Highly emissive excitons with reduced exchange energy in thermally activated delayed fluorescent molecules

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Unlike conventional thermally activated delayed fluorescence chromophores, boron-centered azatriangulene-like molecules combine a small excited-state singlet-triplet energy gap with high oscillator strengths and minor reorganization energies. Here, using highly correlated quantum-chemical calculations, we report this is driven by short-range reorganization of the electron density taking place upon electronic excitation of these multi-resonant structures. Based on this finding, we design a series of π-extended boron- and nitrogen-doped nanographenes as promising candidates for efficient thermally activated delayed fluorescence emitters with concomitantly decreased singlet-triplet energy gaps, improved oscillator strengths and core rigidity compared to previously reported structures, permitting both emission color purity and tunability across the visible spectrum.
The discovery of purely organic thermally activated delayed fluorescence (TADF) materials, with its premise to break the spin statistical bottleneck of 25% internal quantum efficiency without the requirement of rare noble metal emitters, has prompted a paradigm shift in the design of emitter materials for use in organic light-emitting diodes (OLEDs). TADF is rooted in a thermally promoted reverse intersystem crossing (RISC) process enabling upconversion of triplet excitons into emissive singlet excitons, which otherwise would be lost through non-radiative pathways. One key property TADF molecules should fulfill for efficient RISC is a small energy gap between the lowest singlet and triplet excited states \( \Delta E_{ST} \) (usually < 0.2 eV), so that delayed fluorescence can be thermally activated at room temperature (though exceptions to this general rule exist that involve higher-lying triplet states). The most widely applied design strategy so far is based on molecules featuring weakly coupled and spatially separated donor (D) and acceptor (A) moieties. This motif sustains charge-transfer (CT) excitations with small exchange interactions and correspondingly small \( \Delta E_{CT} \) compared to localized excited states.

However, this approach suffers from a number of drawbacks that directly reflect the nature of the emissive excited state. In particular, achieving high photoluminescence quantum yields (PLQY) and color purity in conventional TADF molecule-based OLEDs has been challenging thus far. As a consequence of their dominant CT character, the singlet electronic excitations in these molecules often display fairly small radiative emission cross-sections (oscillator strengths, \( f_{osc} \)). Hence, high PLQY in these materials is only possible through efficient suppression of non-radiative decay processes. Moreover, charge-transfer excitations are usually accompanied by large structural reorganization, associated with conformational degrees of freedom in D-A molecular architectures, leading to broad emission spectra. Yet, such conformational gating effects also feed small admixtures of local (covalent) excited-state character into (primarily triplet) CT (ionic) excitations, prompting the needed spin-orbit interaction that mediates spin conversion. Thus, designing optimally performing TADF compounds in this scenario relies on the necessarily delicate balance between antagonistic effects.

A notable departure from the usual strategy has recently been proposed by Hatakeyama et al. who designed TADF emitters as triazulene cores incorporating ortho-substituted boron and nitrogen atoms to promote multiple resonance effects (see chemical structures in Fig. 1 and resonant structures in Supplementary Fig. 5). Unlike conventional D-A architectures, these boron-centered azatriangulenes yield concomitantly narrow emission spectra (full-width at half-maximum = 28 nm), relatively large \( f_{osc} \) (~0.2 for both DABNA-1 and 2) and small \( \Delta E_{ST} \) (~0.15 eV for DABNA-1 and 0.21 for 2) values. OLEDs with high maximum external quantum efficiencies (EQE\(_{max}\)) of 13.5% and pure blue emission [CIE coordinates of (0.13, 0.09)] for DABNA-1 were demonstrated. In marked contrast with experiment, recent publications reported Time-Dependent Density Functional Theory (TD-DFT) \( \Delta E_{ST} \) predictions in the range 0.4–0.6 eV depending on functional, largely overestimating the experimental values. Based on these TD-DFT calculations, two mechanistic pictures for TADF in boron-centered azatriangulenes molecules have been put forward: Lin et al. claimed that RISC occurs directly from \( T_1 \) to \( S_1 \) while Northey et al. advanced that RISC involves an intermediate higher-lying triplet state \( T_2 \).

Here, by scrutinizing the nature of the lowest electronic excitations in these molecules, we propose a new paradigm for TADF that builds on the concept of short-range charge-transfer illustrated in Fig. 1. While long-distance charge separation in multichromophoric D-A systems reduces \( \Delta E_{ST} \) at the expense of \( f_{osc} \), we show that boron-centered azatriangulenes undergo a large but local spatial reorganization of the electronic density in the excited states, which significantly lowers the exchange energy while maintaining high overlap between wavefunction tails and therefore high \( f_{osc} \) transitions, together with small structural relaxation energies. Based on these results, we propose analogs that we hope will lead to high performance TADF emitters in OLED devices.

