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## COMMUNICATION

## Aggregation induced emission (AIE) of trifluoromethyl substituted distyrylbenzenes†

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The AIE properties of two trifluoromethyl substituted distyrylbenzene model compounds were compared. The fluorescence quantum efficiency of these molecules can be modulated by tuning their subtle solid-state intermolecular interactions.

Fluorescent molecular materials have been intensively studied as active media for organic light-emitting diodes (OLEDs), lasers, and sensor applications.<sup>1,2</sup> Many of the fluorescent molecules have efficient emission in solution, however, the emission tends to vanish in solid-state due to aggregationcaused quenching (ACQ). Although ACQ is quite detrimental to material performance in devices,<sup>3</sup> recent reports from Tang et al. and Park et al., showed that several molecular systems can display strong fluorescence upon concentration or solidification, while their dilute solutions show weak emission.<sup>4-6</sup> The aggregation-induced emission (AIE) phenomenon is generally ascribed to changes of molecular geometry in solid-state, which result in suppressed non-radiative relaxation pathways of excited species to enhance fluorescence efficiency. More recently, the result from Dinca et al. suggested that spatial isolation of the rigid  $\pi$ -conjugation framework of a molecule with bulky substituents is effective in enhancing molecular fluorescence.7

In this communication, we report the design, synthesis, crystal structure, and optical properties of a novel AIE molecule – a methoxy-substituted trifluoromethyldistyrylbenzene (MeO-CF<sub>3</sub>DSB) (Fig. 1a). Especially, the emphasis is placed on the role of intermolecular interactions in enhancing solid-state fluorescence. For comparison, the unsubstituted trifluoromethyl-distyrylbenzene (CF<sub>3</sub>DSB) (Fig. 1b) was also synthesized. The CF<sub>3</sub>DSB was first reported by Holmes *et al.*<sup>8</sup> which contains a bulky trifluoromethyl (CF<sub>3</sub>) group on its vinylenic linkage.

The target compound, **MeO-CF<sub>3</sub>DSB**, was synthesized in 79% yield using the Wittig–Horner reaction to condense 2,5-bis(diethoxyphosphorylmethylene)-1,4-dimethoxybenzene and 4'-methoxy-2,2,2-trifluoroacetophenone (see the electronic



Fig. 1 Chemical structures of  $MeO-CF_3DSB$  (a) and  $CF_3DSB$  (b), and single crystal X-ray structures of  $MeO-CF_3DSB$  (c) and  $CF_3DSB$  (d).

supplementary information, ESI, for the detailed synthesis and characterization<sup>†</sup>).

CF<sub>3</sub> is known to be a strong electron-withdrawing group and is able to modulate material properties.<sup>9</sup> Unlike the linear cyano group (CN),<sup>10</sup> the CF<sub>3</sub> group imposes a significant spatial constraint on the molecular skeleton due to its steric hindrance. To our surprise, the study of the single crystal structure of CF<sub>3</sub>DSB reveals that CF<sub>3</sub> substituents impede the molecule from adopting the expected *anti*-conformation. Moreover, severe torsion between lateral phenyl groups and the phenylenevinylene core is observed. As a result, the effective  $\pi$  conjugation is interrupted by the *syn*-defect.<sup>11</sup>

The highly electronegative nature (EN = 4.0 according to the Pauling scale) of the F atoms on the CF<sub>3</sub> group also tends to induce hydrogen bonding with surrounding hydrogen atoms. As a result, it not only significantly affects the molecular geometry, but also creates a pronounced influence on the molecular packing modes in solid-state.

The CF<sub>3</sub> group also inductively affects the peripheral phenyl rings even though it has a considerable twisted angle to the  $\pi$  electron core. This creates subtle changes on packing of **MeO-CF<sub>3</sub>DSB**, which has electron-donating methoxy groups at the *para* positions of its peripheral phenyl rings. The methoxy groups add additional resonance structures at the peripheral phenyl rings. Two additional methoxy groups were also introduced onto the central phenyl group in order to increase the resonance conjugation path of  $\pi$  electrons along the phenylenevinylene core.

Fig. 2 shows the <sup>1</sup>H NMR (A) and <sup>19</sup>F NMR (B) spectra of **MeO-CF<sub>3</sub>DSB** and **CF<sub>3</sub>DSB**. The analysis of the <sup>1</sup>H NMR spectra reveals that both molecules are centrosymmetric, and

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**Fig. 2** <sup>1</sup>H NMR (A) and <sup>19</sup>F NMR (B) spectra of **MeO-CF<sub>3</sub>DSB** (top) and **CF<sub>3</sub>DSB** (bottom) in chloroform- $d_3$ . The spectral peaks are not on the same vertical scales.

