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Molecular tuning of the crystallization-induced emission enhancement of diphenyl-dibenzofulvene luminogens

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The absorption and emission properties of various diphenyldibenzofulvene (DP-DBF) derivatives were investigated, and their crystallization-induced emission enhancement (CIEE) performances were found to show a clear correlation with the twist angle around the C=C bond of the DP-DBF structure.

Organic luminogens that show aggregation-induced emission (AIE) and crystallization-induced emission enhancement (CIEE) properties¹⁻⁴ have received considerable attention in recent years, owing to their appealing applications in fluorescent chemical sensors,⁵ biological probes,^{6–8} organic field-effect transistors (OFETs),⁹ and organic light emitting devices (OLEDs).^{10,11} Such luminogens are generally non-emissive in dilute solution, but exhibit moderate-to-high degrees of fluorescence in their aggregated states such as amorphous solid or crystalline forms. Many reported AIE and CIEE luminogens are designed to contain structurally hindered π -conjugated backbones, so that upon aggregation their fluorescence can be enhanced due to restricted intramolecular motion (RIM).¹²⁻¹⁴ Diphenyl-dibenzofulvene (DP-DBF) derivatives constitute an intriguing class of AIE and CIEE lumiogens, featuring relatively simple molecular structures and easy synthesis. Since the first study by Tang and co-workers in 2006,¹⁵ numerous DP-DBF-based luminogens have been reported in the literature, some of which show very interesting polymorphism-dependent emission, strong CIEE effects, and thermochromic and mechanochromic fluorescence properties.^{4,16–20}

It is noteworthy that the emission efficiencies of various literature reported **DP-DBF**s show a substantial degree of variations (see the summary in Figure 1). By analyzing these data, one would reasonably expect to find some correlations between the



Fig. 1 Literature reported DP-DBF derivatives and their fluorescence quantum yields (Φ) in the solution phase (soln), aggregated (aggr), amorphous solid (amor), thin film (film), and crystalline (cryst) states.

fluorescence properties of **DP-DBF**s with their molecular parameters (e.g., molecular geometry and substitution effects). Previously, Tang^{16,17} and Zhang¹⁸ attributed the fluorescence enhancement and emission wavelength shifts of **DP-DBF** luminogens **5** and **6** in the aggregated and crystalline states to the twist angle (θ_1) between the phenyl and vinyl units in the structure of **DP-DBF**. However, such rationalization was not strongly supported by theoretical analysis and experimental evidence. Shuai and co-workers in 2012 performed a molecular dynamics study to show that both the bond stretching in the **DBF** unit and the twisting around the C=C bond play essential roles in the elec-

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[†] Electronic Supplementary Information (ESI) available: Synthetic procedures, spectroscopic characterization, DFT calculations, and X-ray single crystallographic data for compounds **5a–c**, **8a–c**, and **9**. See DOI: 00.0000/00000000.

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Fig. 2 Potential energy surfaces of DP-DBF in the solution phase with a conical intersection (CI) seam.

tronic non-adiabatic transition of **DP-DBF**.²¹ Recently, it has been reported that restriction of the twisting around the C=C bond plays a crucial role in the AIE of various π -conjugated systems.²² In 2013, Li and Blancafort developed a conical intersection (CI) model to explain the AIE properties of **DP-DBF**.²³ According to their model, the first excited state (S1) of **DP-DBF** can be deactivated to the ground state (S_0) through an S_1/S_0 CI seam. As illustrated in Figure 2, DP-DBF in the solution phase can readily reach an energetically accessible region of the CI seam, where molecular geometries show a high twist angle ($\theta_2 > 50^\circ$) about the C=C bond of **DP-DBF**. This non-radiative decay pathway quenches the fluorescence of DP-DBF in the solution phase. In the solid state, however, the twist around the C=C bond is restricted and there is only a high-energy region of CI seam existing on the potential energy surface (PES), which in turn results in enhanced solidstate fluorescence. This modelling study thus motivated us to propose that the twist angle about the C=C bond of **DP-DBF** (θ_2) in the minimum-energy structure of the ground state is a key factor controlling its fluorescence behavior, especially the fluorescence quantum yield in the aggregated state. Upon aggregation, restricted intramolecular motion should significantly influence the internal conversion of the first excited state (S_1) to the CI seam on the PES. If θ_2 is relatively large, the amount of energy required for the S₁ state to reach the CI seam should be small and the fluorescence is thus well quenched. If θ_2 is small, the non-radiative decay pathway through the CI seam becomes difficult to access. As a result, the radiative decay acts as the dominant deactivation pathway (i.e., fluorescence enhancement).