Results

Origin of small \( \Delta E_{ST} \) in DABNA molecules. We start our analysis with DABNA-1. Irrespective of the choice of the DFT functional and the use (or not) of the Tamm-Dancoff approximation, all our TD-DFT calculations yield erroneously large \( \Delta E_{ST} \) values (e.g., 0.56 eV at B3LYP level), in line with refs.6,15,16 (see Supplementary Table 1). The use of tuned range-separated functionals does not help either. By varying the amount of Hartree-Fock-like exchange in the functional, we observe a smooth decrease of \( \Delta E_{CT} \) that reaches a more reasonable 0.25 eV with pure semilocal models (e.g., LDA), but at the cost of an unphysical delocalization of the electronic density over the outer phenyl rings (Supplementary Fig. 1). The discrepancy between experiment and theory has more fundamental grounds, as we discovered by running higher-level Spin-Component Scaling second-order approximate Coupled-Cluster (SCS-CC2) calculations with the def2-TZVP basis set (see SI for further details on these calculations).

In contrast to TD-DFT, SCS-CC2 calculations on DABNA-1 and compound 2 provide (vertical, i.e., based on ground-state geometry) \( \Delta E_{ST} \) values in excellent agreement with experiments, Table 1. Despite relatively small \( \Delta E_{ST} \) values (<0.2 eV), the lowest singlet electronic excitation in these molecules is strongly dipole-allowed with a \( f_{osc} \) of 0.31 in DABNA-1 and (summing over the two degenerated singlet excited states arising from the \( C_{SV} \)-symmetry) 0.26 in 2. Most interestingly, similar \( \Delta E_{ST} \) values were obtained for vertical and adiabatic (fully relaxed) excitations, owing to modest nuclear reorganization energies in the \( S_1 \) state (0.12 eV and 0.10 eV for DABNA-1 and molecule 2, respectively, Table 1), which should ensure narrow singlet emission as an added virtue.
The origin for the unusual electronic properties of these molecules is best pictured by difference density plots for the $S_0$-$S_1$ and $S_0$-$T_1$ excitations, calculated at the SCS-CC2 level and shown in Fig. 1b for DABNA-1 (cf. Supplementary Fig. 1). These plots reveal a remarkably homogenous short-distance reshuffling of the electronic density upon excitation that yields spatially alternating hole-rich and electron-rich regions. The density reorganization is instructive to analyze the results obtained for fragments (labeled fr1–fr5) extracted from the parent molecules. Close inspection of the differential density plots for both singlet and triplet excitations show the same alternating pattern as the one observed for DABNA-1, yet with an increasing spreading in space as the fragment becomes larger and/or more conjugated, Fig. 2b. This effect can be quantitatively assessed by computing the CT delocalization volume (see Supplementary Information "Difference density plots" section for computational details). Figure 2c shows strong linear correlations ($R^2 = 0.99$) between both $\Delta E_{ST}$ or $f_{osc}$ and the CT volume, with more extended systems providing, remarkably, smaller $\Delta E_{ST}$ and larger $f_{osc}$. The trend is in fact reminiscent of the behavior of localized (covalent) excitations in conjugated materials, where the exchange energy measured/calculated in polymer chains is usually significantly smaller than that in the parent small molecules\(^{17}\).

### Highly emissive molecules with small $\Delta E_{ST}$

The most striking feature arising from Fig. 2c is that while CT delocalization triggers a large decrease in $\Delta E_{ST}$ from fr1 (0.65 eV) to fr5 (0.18 eV), the lowest excitation $f_{osc}$ strength instead increases along the same sequence, from 0.02 in fr1 to 0.23 in fr5. This result contrasts with the behavior observed for conventional D-A-based TADF molecular architectures\(^{12}\). Inspired by this finding, we applied the multiple charge resonance strategy to design in silico new TADF chromophores based on π-extended B-doped and N-doped nanographenes (Fig. 3a). The results reported in Fig. 3b confirm the trends observed for the fragments in Fig. 2, i.e., reduced $\Delta E_{ST}$ (as supported by the Zero Field Splitting calculations, see Supplementary Table 4) and enhanced $f_{osc}$. In the largest compound investigated, 6, the singlet and triplet excitations are found to be quasi-degenerate ($\Delta E_{ST} \sim 3$ meV), yet the singlet $f_{osc}$ is as large as 1.0. Moreover, as all investigated molecules have a rigid backbone with small (intramolecular) nuclear reorganization.
energies (Supplementary Table 3), we expect these give rise to narrow linewidth and pure color emission. It is important to stress that the increment in $f_{\text{osc}}$ is not solely caused by the increase of the number of $\pi$-electrons but, instead, occurs primarily through extended delocalization of the wavefunction and increased polarizability along the main-axis of the molecules.

