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Integration of aggregation-induced emission  
and delayed fluorescence into electronic  
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**A series of luminogens comprised electron donors and acceptors are found to possess two types of interesting photophysical processes of aggregation-induced emission (AIE) and delayed fluorescence. According to theory calculation, restriction of intramolecular motions accounts for their AIE characteristics. Moreover, a separated distribution of the HOMOs and the LUMOs of these luminogens leads to small  $\Delta E_{ST}$  values and therefore delayed fluorescence.**

Organic materials displaying strong light emissions have attracted intensive scientific interest in previous decades, owing to their great potential applications in organic light-emitting diodes (OLEDs), bio-imaging probes, *etc.*<sup>1,2</sup> According to the spin statistics rule, the percentages of triplet and singlet excitons are 75% and 25%, respectively, under electrical excitation. Therefore, in fluorescent organic materials-based OLEDs, only 25% of excitons can be harvested for light emission. This means that the maximum external quantum efficiency (EQE) of conventional fluorescent OLEDs reaches merely 5% in principle, supposing the light-out-coupling efficiency of the devices is about 20%. As we all know, phosphorescent materials, such as typical heavy metal complexes<sup>3</sup> and just emerging pure organic molecules with room temperature phosphorescence (RTP),<sup>4</sup> can utilize both triplet and singlet excitons. Delayed fluorescence is another important alternative approach to utilizing excited triplet energy for light emission.<sup>5</sup> Recently, the internal quantum efficiency (IQE) of an OLED employing molecules with delayed fluorescence has approached 100%.<sup>6</sup> However, common luminogens with delayed fluorescence

often encounter severe concentration or aggregation-caused quenching (ACQ)<sup>7</sup> because of the strong intermolecular interactions, which limits their high-tech applications.

Aggregation-induced emission (AIE) luminogens, which are almost nonfluorescent in solutions, but highly emissive as aggregates are formed, are promising luminescent materials free of the ACQ problem.<sup>8</sup> Restriction of intramolecular motions (RIM), including rotation and vibration, is now validated as the main cause of the AIE effects.<sup>8,9</sup> With the deciphering of the AIE mechanism, a new strategy to create high-performance solid-state light emitters is proposed. Simply by grafting AIE units to the ACQ chromophores, new AIE luminogens with efficient fluorescence in the aggregated state can be attained. In view of this, the design of luminogens with both delayed fluorescence and AIE characteristics is a useful way to employ efficient triplet excitons in solids without inducing the ACQ problem. These luminogens may boost the development of nondoped OLEDs.

Luminogens with delayed fluorescence generally have clearly separated HOMO and LUMO distributions, which can give rise to a small energy gap ( $\Delta E_{ST}$ ) between the triplet ( $T_1$ ) and singlet ( $S_1$ ) states, and thus enhance the reverse intersystem crossing process (RISC).<sup>5,7</sup> Designing an electron donor–acceptor (D–A) system is a possible way to realize effective HOMO–LUMO separation<sup>5b</sup> as well as high solid-state fluorescence.<sup>10</sup> Therefore, most molecules featuring delayed fluorescence contain electron donors, such as carbazole and diphenylamine, and acceptors such as triazine and oxadiazole.<sup>11</sup>

In this study, we designed a series of luminogens with a D–A framework. The electron-sufficient phenoxazine (PXZ) and phenothiazine (PTZ) are adopted as the donors, and their nonplanar conformations are anticipated to suppress strong intermolecular  $\pi$ – $\pi$  interactions and decrease emission quenching as well.<sup>7b,c,8</sup> The electron-deficient diphenylsulphone (DPS) and dibenzothiophene-S,S-dioxide (DBTO) are used as the acceptors. The chemical structures of these D–A luminogens are shown in Fig. 1. Details of the synthetic routes (Scheme S1, ESI†), procedures and characterization data are given in the ESI.† In general, DPS-PXZ and DPS-PTZ were obtained by the NaH mediated coupling