Validation of the above hypothesis requires systematic examination of **DP-DBF**s with varied θ_2 values. To do so, we chose the approach of attaching functional groups to different positions of the two phenyl rings in **DP-DBF** to finely tune the twist angle θ_2 by steric effects. A series of **DP-DBF**s derivatives functionalized with methoxy (OMe) or benzyloxy (OBn) substituents was thus designed and prepared in this work. Figure 3 outlines our synthetic methods, in which 9-(dibromomethylene)-9*H*-fluorene (**10**) was first subjected to Suzuki-Miyaura cross coupling with methoxyphenylboronic acids **11a–c** to yield OMe-substituted **DP-DBF**s **5a–c** in good yields. Note that compounds **5a–c** are regioisomers with OMe groups substituted at the *ortho, meta,* and *para*-positions of the phenyl rings, respectively. Compounds **5a–c** were then treated with BBr₃ to afford demethylated products

With these substituted DP-DBFs in hand as models, we then carried out comparative analyses focusing on their structural, electronic, and fluorescence properties. Figure 4 shows the electronic absorption spectra of DP-DBFs 5a-c, 8a-c, and 9 measured in the solution phase. Ortho-OMe substituted 5a gives three distinct $\pi \rightarrow \pi^*$ absorption peaks at 316, 302, and 282 nm. In addition, there is broad absorption shoulder ranging from ca. 330 to 420 nm. Comparatively, the spectrum of ortho-tethered 9 shows $\pi \to \pi^*$ absorption peaks at similar wavelengths; however, its long-wavelength shoulder band at 329 nm appears to be much steeper and narrower. The different spectral patterns can be attributed to the different rotational modes between 5a and 9; the phenyl groups of 5a can rotate to form various conformers in the solution phase, but the tethered phenyl rings of 9 are inhibited from such rotational modes. The spectrum of meta-OMe substituted 5b shows two absorption peaks at 320 and 287 nm, along with a very broad absorption shoulder in the region of 330 to 440 nm. The edge of the long-wavelength absorption shoulder of 5b is significantly redshifted relative to that of 5a, suggesting a higher degree of π -conjugation in **5b**. For the spectrum of *para*-OMe substituted 5c, a broad absorption band at 369 nm can be seen and its absorption edge is the most redshifted among the DP-DBFs. The spectra of OBn-substituted DP-DBFs show similar features to those of their OMe-substituted analogues, indicating little contribution of the benzyl groups to the electronic absorption features. To determine the $S_0 \rightarrow S_1$ vertical transition energies for the **DP**-DBFs, the half-height wavelength of the lowest-energy maximum absorption band $(\lambda_{1/2}^{abs})$ in each absorption spectrum was considered. The experimental values show good agreement with timedependent density functional theory (TD-DFT) calculated S $_0 \rightarrow$ S_1 energies (see Table S-2, ESI). For both groups of OMe and OBn-substituted **DP-DBF**s, a redshift trend in $\lambda_{1/2}^{abs}$ can be clearly observed as: ortho < meta < para. It is worth mentioning that the solid-state UV-Vis absorption spectra of the DP-DBFs were also measured, showing very small variations in comparison with the solution-phase spectra (see Figure S-23, ESI).

The single crystals of **DP-DBFs 5a–c**, **8a–c**, and **9** were grown and their molecular structures were elucidated by single crystal Xray diffraction (XRD) analysis (Figure 5). In the crystal structure of *ortho*-OMe substituted **5a**, the two OMe groups take two different orientations (*cis* and *trans*) with respect to the fluorene plane. These two conformations exist in a ratio of ca. 1:1, and they show similarly large twist angles around the C=C bond. In contrast to **5a**, the crystal structure of *ortho*-OBn-substituted **8a** only shows the *trans* conformation with a small twist angle around the C=C bond. Both *meta*-substituted **5b** and **8b** adopt a *trans* conformation in terms of the relative orientation of the OMe or OBn substituents, while the benzyl groups in the structure of **8b** show Published on 08 December 2020. Downloaded by Auckland University of Technology on 12/15/2020 3:54:18 PM



Fig. 3 Synthesis of substituted DP-DBFs 5a-c, 8a-c, and 9. Inset: definition of dihedral angles θ_a and θ_b in the structure of DP-DBF.



Fig. 4 UV-Vis absorption spectra of (A) 5a-c and 9, and (B) 8a-c measured in chloroform.

a certain degree of rotational disorders. It is also worth mentioning that there was another crystalline form of 5b obtained during the crystallization process. Such crystals were formed in a relatively small quantity, and the molecular structure adopts a cis conformation (see Fig. S25A, ESI). Two distinct crystal structures of para-OMe-substituted 5c were previously reported by Zhang and co-workers.¹⁸ One is colorless with blue emission, and the other is yellow in color with green emission. In our experiment, we obtained the single crystal of **5c** that is similar to the first one. The molecular structure of para-OBn-substituted 8c shows a similar **DP-DBF** conformation to that of **5c**, but the twist angle about the C=C bond appears to be smaller. In the crystal structure of 9, the two oxygen groups are in a *cis* conformation and the C=Cbond shows a moderate degree of twisting. Overall, the twist angles around the C=C bonds in the crystal structures of 5a-c, 8a-c, and 9 show a wide range of variation as expected. To quantitatively assess the degree of twisting, the sum of two dihedral angles (θ_a and θ_b , see the inset of Figure 3 for definition) about the C=C bond were measured and compiled in Table 1.

