Tuning Solid-State Emission with Molecular Torsion in Dibenzo-suberenylidene-Derived Organic Dyes

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ABSTRACT: The solid-state emission of organic compounds is required for many opto-electronic applications. However, it remains challenging to modify the emission properties of existing solid-state emissive organic frameworks, due to their inherently complicated structure-activity relationships. Herein, we report the design and construction of a new family of solid-state luminogens based on the dibenzosuberenylidene scaffold. The dyes exhibit interesting crystallization-induced emission enhancement (CIEE) behavior, which can be fine-tuned via easily implemented structural modifications to result in a range of fluorescence colors and intensities.

Solid-emissive organic compounds are desirable for use in many applications, such as organic light-emitting diodes, sensors, medical imaging, and photovoltaics. Over the past two decades, increases in the theoretical understanding of this phenomenon, which is commonly known as “Aggregation-Induced Emission” (AIE), has led to the development of several strategies that can be used to design solid-emissive organic frameworks, and avoid the aggregation-induced quenching that is otherwise typically observed for organic fluorophores. Such strategies include the incorporation of propeller-like ‘rotors’, such as phenyl or arene rings, into molecular frameworks to yield twisted structures in aggregate forms, increasing intermolecular distances between adjacent molecules and restricting the π–π interactions which could otherwise quench the emission. Simultaneously, the steric hindrance provided by these substituents restricts the vibrational motions of the molecule, which restricts access to conical intersections that could otherwise result in efficient nonradiative decay of the excited state energy. These design strategies tend to generate complicated molecules, whose versatility is dependent on the practicality of their synthesis. Furthermore, it often remains especially difficult to fine-tune the photophysical properties within each luminogenic scaffold, which in our opinion has been a significant bottleneck in the development of versatile solid-emissive organic frameworks. It is of broad interest to develop novel, synthetically practical organic motifs which allow the facile tuning of emission properties via simple structural modifications.

Our group has previously developed a series of stimuli-responsive organic dyes and AIE materials based on tropylium ion, as well as explored the unique solid-state fluorescence behaviour of the tetrabenzo[5.7]fulvalene (Figure 1). The dibenzosuberenyldene framework contained in tetrabenzo[5.7]fulvalene is known, both from our work and other studies in literature, to bend into a saddle shape, which can enhance solid-state fluorescence via the inhibition of intermolecular π-stacking. We were attracted to the possibility of incorporating this dibenzosuberenyldene-based π-system into ionic organic dyes to explore their photophysical properties and potential applications (Figure 1).
In line with recent theories regarding the control of conical intersections, initially proposed by Li and Blancafort in 2013, we hypothesised that the torsional motion of the double bond and vibrational ring puckering of the dibenzosuberenyldiene moiety could result in an energetically-accessible conical intersection that could also facilitate efficient nonradiative decay. We envisaged that the installation of variously-sized substituents at positions adjacent to the C=C double bond would sterically-hinder the framework, restricting the vibrational and rotational degrees of freedom and hence the accessibility of any potential conical intersections. Herein, we present the development and study of a novel framework for ionic organic compounds based on the dibenzosuberenyldiene moiety, which are intensely coloured, brightly fluorescent tetrafluoroborate salts (Figure 1). Through easily implemented structural modifications to influence molecular torsion and ring puckering, we were able to increase the solid-state photoluminescent quantum yield, as well as predictably adjust the fluorescence colour of these dyes.

The dyes in the family were easily-synthesised in two steps, starting from readily available 4-bromo anilines 1 and dibenzosubereneone 2 (Scheme 1). Following a bromine-lithium exchange with n-butyllithium, nucleophilic addition of the lithiated anilines to dibenzosubereneone provided the corresponding tertiary amines 3. These were then dehydrated with excess anhydrous HBF₄ to immediately yield intensely coloured dyes as tetrafluoroborate salts, which were then further purified via recrystallisation and remained bench-stable for several years.

The first dye we synthesised and studied was DMA-Sub (Scheme 1), which was a fine red crystalline powder with faint red fluorescence. Preliminary photophysical studies revealed the presence of two broad absorption bands in solution at λabs = 400 nm and 495 nm (Table 1), the latter of which was hypsochromically shifted by ~18 nm in thin-film form. The compound showed faint fluorescence in solution at 637 nm upon irradiation at both 400 and 495 nm. The crystalline emission of the compound was similar to that in solution, but again with a slight hypsochromic shift in λmax. Photoluminescence quantum yield (Φf) measurements saw the Φf values increase from ~0.1% in solution to ~0.8% in thin film, and ~0.5% in crystalline form (Table 1).

