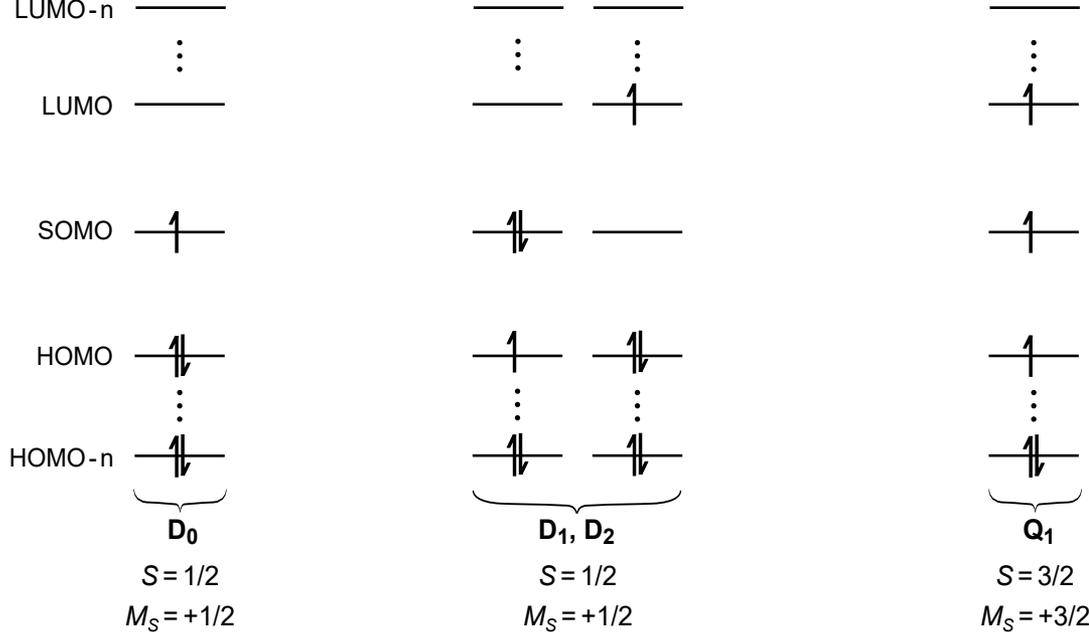
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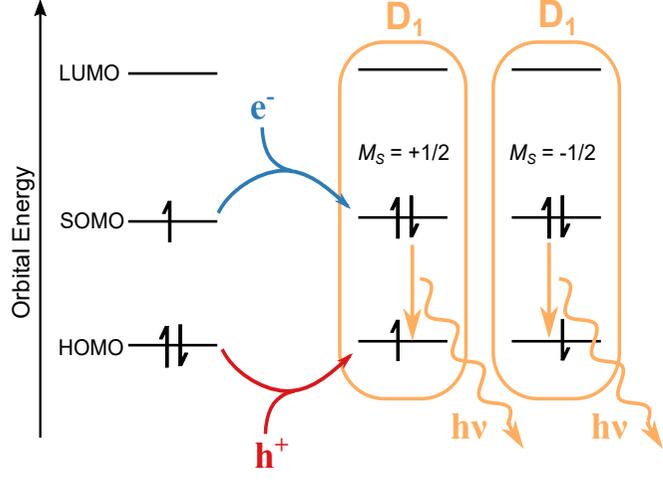


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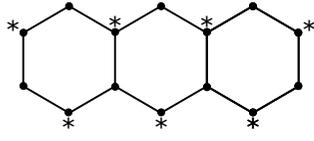


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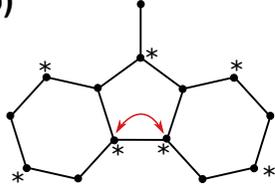