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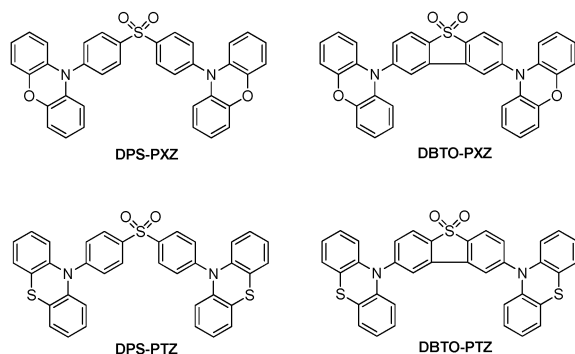


Fig. 1 Molecular structures of DPS-PXZ, DBTO-PXZ, DPS-PTZ and DBTO-PTZ.

reaction of bis(*p*-fluorophenyl)sulfone with PXZ or PTZ. DBTO-PXZ and DBTO-PTZ were synthesized using Buchwald-Hartwig aminations of 2,8-dibromo-dibenzothiozole 5,5-dioxide with PXZ or PTZ in the presence of Pd(OAc)<sub>2</sub>/P(*t*-Bu)<sub>3</sub>/*t*-BuONa. These compounds were fully characterized by NMR and mass spectroscopy with satisfactory results. Single crystals of DBTO-PTZ were grown from dichloromethane/methanol and analyzed by X-ray single-crystal diffraction (Fig. S1, ESI<sup>†</sup>).

Fig. 2A and B show the absorption spectra and the PL spectra of these molecules in dilute THF solutions and in the solid state, respectively. The photophysical data are summarized in Table 1. Compared with DPS-PTZ, DPS-PXZ shows a long wavelength absorption peak at 385 nm, which could have resulted from the intramolecular charge transfer (ICT) from PXZ to DPS. A similar ICT state can also be observed at 405 nm for DBTO-PXZ. The apparent ICT absorption peaks of DPS-PXZ and DBTO-PXZ could

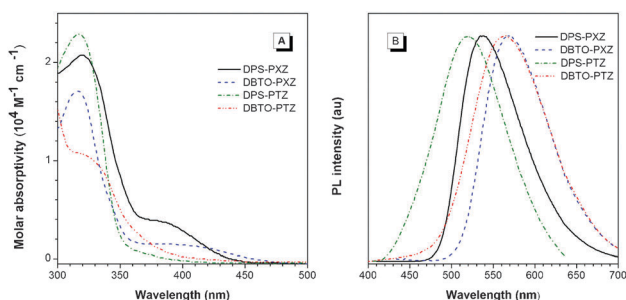


Fig. 2 (A) Absorption spectra in THF solutions and (B) PL spectra in solid state of DPS-PXZ, DBTO-PXZ, DPS-PTZ and DBTO-PTZ.

be attributed to the stronger electron-donating ability of PXZ than PTZ. The emission maximum of DPS-PXZ is 535 nm, which is red-shifted by 16 nm relative to that of DPS-PTZ (519 nm). A small red-shift is also observed for DBTO-PXZ (569 nm) compared to that of DBTO-PTZ (563 nm). These emission behaviors once again suggest that PXZ is a better electron-donating unit than PTZ. On the other hand, the DBTO-containing luminogens show much redder absorption and emission than DPS-containing ones, owing to the enhanced conjugation of DBTO compared to DPS.