Table 1. Photophysical properties of dibenzosuberenyldiene dyes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solution (DCM)</th>
<th>Crystalline (Thin-film)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λabs / nm</td>
<td>λem / nm</td>
</tr>
<tr>
<td>DMA-Sub</td>
<td>401, 495</td>
<td>637</td>
</tr>
<tr>
<td>DEA-Sub</td>
<td>400, 494</td>
<td>634</td>
</tr>
<tr>
<td>DBA-Sub</td>
<td>401, 497</td>
<td>627</td>
</tr>
<tr>
<td>DFDMA-Sub</td>
<td>397</td>
<td>568</td>
</tr>
<tr>
<td>DMeDMA-Sub</td>
<td>369</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>(398, 477)</td>
<td>(625 (663)</td>
</tr>
<tr>
<td></td>
<td>(393, 474)</td>
<td>(665 (662)</td>
</tr>
<tr>
<td></td>
<td>(393, 474)</td>
<td>(622 (669)</td>
</tr>
<tr>
<td></td>
<td>(400, br)</td>
<td>(625 (597)</td>
</tr>
<tr>
<td></td>
<td>(364)</td>
<td>(537 (591)</td>
</tr>
</tbody>
</table>

*N.D. = not detected/no fluorescence, see the SI for further experimental details.

Single-crystal XRD studies (Figure 2a) revealed that crystalline DMASub sat in a quinoidal iminium form that localised the positive charge on the nitrogen, which was also confirmed by NMR data for the solution state (see page S6 in the SI for details). The structure shows significant bend across the dibenzosuberenyldiene moiety, with a dihedral angle between the two benzo groups of ~126° (Figure 2a), inhibiting planar π–π interactions within the packing unit (Figure 2b). Interestingly, the quinoidal moiety itself also slightly bends to ~178° (Figure 3, vide infra), indicating that there is also some ring puckering and significant strain across this six-membered ring. The BF₄⁻ anions also play a large role in inhibiting π–π interactions, with significant C–H···F interactions between the dibenzosuberenyldiene framework and the adjacent BF₄⁻ anions, as demonstrated by the lack of ‘tumbling’ typically observed for the BF₄⁻ anions in the crystal lattice (Figure 2b). This is thought to be a major factor as to why this framework is more fluorescent in solid form than in solution form.

Figure 1. Dibenzosuberenyldiene-derived compounds as novel solid-state emissive organic dyes.

The first structural modification we investigated was extending the $N,N$-dialkyl chain length to form DEA-Sub and DBA-Sub (Scheme 1). As observed in our previous work, we believed that the length of the alkyl chain might play an important role in optical behaviours of these dyes. Indeed, while both DEA-Sub and DBA-Sub are also bright red crystals like DMA-Sub, they showed significantly stronger fluorescence intensities as crystalline powders compared to DMA-Sub, with $\Phi_f = 2.3\%$ and $\Phi_f = 10.3\%$ respectively (Table 1). Importantly, the crystalline $\Phi_f$ values for DEA-Sub and DBA-Sub were much greater than the thin-film values (Table 1), which clearly demonstrates that these compounds exhibit CIEE behavior, and that crystal packing effects play a significant role in mediating the emission properties of the framework.

Indeed, XRD analyses of DEA-Sub and DBA-Sub show that there is little difference in their single molecular configurations compared to DMA-Sub (Figure 2c), except slight changes in the bending angle of the quinoidal moieties (Figure 3). The structural similarity of the molecules and their colors is also supported by our TD-DFT calculations, which revealed that the alkyl chains provided minimal contribution to the HOMO and LUMO states or the excited states in all three $N,N$-dialkyl derivatives (see page S32 in the SI for more details). However, there are clear differences in the packing behavior of the molecules, with the longer alkyl chains better shielding the charge localized on the nitrogen centers from long range Coulombic interactions, and also increasing the intermolecular distances to further inhibit $\pi$-$\pi$ interactions. Intriguingly, the crystal structure of DBA-Sub showed additional short-range interactions between the terminal methyl groups from butyl chains of adjacent molecules, with an extremely short intermolecular distance of 1.998 Å (Figure 2d). There are also multiple intermolecular short-range interactions between the $n$Bu groups and the BF$_4^-$ anions. The structural rigidification afforded by these attractive interactions is probably the main cause of the significant increase in $\Phi_f$ of the crystalline form to 10.3% in DBA-Sub from 0.5% in DMA-Sub. Whilst DEA-Sub also showed an increase in fluorescence intensity compared to DMA-Sub, the alkyl chains were not long enough to participate in the additional rigidifying interactions and hence the increase in $\Phi_f$ to 2.3% in DEA-Sub could be attributed primarily to the alteration of packing arrangements alone.

![Figure 2](image.png)

Figure 2. (a) Single crystal XRD analysis of DMA-Sub showing selected bond lengths (in Ångstrom) and bend angle across the suberenylidene system; (b) unit cell of DMA-Sub with selected short-range interactions (defined as contacts shorter than sum of the van der Waals radii) shown in blue, and the shortest $N^\equiv BF_4^-$ distance shown in red; (c) Overlay comparison of the single crystal XRD structures of DMA-Sub (grey), DEA-Sub (blue) and DBA-Sub (pink); (d) selected distances in DBA-Sub, showing short-range interactions between the two butyl chains, and $N^\equiv BF_4^-$ distances shown in red.