the protons on the vinylenic segments appear to be a clear doublet with a coupling constant of 1.5 Hz. Consequently, the <sup>19</sup>F NMR spectra of MeO-CF<sub>3</sub>DSB and CF<sub>3</sub>DSB show a distinct doublet peak with the similar corresponding coupling constant. The coupling constant indicates the existence of intramolecular C-F···H-C hydrogen bonding on the vinylenic segments of the molecule.<sup>12</sup> Moreover, the clear difference of chemical shift between the aromatic proton b ( $\delta$ , 6.90 ppm) and c ( $\delta$ , 7.21 ppm) on the lateral phenyl ring of MeO-CF<sub>3</sub>DSB, compared to those of CF<sub>3</sub>DSB (proton b', 7.23 ppm; proton c', 7.34 ppm), strongly suggests the anisotropic electron distribution within the *para*-substituted peripheral phenyl rings of MeO-CF<sub>3</sub>DSB with the substituent of methoxy groups. The natural bond orbital (NBO) study clearly corroborates that the substitution of methoxy groups poses a considerable influence on the  $\pi$  electron delocalization in both the phenylenevinylene core and the peripheral phenyl moieties of MeO-CF<sub>3</sub>DSB as shown in Fig. S2.<sup>+13</sup>

Both MeO-CF<sub>3</sub>DSB and CF<sub>3</sub>DSB molecules are soluble in common organic solvents such as THF, chloroform, and acetone, but insoluble in water. The absorption spectra of MeO-CF<sub>3</sub>DSB and CF<sub>3</sub>DSB in dilute THF solution are shown in Fig. 3, with  $\lambda_{max}$  at 370 nm and 297 nm, respectively, corresponding to the main electronic transition of the phenylenevinylene core (Fig. S1†).<sup>14</sup> It is worthy to note that MeO-CF<sub>3</sub>DSB and CF<sub>3</sub>DSB show significant hypsochromic shift of the lowest energy electronic transitions compared to the non-CF<sub>3</sub> substituted DSB analogues.<sup>15</sup>

The effective conjugation is confined between the  $CF_3$  groups on the phenylenevinylene core owing to highly twisted terminal phenyl groups. By comparing with **CF\_3DSB**, the



**Fig. 3** Absorption (in THF solution) and emission (in solid powders) spectra of **MeO-CF<sub>3</sub>DSB** (red) and **CF<sub>3</sub>DSB** (black). Inserted photographs of **MeO-CF<sub>3</sub>DSB** in powder form (a), 10  $\mu$ M THF solution (b), 10  $\mu$ M THF-water mixture ( $f_w = 90\%$ ) (c) taken under UV illumination with the excitation wavelength of 365 nm.

absorption spectrum of MeO-CF<sub>3</sub>DSB shows a noticeable shoulder at 274 nm, which is corresponding to the localized transitions of the terminal ends of the molecule. Both MeO-CF<sub>3</sub>DSB and CF<sub>3</sub>DSB (see inset of Fig. 3) show blue fluorescence in their solid form, but only show very weak fluorescence in dilute THF solution. The fluorescence quantum efficiencies  $(\Phi_{\rm fl})$  of MeO-CF<sub>3</sub>DSB and CF<sub>3</sub>DSB powders are 56.3% and 11.2%, respectively ( $\Phi_{\rm ff}$  in solid-state is obtained in a calibrated integrating sphere, using 9,10-diphenylanthracene as the standard), which clearly indicates the AIE characteristics of MeO-CF3DSB and CF<sub>3</sub>DSB. However, there is a pronounced  $\Phi_{ff}$  difference between CF3DSB and MeO-CF3DSB. In addition, the nonemissive dilute solutions of MeO-CF3DSB and CF3DSB  $(10 \,\mu\text{M in THF})$  become strongly fluorescent when a significant amount of water was added to induce dispersed aggregates as is commonly used to study AIE molecules; (See inset of Fig. 3 and Fig.  $S3^{\dagger}$ ).<sup>6</sup>

To investigate the effect of spatial arrangement of MeO-CF<sub>3</sub>DSB on its fluorescence in solid-state, single crystals of MeO-CF<sub>3</sub>DSB and CF<sub>3</sub>DSB were grown by slow evaporation of chloroform solvent under ambient condition, and the X-ray diffraction results of single crystals were refined and analyzed. **MeO-CF<sub>3</sub>DSB** forms monoclinic crystals having the  $P2_1/c$ space group and there are two molecules present in a unit cell, as shown in Fig. 1c. A full crystal analysis of collected data is provided in Table S1 in the ESI,† where the crystallographic information of CF<sub>3</sub>DSB (Fig. 1d) is also provided for comparison. As shown in Fig. 1c, the X-ray crystal structure of MeO-CF<sub>3</sub>DSB unequivocally confirms that the molecule is in syn-conformation and possesses a high symmetry with an inversion center, which is consistent with the NMR results. An important feature of the MeO-CF<sub>3</sub>DSB crystal, akin to CF<sub>3</sub>DSB, is that the through-space distance of the intramolecular F...H bonds (C12-F1···H4-C4: 2.26 Å) are much shorter than the sum of the van der Waals radii for H and F (H = 1.20 Å, F = 1.47 Å). Even though it is known in the literature that the interactions between donor(D)-H...acceptor(A) angle below 120 °C are less significant,<sup>16</sup> it can be regarded as a beneficial contact on the vinylenic segments for the molecular svn-conformation.