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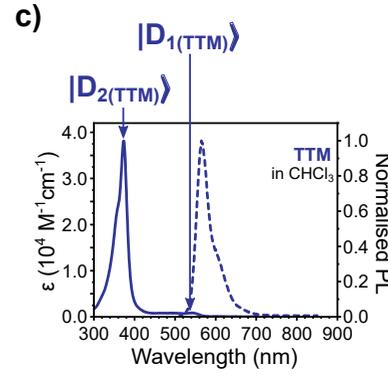
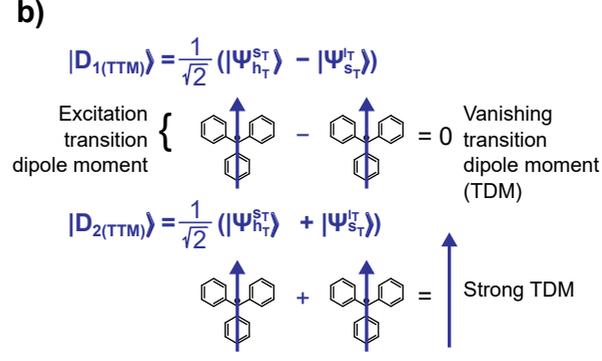
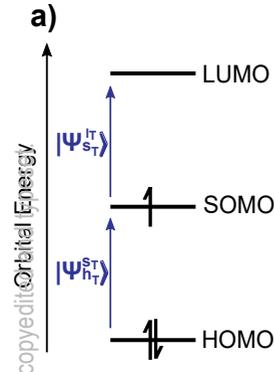
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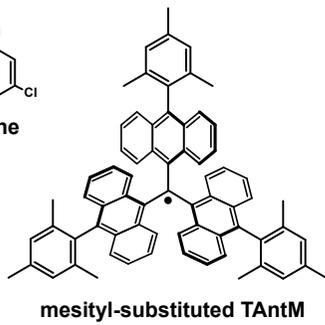
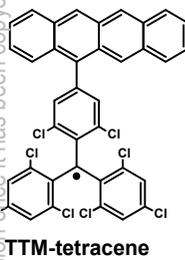
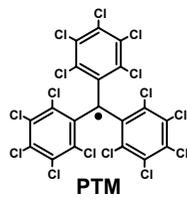
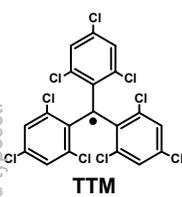


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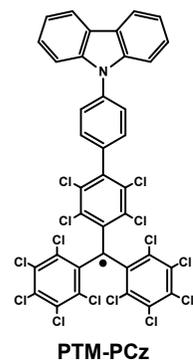
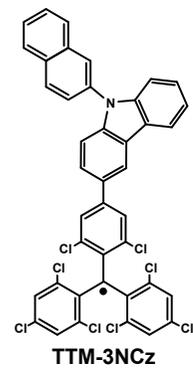
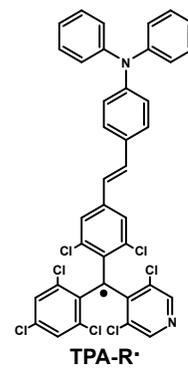
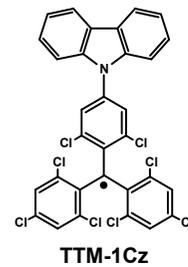
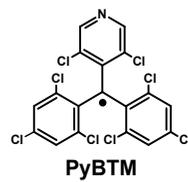