We next aimed to explore the role of hindering the double-bond torsion and ring puckering motions of the dibenzosuberenyldene moiety, which we hypothesised would attenuate the nonradiative decay pathways and potentially facilitate increased emission intensity by inhibiting the accessibility of conical intersections. Accordingly,
DFDMA-Sub and DMeDMA-Sub were synthesized according to the general procedure (Scheme 1). Gratifyingly, we immediately observed significantly higher solid-state Φ_t values in crystalline powder form, with Φ_t = 16.9% in DFDMA-Sub and Φ_t = 24.6% in DMeDMA-Sub, supporting the rationale of our design. Notably, however, we also observed significant changes in colour for each of these compounds, with DFDMA-Sub being vivid orange and DMeDMA-Sub bright yellow (see Figure 3).

Single crystal XRD studies of DFDMA-Sub and DMeDMA-Sub revealed that the 3,5-substitutions visibly bend the quinoidal moiety out of plane, from 178° in DMA-Sub to 161° in DFDMA-Sub and 140° in DMeDMA-Sub (Figure 3). In fact, the decrease in bend angle almost perfectly correlates with a suppression of the low-energy S_0 to S_1 charge transfer-type transition prominent in the spectra of the non-substituted dyes (Table 1, also see Figure 3 and 4a), as well as a hypsochromic shift of the higher-energy absorption. These results suggest that the bend angle of the compounds is the direct cause of the change in colour of the compounds, presumably via the modulation of the energy differences between the various electronic states of the framework. Furthermore, the fluorescence quantum yield Φ_t also roughly correlates with the quinoidal bending angle across the dye family (Figure 3), which supports the hypothesis that motion around the C=C double bond, as well as ring-puckering motions in both ring systems of the framework, is a major factor in mediating the fluorescence intensity of the compounds.

![Comparison of quinoidal bending angles](image)

**Figure 3.** Comparison of quinoidal bending angles, Φ_t, thin-film UV-vis absorption (dashed line) and thin-film emission(solid-line) spectra of all dyes.

TD-DFT geometry optimisations of the S_1 states of DMA-Sub and DMeDMA-Sub as two representative examples (Figure 4, also see page S32 in the SI for details) show a lengthening of the C=C double bond linker between the dibenzosuberenyliydene and iminium moieties. At the same time, the puckering angles of the upper halves of the seven-membered rings become more acute while the lower halves become more planar. The quinoidal moieties are also calculated to become more planar in the S_1 state, although the 3,5-substituents seem to inhibit this process to some extent. While the quinoidal moiety of DMA-Sub is almost perfectly planar in the S_1 state, that of DMeDMA-Sub still exhibits a considerable bend across the iminium ring of 157° in the S_1 state (Figure 4b). These findings reveal the importance of the ‘flapping’ motions to the photophysical properties of the scaffold, and suggest that the framework might undergo excited-state planarization. Such an effect is interesting as this type of bent-to-planar motion is not commonly observed in typical excited-state planarization scaffolds, although it has recently been reported in a similar seven membered ring-containing system.

It should also be noted that the rigid unsaturated C=C bond ‘tether’ between the two benzo groups in the suberenyliydene scaffold also plays a major role in mediating the emission intensity of the framework. A series of variants that lack this ‘tether’ were synthesized and studied (compounds DMA-Trit, DMeDMA-Trit and DMA-Suberane, see pages S21-29 in the SI for further details). Intriguingly, none of these variants showed any fluorescence in the solution or solid state, highlighting the importance of restricting molecular motions and validating the significance of our structural design for this novel dye family (Scheme 1).
In summary, we have designed and synthesized a new family of solid-state luminogens based on the dibenzosubereryliden framework. A systematic investigation of their photophysical properties, as well as single-crystal XRD analysis, revealed several interesting structure-activity relationships that influence their solid-state fluorescence. These easily accessible synthetic compounds not only exhibit promising CIEE behaviour that can be potentially exploited in opto-electronic applications, but also represent a stimulating model scaffold for further theoretical studies of the effect of conical intersections and excited state planarization on photoluminescent properties.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge: Experimental procedures and methods, characterization data, NMR and UV-vis absorption and excitation-emission spectra, and Cartesian coordinates for DFT-optimized structures.

Accession Codes
CCDC 1910654, 1910657, 1910658, 1910659, 1910660, 1910661, 1910662 and 2177391 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions
RDC and TVN conceived the project with suggestions from TWS. DPP and RDC performed all the experimental synthesis, characterization and computational modelling. WK, BZ, DPP and WWHW investigated the photophysical properties of the compounds. DPP, RDC and MB jointly solved and refined the X-ray crystal structures of the compounds. DPP and TVN wrote the manuscript with input from all other authors. All authors have given approval to the final version of the manuscript.

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REFERENCES


[17] See the Supporting Information for further details.

[18] Theoretically, the expected product from acidification of 3 could bear the tricyclic benzene-tropylium-benzene aromatic system, as illustrated here. Presumably, the quinoidal iminium form, which occurs due to the charge transfer from this hypothetical triaryl carbocation to the aniline nitrogen centre, is more energetically favoured.


