Rationalization and tuning of doublet emission in organic radicals†

Claire Tonnele a,* and David Casanova a,ab

Neutral organic radical emitters are promising alternative candidates for efficient OLEDs. Their potential relies on their ability to avoid spin statistics loss of charge recombination as in closed shell emitters. Yet, these radicals generally present limited luminescence that was shown to be enhanced via chemical functionalization. Here we provide a detailed physical interpretation of the origin of the intrinsic poor emissive properties of TTM, a paradigmatic doublet emitter, from a computational perspective. The weak emission is rationalized on the basis of the mixing of intramolecular charge transfer (CT) excitations between the radical center and the ligands. We demonstrate that significant cancellation of the transition dipole moments of these CT contributions results in low oscillator strength and show how the modulation of their relative contributions to the composition of the lowest excited doublet state via donor substitution can brighten the organic radical. We illustrate this analysis through the study of a series of TTM derivatives. This study contributes to further the understanding of the photophysics of organic radicals and provides new insights for the tuning of their luminescence by rational design.

1 Introduction

Since the pioneering work of Tang and Van Slyke, who reported the first organic light-emitting diode (OLED) based on small molecules in 1987,1 remarkable effort has been put, in both academia and industry, into the research and development of high-performance OLEDs, enabling the realization of technical maturity and reaching the stage of commercial applications for display and lighting technologies.2,3 In conventional fluorescence-based OLEDs, holes and electrons injected from the electrodes recombine within the emissive layer with a probability of forming 1/4 singlet excitons and 3/4 dark triplet excitons dictated by spin statistics, limiting their internal quantum efficiency (IQE) to 25%.4

Several strategies have been explored and developed to harvest the triplet excitons and overcome the spin statistics limitation of typical organic semiconductors to theoretically achieve 100% IQE. A direct approach consists in using emitters containing heavy-metal atoms whose strong spin–orbit coupling enables efficient phosphorescence from triplet excitons.5 An alternative concept relies on the thermally activated delayed fluorescence (TADF) mechanism, through which triplet excitons are upconverted to radiative singlet excitons via reverse intersystem crossing.6

Recently, a very promising route for efficient OLEDs employing open-shell neutral organic radicals as emitters has emerged. In organic radicals, both ground and lowest excited states have doublet multiplicity, and the D1 → D0 transition is thus spin-allowed. The use of radical emitters with doublet emission constitutes a conceptually superior solution to elegantly circumvent...
the spin statistics limited efficiency issue encountered in closed-shell organic semiconductors. Following the seminal work of Gamero et al. in brightening the tris(2,4,6-trichlorophenyl)-methyl (TTM) radical by functionalization with a carbazole unit, Peng et al. reported in 2015 the first doublet-emission OLED. The practical chemical space has been principally limited to the TTM, perchlorotriphenylmethyl (PTM) and bis(2,4,6-trichlorophenyl)methyl (BTM) radical families. Recently, Li and co-workers reported what is to date the most efficient radical-based OLED (TTM-3NCz), reaching an impressive external quantum efficiency (EQE) of 27%. So far, the demonstration of radical-based OLEDs with doublet emission has been rare compared to singlet-based OLEDs. On the theoretical and computational sides, several groups have addressed the emissive properties of neutral organic radicals and possible brightening of the D States. These studies principally rely on unrestricted density functional theory (DFT) calculations to investigate substitution effects from a molecular orbital picture, intensity borrowing or hybridization between states perspectives, and possible non-radiative pathways.

In the present study, we aim to contribute to the rationalization of the doublet emission of organic radicals with the theoretical investigation of TTM and TTM derivatives (Fig. 1). We report the detailed characterization of the electronic structure and optical properties of the TTM radical and propose a physical interpretation of the origin of its weak emission.

2 Computational details

Ground state geometries of all compounds were optimized within the framework of DFT using the CAM-B3LYP functional and the 6-311G(d,p) basis set in the gas phase. Excitation energies were computed using the time-dependent version of DFT (TD-DFT), without and with the Tamm–Dancoff approximation (TDA), using the PBE0 functional and the 6-311G(d,p) basis set. Diabatization of the electronic states of 1 was carried out at the same level of theory using the Boys diabatization scheme. All calculations were performed using the Gaussian16 and Q-Chem packages. The DrawMol program was used for visualization.

3 Optoelectronic properties of TTM

3.1 Low-lying electronic states

The pristine TTM radical (1) exhibits a propeller-like geometry with D3 symmetry. The electronic ground state of 1 (X2A2) exhibits a singly (un)occupied molecular orbital (S(U)OMO) belonging to the A2 irreducible representation. The a2-SOMO contains a large contribution of the central carbon atom (p2), mixed with π-orbital contributions from the three trichlorophenyl rings (Fig. 2). HOMO and LUMO come as pairs of doubly degenerate π orbitals, i.e., 45e and 46e respectively, delocalized over the 2,4,6-trichlorophenyl ligands with no contribution over the central carbon atom.