Dark Radical Structures

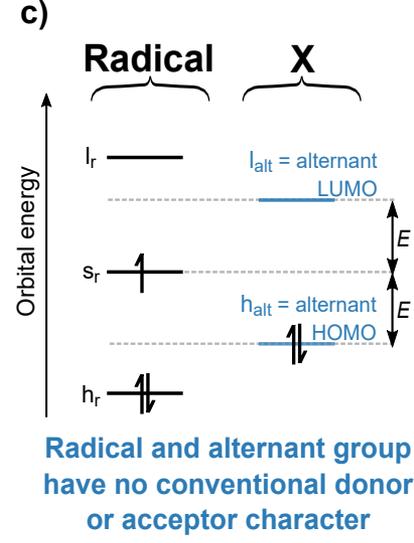
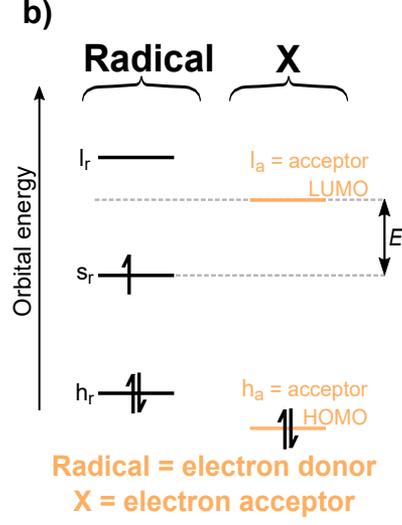
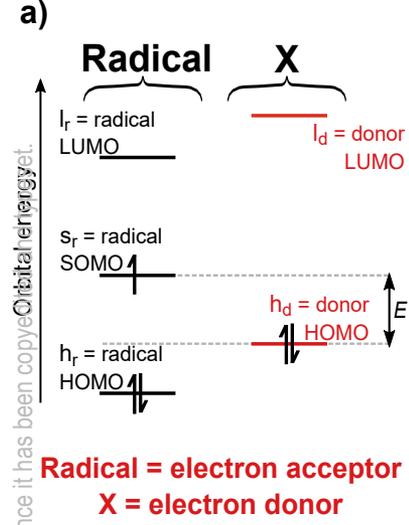
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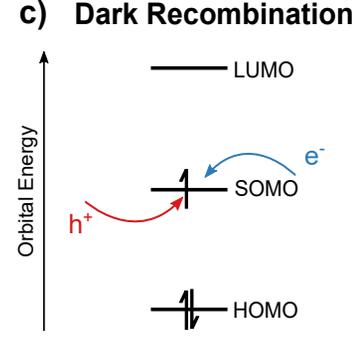
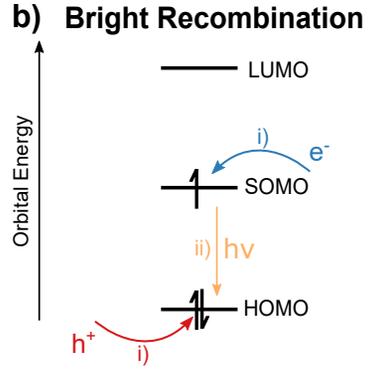
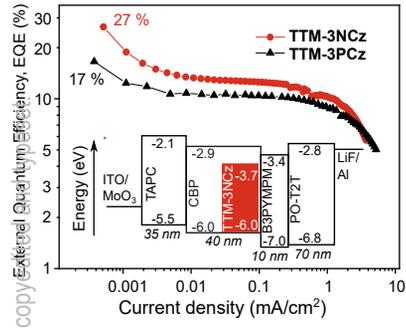
Bright Radical Structures