In addition, the severe torsion between the lateral phenyl group and the central phenylenevinylene framework is a



**Fig. 4** Crystal structure and short contact in **MeO-CF<sub>3</sub>DSB** single crystal; (a) unit cell packing diagram viewed down the *b* axis; (b) packing of terminal phenyl rings viewed down the *b* axis.

 Table 1
 Physical properties of MeO-CF<sub>3</sub>DSB and CF<sub>3</sub>DSB

Dye	$\lambda_{\rm ab} \ ({\rm nm})^a$		$\lambda_{\rm em} ({\rm nm})^b$			
	Solution <sup>c</sup>	Aggregate <sup>d</sup>	Solution $(\Phi_{\rm fl})^c$	Solid $(\Phi_{\rm fl})^e$	$T_{\rm m}^{f}(^{\circ}{\rm C})$	$\Delta H_{\text{fusion}}^{f}$ (kcal mol <sup>-1</sup> )
MeO-CF <sub>3</sub> DSB	370 (275)	369 (275)	487 (<0.010)	490 (0.563)	183	11.24
CF <sub>3</sub> DSB	297	297	409 (<0.010)	409 (0.112)	149	6./1

<sup>*a*</sup> Absorption maximu,  $\pm 1$  nm. <sup>*b*</sup> Emission maximum,  $\pm 1$  nm; emission spectrum taken at a  $\lambda_{ex}$  of 380 nm for **MeO-CF<sub>3</sub>DSB** and 310 nm for **CF<sub>3</sub>DSB**. <sup>*c*</sup> In THF (10  $\mu$ M). <sup>*d*</sup> In a THF/water mixture (10:90 by volume). <sup>*e*</sup> In solid powder form,  $\pm 0.002$ . <sup>*f*</sup> Analytic results of differential scanning calorimetry (DSC) at a heating rate of 10 °C min<sup>-1</sup> on thermo-equilibrated samples:  $T_{m}$ , melting temperature,  $\pm 1$  °C;  $\Delta H_{fusion}$  energetics for melting transition,  $\pm 0.1$  kcal mol<sup>-1</sup>.

distinct feature. Consistent with the large torsion angle for  $CF_3DSB$  (84.3°), the torsion angle for  $MeO-CF_3DSB$  is 78.1°. These large dihedral angles hamper the effective charge transfer between the lateral phenyl group and the phenylenevinylene core. As a result, their effective conjugation lengths are much shorter than all *anti*-linkage in un-substituted DSB analogues. Moreover, the methoxy substituents on MeO-CF<sub>3</sub>DSB pose a significant influence on molecular packing in solid-state. As shown in Fig. 4a and Fig. S4,† an interlayer network was formed along the *b* axis. In addition to the close contacts along the columns, a network of close contacts within each column is also observed.

**MeO-CF<sub>3</sub>DSB** molecules in a crystal form two slipped columnar stacks with different heights along the *b* axis. This arrangement results in a network of short intermolecular contact (C13–H13A···· F2–C12 [at (1-x, -1/2 + y, -1/2 - z)], 2.66 Å) between the lateral methoxy substituted phenyl rings of adjacent molecules.

The methoxy substituents on the lateral phenyl rings of **MeO-CF<sub>3</sub>DSB** induce rigid and extensively networked contacts with eight neighboring molecules compared to the relatively loose intermolecular contact for **CF<sub>3</sub>DSB** molecules in crystal (Fig. S5†). The interactions extend throughout the lattice and bring each molecule into contact with two other molecules along *a* and *b* axes. These networked contacts not only reinforce the co-planarity of conjugating path at the core of **MeO-CF<sub>3</sub>DSB**, but also significantly reduce the non-radiative relaxation pathways to improve the fluorescence efficiency. On the other hand, the very low luminescence observed for both molecules in solutions can be explained by the nonradiative decay of the excited species through various molecular vibrations and rotations pathways of solvated molecules.

The reinforced intermolecular interactions resulting from the incorporation of the methoxy groups on MeO-CF<sub>3</sub>DSB were verified by investigating the thermal properties of these molecules. There is a significant difference in melting points between MeO-CF<sub>3</sub>DSB and CF<sub>3</sub>DSB (183 °C and 149 °C), which suggests the stronger packing of MeO-CF<sub>3</sub>DSB. In addition, MeO-CF<sub>3</sub>DSB shows 167% higher molecular lattice dissociation energy,  $\Delta H_{\text{fusion}}$ , than that of CF<sub>3</sub>DSB (11.24 kcal mol<sup>-1</sup> vs. 6.71 kcal mol<sup>-1</sup>) as determined by differential scanning calorimetry (DSC) and shown in Fig. S6† and Table 1.

In conclusion, we have demonstrated that a highly fluorescent AIE molecule can be made with high quantum yield (56.3%) and

its emission efficiency can be modulated by fine-tuning the subtle intermolecular interactions in solid-state. This thorough investigation provides useful insights for rational design of highly efficient AIE dyes for optoelectronics and sensing applications.

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