Frontier molecular orbitals determine the nature of low-lying states. In particular, spin-conserving (doublet-to-doublet) electronic transitions involve, for the most part, the orbitals shown in Fig. 2. The lowest excited state is doubly degenerate and mainly described by the 45e to 22a2 electron promotions. The X2A2 → 12E transition dipole moments (TDMs) are perpendicular to the C3 symmetry axis and oscillator strengths are quite small, in accordance with the rather weak emission of 1. TDDFT predicts the presence of three excited doublets at slightly higher energies (Table 1). Transitions to 22E and 12A1 exhibit vanishing oscillator strengths, while excitation to 12A2 is dipole forbidden by symmetry. On the other hand, the 32E state (22a2 → 46e) holds a much stronger dipole allowed transition, and can be associated with the intense absorption band observed in the experimental spectrum of 1 (~375 nm in CHCl3).

The luminescence properties of 1 are expected to be related to the lowest excited state. Hence, in the following, we focus our attention on the characterization of the 12E state.

3.2 Importance of radical–ligand interactions

Molecular orbitals involved in the excitation to the 12E state are largely delocalized over the entire molecule, predicting the non-innocent participation of the 2,4,6-trichlorophenyl ligands. To illustrate the role of the ligands, we explore the dependence of excited state properties with the concomitant conrotatory torsion (θ) of the three ligands (Fig. 3). Here, the ortho chlorine atoms have been replaced by hydrogen atoms to avoid steric hindrance (compound 0, see the ESI†). At the D3h geometry, in which the aromatic rings are perpendicularly oriented with respect to the σh symmetry plane (θ = 90°), π-orbitals of the ligands are orthogonal to the p2 orbital of the central carbon atom. Decoupling the unpaired electron from the π-system of the phenyl rings results in strictly dipole forbidden transitions to low-lying states (Table S2, ESI†). By decreasing the dihedral angle (θ < 90°), the transition to the lowest 12E becomes symmetry allowed (non-zero TDMs), although oscillator strengths remain very small at all dihedral angles. On the other hand, departure from D3h triggers a fast increase of the transition strength to the 32E state. Moreover, while the doubly degenerate HOMO and LUMO remain virtually unaffected by planarization of the system, the SOMO and SUMO levels are significantly destabilized and stabilized, respectively (Fig. S3, ESI†). This results in an overall decrease of the SOMO-LUMO and HOMO-SUMO gaps that in turn translates into a lowering of the excitation energy to the 12E and 32E states.

Therefore, the non-zero TDMs become possible through the interaction of the radical electron with the π-system of the ligands.
Despite that, excitation to the lowest doublet (1^2E) remains very weak.

### 3.3 Role of excited state symmetry-breaking relaxation

Electronic semi-occupancy of the 45e orbital pair of the lowest excited doublet at the D3 Franck–Condon geometry induces a Jahn–Teller distortion. The Jahn–Teller active distortion modes able to split the doublet state must be different from the totally symmetric representation and must belong to the symmetrized direct self-product of the E representation (A1 ⊕ E). Therefore, the degeneracy-breaking distortion responsible for the excited state stabilization on the 1^2E potential energy surface follows an E-symmetry mode. As a result, the symmetry of the molecule reduces to C2, with the two-fold rotation axis aligned with one of the C-ligand bonds. At the C2 excited state minimum, the molecule is slightly more planar, with shorter C-ligand bonds (especially that at the C2 axis), and a loss of aromaticity of the six-membered rings (Table S5, ESI†).

Relaxation on the lowest excited doublet (2^2B) results in a redshift of the energy gap with the ground state. The computed vertical excitation energy of 2^2B at the C2 minimum (Fig. 4) is in relative agreement with the maximum of the emission band of recorded in solution (560–570 nm). The symmetry loss at the 2^2B geometry induces a localization of the hole and electron on one of the ligands (especially the former), which can be related to the mild increase in the oscillator strength with respect to lowest excitation at the D3 geometry (1^2E state).

### 3.4 Why TTM is a weak emitter?

The results gathered in the previous sections are in very good agreement with the experimentally observed weak emission of
TTM, but do not provide a physical rationalization for the low oscillator strength of the lowest excited doublet, $1^2E$ ($D_3$ geometry) or $2^2B$ ($C_2$ geometry). The poor emission of alternant radicals such as TTM is generally rationalized considering excitations involving the HOMOs, SOMOs and LUMOs.\(^\text{9,23}\) In such systems, the HOMO $\rightarrow$ SOMO and SOMO $\rightarrow$ LUMO excitations are understood as being degenerate with identical TDMs. As they mix, the out-of-phase combination produces the low-lying dark states with vanishing TDM, referred to as $D_1$, while the in-phase combination forms the bright states labelled $D_2$. Breaking the alternancy symmetry lifts the HOMO–SOMO and SOMO–LUMO degeneracy, which allows a larger TDM of the lowest excited state to be achieved.\(^\text{22}\) However, to the best of our knowledge, no computational investigation has so far provided a physical characterization of these contributions.