The fluorescence quantum yields ( $\Phi_F$ ) of DPS-PXZ, DBTO-PXZ, DPS-PTZ and DBTO-PTZ in dilute THF solutions are 3.1%, 1.0%, 1.6% and 1.2%, respectively (Table 1), revealing that they emit weakly in the solution state. The  $\Phi_F$  values of DPS-PXZ, DBTO-PXZ, DPS-PTZ and DBTO-PTZ in solid state are increased to 16.3%, 6.7%, 20.3% and 10.7%, indicating that they are exactly AIE-active. To further confirm their AIE characteristics, their PL changes in THF/water mixtures were measured. Fig. 3A illustrates the PL spectra of DPX-PXZ in THF/water mixtures as an example. The emission intensity of DPX-PXZ is enhanced when a large amount of water is added to its pure THF solution. Similar emission behaviors in the mixture can also be observed from the PL spectra of other luminogens (Fig. 3). Because these luminogens are insoluble in water, they must have aggregated in the mixtures with high water fractions. In the aggregated state, intramolecular motions are restricted, and thus the nonradiative decay channel of the excited state is blocked, resulting in enhanced light emission.<sup>8,9</sup>

Fig. 4 presents the single-crystal structure and molecular packing of DBTO-PTZ. No clear intermolecular  $\pi$ - $\pi$  interactions are observed because the nonplanar structure of PTZ hinders the close stacking of the phenyl moieties. PXZ has a similar structure to PTZ. Therefore, we can imagine that no intermolecular  $\pi$ - $\pi$  interactions occur in DPS-PXZ and DBTO-PXZ, although the single crystals of DPS-PXZ and DBTO-PXZ are not obtained. The dihedral angle between the donor (DPTO) and acceptor (PTZ) planes is estimated to be 82.4°. Such a large dihedral angle can not only efficiently suppress intermolecular  $\pi$ - $\pi$  interactions, but also reduce the overlap of HOMO and LUMO and lead to orbital separation.<sup>5</sup>

The transient fluorescence decay curves of these luminogens in the solid state were measured in ambient conditions (Fig. 5). DPS-PXZ, DBTO-PXZ, DPS-PTZ and DBTO-PTZ exhibit apparent delayed decay components in the excited state with lifetimes of

Table 1 Photophysical properties of DPS-PXZ, DBTO-PXZ, DPS-PTZ and DBTO-PTZ

Compound	$\lambda_{\text{abs}}^a$ (nm)	$\lambda_{\text{em}}^b$ (nm)	$\Phi_F^c$ (%)		$\tau_d^d$ ( $\mu\text{s}$ )	$R^e$ (%)	HOMO/LUMO <sup>f</sup> (eV)	$E_S/E_T^f$ (eV)	$\Delta E_{\text{ST}}$ (eV)
			THF	Powder					
DPS-PXZ	320, 385	535	3.1	16.3	0.8	19.6	-6.31/-1.01	3.52/3.42	0.10
DBTO-PXZ	316, 405	569	1.0	6.7	0.7	14.3	-6.37/-1.39	3.35/3.29	0.06
DPS-PTZ	318	519	1.6	20.3	52.3	38.6	-6.53/-1.00	3.78/3.52	0.26
DBTO-PTZ	330	563	1.2	10.7	2.3	22.7	-6.59/-1.39	3.64/3.51	0.13

<sup>a</sup> In THF solution ( $10^{-5}$  M). <sup>b</sup> In solid state. <sup>c</sup> Fluorescence quantum yield determined by a calibrated integrating sphere. <sup>d</sup> PL lifetimes of delayed ( $\tau_d$ ) decay components for the compounds measured in powder under ambient conditions. <sup>e</sup> The ratio of delayed components. <sup>f</sup> Calculated by TD-DFT at M062X/6-31G(d,p).