Additional insights into this unexpected behavior can be gained from a detailed analysis of the singlet excited-state wavefunctions, in particular of the following two metrics that assess the relative electron-hole quasi-particles: the electron-hole separation ($\Delta r$) and the amount of charge transferred ($\Delta q$).

Figure 3c points to a picture where the low-lying singlet excited state undergoes substantial reshuffling of the electronic density (large $\Delta q$ values) but over short distances (small $\Delta r$ values). Besides, these characteristics get more pronounced as the ribbons grow longer: $\Delta r$ decreases from 0.9 to 0.6 Å when going from 3 to 6, while $\Delta q$ increases from 0.58 $|e|$ in 3 up to 0.71 $|e|$ in 6. The resulting ‘short-range/local CT’ states feature both high electron-hole wavefunction overlaps and small exchange interactions, turning into high $f_{\text{osc}}$ and low $\Delta E_{\text{ST}}$ values for the DABNA core building block. In addition, ‘long-range’ $\pi$-conjugation along ribbons 3–6 translates into electronic excitations with extended delocalization and hence increased polarizability and radiative decay rates. While none of these effects is surprising when taken separately, it is the combination of short-range charge separation and long-range electronic delocalization that makes these molecules unique. We believe this is a real breakthrough as most of the low $\Delta E_{\text{ST}}$ TADF molecules reported so far are characterized by very low $f_{\text{osc}}$ and radiative decay rates. This is exemplified by the comparison of compounds 3–6 with selected D-A TADF reference molecules, for which $f_{\text{osc}}$ and $\Delta E_{\text{ST}}$ calculated at a similar level of theory (Fig. 3b and Supplementary Table 2) are concurrently small, in line with their $\Delta r$ values larger than the 1.5–2.0 Å criterion usually set to discriminate CT excitations that we reported previously.

Finally, besides the beneficial effect on $\Delta E_{\text{ST}}$ and $f_{\text{osc}}$, increased delocalization along the series 3–6 expectedly produces a spectral red-shift of the lowest singlet excitation, thereby allowing for variations of the emission color from blue to green as a function of the molecular size (Fig. 3d). Further tuning of the emission...
wavelength can be achieved, for instance by introducing an excess amount of N-atoms or B-atoms into the conjugated plane. For the sake of illustration, we designed two other molecules, 7 and 8, based on 5. These chromophores essentially retain the properties of the parent molecule in terms of $\Delta E_{ST}$ and $f_{osc}$ (see Supplementary Table 3), however, they possess emission wavelengths blue-shifted to 2.85 eV (435 nm, deep blue), 7 and red-shifted to 2.1 eV (590 nm, yellow, 8) compared to 5.

To conclude, using highly correlated wavefunction-based methods, we have elucidated the origin for the reduced singlet-triplet gap in the boron-centered azatriangulene molecules originally reported by Hatakeyama et al. as resulting from a local alternating rearrangement of the electronic density upon excitation. We have further shown that this is compatible with high absorption and emission extinction coefficients and we have proposed a strategy, based on promoting short-range charge-transfer in π-extended chromophores, as a way to simultaneously optimize RISC and radiative decay rates. This approach has been successfully applied to the design of TADF molecules with: (i) close-to-resonant lowest singlet and triplet excited states; (ii) large singlet radiative decay rates (iii) tunable and expected pure color singlet emission. We hope our theoretical work will catalyze the synthesis and trigger the characterization of a new generation of TADF molecules with unprecedented electroluminescence quantum efficiencies.

Methods

Computational details. The SCS-CC2 calculations were performed by the TURBOMOLE 6.5 software19 using the spin-adapted formulation of the linear response theory and the def2-TZVP basis set20. The TD-DFT calculations were carried out using the def2-TZVP basis set. The TD-DFT calculations together with the respective analysis were performed with the ORCA 4.0.1.2 software21.

Data availability

All data are available from the corresponding author upon request.

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Author contributions

The calculations were performed by A.P. with contributions from D.H. and Y.O. The manuscript was written by A.P., D.H., Y.L., J.-C.S.-G., L.M., E.Z.-C., D.B., and Y.O. contributed to the analysis and improvements of the work.

Additional information

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