To explore the origin of the weak emission of I, we decompose the adiabatic electronic states mainly described as HOMO $\rightarrow$ SOMO and SOMO $\rightarrow$ LUMO excitations, $1^2E$ and $3^2E$ (see the ESI\(^\text{†}\) for details), into a set of diabatic states with a well-defined character being constructed by maximizing the difference of the magnitude of the dipole moment between each pair of diabatic states (Boys localization).\(^\text{26}\) The diabatic state energies are obtained as the diagonal elements of the diabatic Hamiltonian composed by state energies and interstate couplings of LC and CL diabats. Fig. 5 shows the oscillator strength of the lowest eigenstate of the model Hamiltonian as a function of the energy gap $\Delta E$ between LC and CL states (with fixed $V_x = V_y = -0.278$ eV). For $E(\text{LC}) = E(\text{CL})$, the doubly degenerate lowest adiabatic state is built as half-and-half mixing of two diabats ($\text{LC}_x$ and $\text{CL}_x$ or $\text{LC}_y$ and $\text{CL}_y$), with a virtually zero oscillator strength, that is, antiparallel arrangement of TDMs. On the other hand, by breaking the LC/CL symmetry, i.e., $\Delta E > 0$, the degree of mixing of the diabatic states can be tuned, promoting the LC character (over CL) of the lowest eigenstate and resulting in an overall non-zero oscillator strength that increases with $\Delta E$. In practice, decreasing the energy of LC diabats with respect to CL excitations can be achieved by enhancing the electron donor character of the ligands, as will be seen in the next section. Oscillator strengths obtained for the lowest doublet modelled at the excited ($C_2$) geometry follow a similar trend, but with systematically higher oscillator strength values induced by symmetry breaking and exciton localization (as discussed above, Section 3.3).

### 4 Substituted TTM derivatives

To address the possible tuning of the photophysical properties of TTM-based compounds, we first investigate the case of 1H, in which one of the para chlorine atoms is substituted by a hydrogen atom. As a result of the reduced symmetry of the system (now $C_2$), the degeneracy of the molecular orbitals is lifted. As for I, the lowest excited state arises from a...
HOMO → SUMO excitation. While the SUMO remains virtually identical to that of 1, the HOMO is asymmetrically delocalized over the whole system with a larger contribution on the H-substituted ligand. These orbitals are slightly destabilized, with a larger effect on the HOMO, but the very small magnitude of these variations does not translate into an overall larger excitation energy (Table 2). The oscillator strength decreases by about 33%, in agreement with the lower donor ability of H versus Cl (see Section 3.4).

Next, we consider donor–acceptor systems 1NO2 and 1NH2 to explore how the photophysics of 1 is affected by substitution as a function of the nature of the grafted moieties, acceptor and donor, respectively. Both types of substitution are predicted to result in a lowest excited doublet (D1) state (22B for all molecules with C2 symmetry) with a CT character and higher TDM than for pristine TTM.9 So far, functionalization by electron donor groups has proven to be a successful strategy for improving the emissive properties of neutral organic radicals.17,36–40 Although acceptor substituted radicals with good emissive properties have not been reported so far, it has been inferred that electron-deficient group may be used to brighten TTM.22 In 1NO2, TTM acts as the donor while the NO2 moiety plays the role of the acceptor, and the transition to the lowest doublet excited state is dominated by a SOMO → LUMO excitation. The introduction of NO2 substantially stabilizes the LUMO level that is principally localized on the dichlorophenyl bearing the substituent. On the other hand, the TTM-centered SOMO is only weakly affected and the SOMO–LUMO energy gap consequently decreases (Fig. S5, ESI†), translating into a lower excitation energy to the lowest doublet as compared to 1. Moreover, our calculations do not predict an improvement of optical properties of 1NO2 with respect to 1, as the oscillator strength remains very low. Visual analysis of the SOMO and LUMO confirms the CT nature of D1, which is further quantified by a larger e–h radius with respect to 1 (1.692 Å against 0.682 Å for 1).