All the **DP-DBF** derivatives **5a–c**, **8a–c**, and **9** show insignificant fluorescence in the solution phase; however, their crystals exhibit luminescence with various intensities and colors under UV-light irradiation (see Figure 5). *Para*-substituted **DP-DBF**s **5c** and **8c** give strong bright blue emission, while *ortho*-substituted **DP-DBF**s **5a** and **8a** exhibit moderate blue emission in the crystalline state.

Fig. 5 Selected molecular structures of **5a-c**, **8a-c**, **and 9** determined from their single crystals, and photographic images of the crystals of these compounds under UV-light irradiation.

Meta-substituted DP-DBFs 5b and 8b afford moderate-to-weak luminescence in yellowish green color, which is very different from the other DP-DBFs. Solid-state fluorescence spectra of the DP-DBF crystals were measured (Figure 6), and detailed emission properties are provided in Table 1. All the DP-DBF crystals give a relatively broad emission band without distinctive vibronic features. Both the OMe and OBn-substituted series show a trend of increasing maximum emission wavelength (λ_{em}) as follows: para < ortho < meta. The trend is different from the shift of λ_{abs} observed in the UV-Vis analysis. The much longer emission wavelengths of meta-substituted 5b and 8b relative to the other **DP-DBF**s are consistent with their yellowish green-colored luminescence in the solid state. Stokes shifts (Δv) were calculated according to the difference between λ_{abs} and λ_{em} in the solid state (see Table 1). It is noteworthy that the Stokes shifts of parasubstituted 5c and 8c are considerably smaller than those of ortho and meta-substituted DP-DBFs, suggesting that para-substituted DP-DBFs undergo a much smaller degree of structural variations during the $S_0 \rightarrow S_1$ excitation in the crystallin state. The strong resonance effects arising from para-substitution are therefore be-



Fig. 6 Fluorescence spectra of (A) **5a**-c and **9**, and (B) **8a**-c measured in the crystalline state. (C) Correlation between the twist angle $([\theta_a + \theta_b])$ around the C=C bond of **DP-DBF** and fluorescence quantum yield (Φ_f) in the crystalline state.

lieved to result in significantly rigid π -conjugated framework of **DP-DBF**.

Figure 6C illustrates the correlations of the fluorescence quantum yields (Φ_f) of **DP-DBF** crystals with the degree of twisting about the C=C bond ($[\theta_a + \theta_b]$). In line with our hypothesis, the experimental results show clear correlations between the twisting of C=C bond and the fluorescence efficiency in the crystalline state. The Φ_f values of **DP-DBF** crystals show an increasing trend with decreasing twist angle about the C=C bond. In particular, meta and ortho-substituted DP-DBFs give an excellent linear relationship between Φ_f and $[\theta_a + \theta_b]$. This result proves that restricted torsional vibration about the C=C bond is the origin of the AIE and CIEE properties of DP-DBF. Given that ortho-tethered 9 also clearly follows the same linear correlation, rotational modes of the phenyl groups can be ruled out as a significant factor to the fluorescence efficiency in the solid state. It is also remarkable to note that the literature reported **DP**-DBF 7, the structure of which contains an ethylene bridge linking the ortho positions of the two phenyl rings, also follows the same linear trend.²⁰ In contrast to meta and ortho-substituted DP-DBFs, para-substituted 5c and 8c do not follow the linear trend of fluorescence quantum yields. Actually, both compounds exhibit very high Φ_f values in the crystalline state, and these values are comparable with those of the para-substituted DP-DBFs reported in the literature.^{17,18} Their high CIEE performances can be attributed to enhanced π -delocalization arising from *para*-alkoxy substitution. Finally, it is worth noting that 5a and 9 are not CIEE luminogens, since their powders give greater Φ_f values than their crystals (see Table S-1, ESI).

In conclusion, with the access to a range of substituted **DP**-**DBF** single crystals, we have unambiguously confirmed that the twist angle around the C=C bond is a key molecular factor controlling their solid-state fluorescence properties. For non-*para*-substituted **DP-DBF**s, their fluorescence quantum yields in the crystalline state can be predicted by a linear correlation with the twist angle. *Para*-substituted **DP-DBF**s, on the other hand, show very strong CIEE performances but do not follow the linear corre-

 Table 1
 Summary of twist angles and photophysical properties for DP-DBF derivatives in the solid state.

entry	$[\theta_a + \theta_b]$ (°)	λ_{abs} (nm)	λ_{em} (nm)	Φ_f (%)	$\Delta v \text{ (cm}^{-1}\text{)}$
5a	40.2	319	473	1.44	10206
5b	32.6	333	497	4.22	10306
5c	12.4	376	468	89.81	4904
8a	3.2	319	454	27.89	10117
8b	31.6	332	515	2.95	10665
8c	5.4	379	449	86.01	4113
9	16.2	319	457	17.63	9561

lation. Our structure-property studies not only provide in-depth understanding of the physical origin of the AIE and CIEE performances of **DP-DBF**-based luminogens, but disclose an effective molecular approach to rationally design and finely tune the fluorescence properties of various related AIE and CIEE luminogens.

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Conflicts of interest

There are no conflicts to declare.

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The CIEE performances of diphenyl-dibenzofulvene luminogens are controlled by the twist angle of the C=C double bond.