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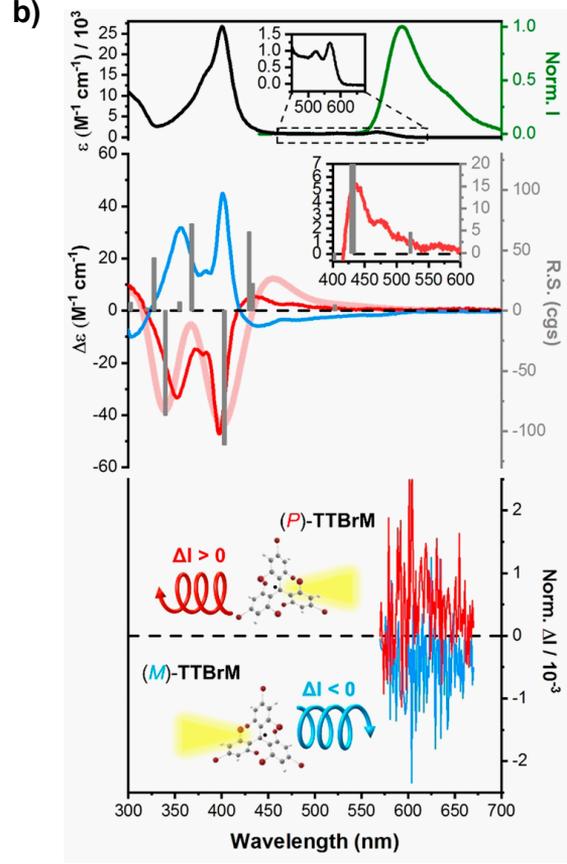
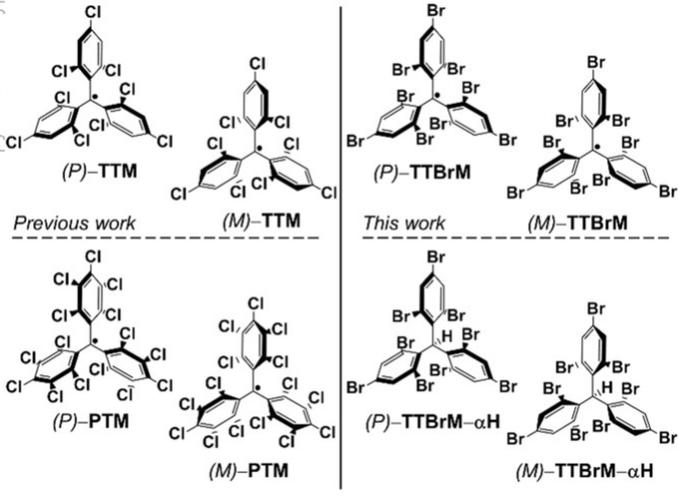


This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copy edited. External Quantum Efficiency, EQE (%)
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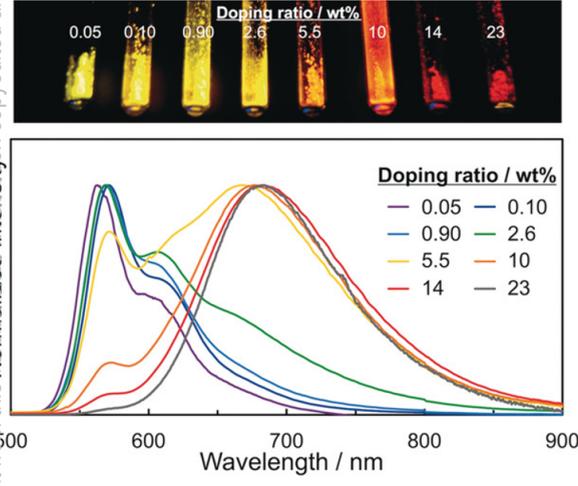
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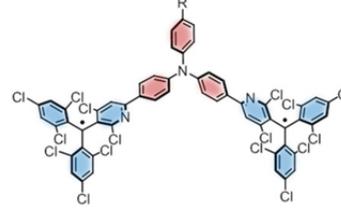
This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this Normalized intensity

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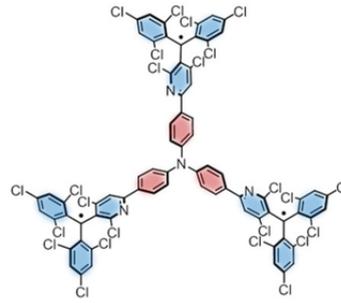


b)

R = CN: TPA(CN)₂(PyBTM⁺)
 R = Me: TPA(Me)₂(PyBTM⁺)
 R = OMe: TPA(OMe)₂(PyBTM⁺)



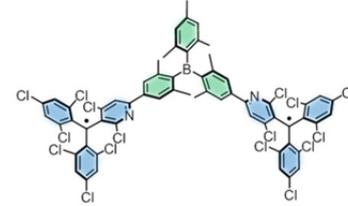
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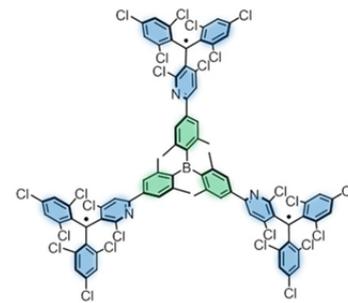
TPA(PyBTM⁺)₃



PyBTM⁺ group



TPB(Me)(PyBTM⁺)₂



TPB(PyBTM⁺)₃