In contrast, increasing the donor character of the ligand in 1NH2 enhances the LC nature of the lowest transition (larger e–h radius), inducing a larger oscillator strength, as predicted in the previous section. Destabilization of the HOMO (Fig. S5, ESI†), mostly localized on the NH2 substituted ring, results in a redshift of the (HOMO → SUMO) D1 excitation energy. Although our calculations overestimate the redshift measured in CHCl3 for 1NH2 with respect to 1, the 4-fold increase in intensity is correctly reproduced.7

Table 2 Vertical transition energies to the lowest excited doublet state (in eV), oscillator strength (f), dominant contribution and electron–hole radius (in Å) computed for the lowest lying excited state of studied compounds at the (TDA and TDDFT) PBE0/6-311G(d,p) level.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>TDA</th>
<th>TDDFT</th>
<th>Contribution</th>
<th>e–h radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.904 (0.027)</td>
<td>2.795 (0.015)</td>
<td>HOMO → SUMO</td>
<td>0.682</td>
</tr>
<tr>
<td>1H</td>
<td>2.906 (0.018)</td>
<td>2.803 (0.012)</td>
<td>HOMO → SUMO</td>
<td>0.094</td>
</tr>
<tr>
<td>1NO2</td>
<td>2.764 (0.018)</td>
<td>2.654 (0.010)</td>
<td>SOMO → LUMO</td>
<td>1.692</td>
</tr>
<tr>
<td>1NH2</td>
<td>2.548 (0.082)</td>
<td>2.473 (0.063)</td>
<td>HOMO → SUMO</td>
<td>2.224</td>
</tr>
<tr>
<td>1'NH2</td>
<td>2.243 (0.133)</td>
<td>2.188 (0.101)</td>
<td>HOMO → SUMO</td>
<td>4.995</td>
</tr>
<tr>
<td>1'NH2</td>
<td>2.158 (0.119)</td>
<td>2.127 (0.099)</td>
<td>HOMO → SUMO</td>
<td>8.709</td>
</tr>
</tbody>
</table>

Fig. 6 Frontier molecular orbitals of characterizing the excitation to the D1 state in 1H, 1NO2, 1NH2, 1'NH2, and 1'NH2 computed at the PBE0/6-311G(d,p) level.
The LC character of $D_1$ can be further tuned by modifying the length of the electron donor ligand as in $1'\text{NH}_2$ and $1''\text{NH}_2$. Inserting a phenyl ring between the radical center and the NH$_2$ substituted dichlorophenyl increases the effective conjugation length of the ligand, lifting the HOMO energy and hence reducing the transition energy. Interestingly, the oscillator strength in $1'\text{NH}_2$ is notably larger than that in $1\text{NH}_2$, as predicted by the classical dipole expression ($\mu = e r$). Adding a second conjugated ring further redshifts the $D_1$ excitation energy and pulls away the hole and electron centers, but the oscillator strength of $1''\text{NH}_2$ decreases with respect to $1'\text{NH}_2$, as the overlap between HOMO and SUMO fades (Fig. 6).

5 Conclusions

In this work, we propose a physical interpretation of the poor emissive properties of TTM and rationalize the possible brightening of doublet emission. Using density functional theory calculations, we first provide detailed characterization of the TTM radical electronic structure and optical properties. The lowest excited state of pristine TTM involves the HOMO and SUMO orbitals, and presents a small, but non-zero, oscillator strength arising from the interaction of the unpaired electron with the $\pi$-system of the 2,4,6-trichlorophenyl ligands. Excited state relaxation lowers the molecular symmetry (from $D_1$ to $C_2$) and localizes the excitation on one of the ligands, inducing a slight increase of the oscillator strength.

Using a model Hamiltonian, we describe the doublet emitter state as a combination of charge transfer excitations from the radical center to the ligands (CL) and from the ligands to the radical center (LC). The respective linear optical responses of these CT contributions significantly cancel each other due to the opposite orientation of their individual transition dipole moments (TDMs), giving rise to a significant oscillator strength.

We show that lowering the degree of mixing of these excitations provides a way of lessening the extent of TDM cancellation and consequently gradually allows increasing oscillator strength. These results demonstrate how a brightening of the lowest excited doublet state can be achieved by tuning the CL/LC relative contributions through substitution of the ligands with electron donating groups.

Chemical substitution of the conjugated ligands with electron acceptor and donor moieties reduces the SOMO/LUMO and HOMO/SUMO energy gaps, respectively, resulting in a redshift of the lowest doublet-to-doublet transition. The presence of donor groups stabilizes LC contributions over CL excitations with respect to TTM, alleviating the TDM cancellation and increasing the overall oscillator strength. Increasing the conjugation length of the ligand can also be used to enhance the emission properties of the radical, but too much electron/hole separation might eventually be detrimental as the spatial overlap becomes smaller.

These results rationalize previous studies on TTM derivatives and provide new insights and ideas to improve the luminescence properties of organic radicals.

Author contributions

C. T. and D. C. conceptualized the work. C. T. performed and analyzed the quantum-chemical calculations. C. T. and D. C. discussed and wrote the manuscript.

Conflicts of interest

There are no conflicts of interest to declare.

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References


34 Notice that the ground state at the C2 geometry also belongs to the B representation, i.e., X2B.