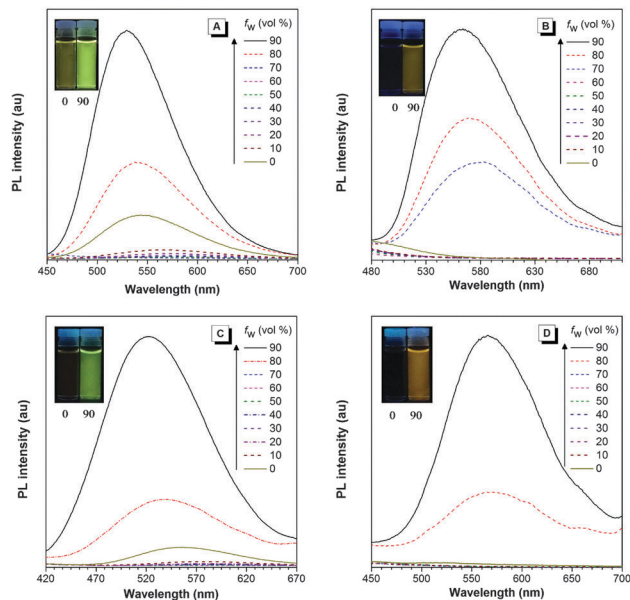


Fig. 3 Photoluminescence (PL) spectra of (A) DPS-PXZ, (B) DBTO-PXZ, (C) DPS-PTZ and (D) DBTO-PTZ in THF/water mixtures with different water fractions ( $f_w$ ). Inset: images of compounds in THF/water mixtures ( $f_w = 0\%$  and  $90\%$ ), taken under the illumination of a UV lamp (365 nm).

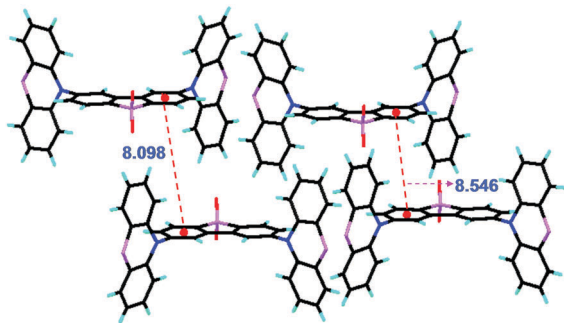


Fig. 4 Single-crystal structure and molecular packing of DBTO-PTZ (CCDC 1432393) with indicated distances (Å) between aromatic rings.

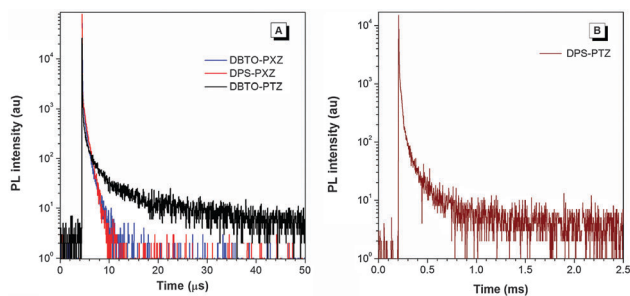


Fig. 5 Photoluminescence (PL) decay spectra of (A) DBTO-PXZ, DPS-PXZ, DBTO-PTZ and (B) DPS-PTZ in powder.

0.8, 0.7, 52.3 and 2.3  $\mu\text{s}$ , respectively (Table 1). Such long lifetimes demonstrate the delayed fluorescence of these D–A luminogens, which is in good agreement with the reported results.<sup>11a,b</sup> The ratios of delayed components (R) of DPS-PXZ,

DBTO-PXZ, DPS-PTZ and DBTO-PTZ are calculated to be 19.6%, 14.3%, 38.6% and 22.7%, respectively.

To have a better understanding of the structure–property relationship of these luminogens, time-dependent density functional theory (TD-DFT) calculations for the excited state and DFT calculations for the ground state ( $S_0$ ) were carried out at the M062X/6-31G(d,p) level (Fig. S2, ESI<sup>†</sup>). The dihedral angle between the donor DBTO and acceptor PTZ in the optimized structure of DBTO-PTZ is calculated to be  $74.9^\circ$ , which matches well with the measured value ( $82.4^\circ$ ) from its crystal structure. The dihedral angles of  $S_0$  and  $S_1$  for other luminogens are also listed in Table S1 and S2 (ESI<sup>†</sup>) and large changes in dihedral angles between the donors and acceptors can be found in the transition from  $S_0$  to  $S_1$ . In the PTZ and PXZ moieties, the dihedral angles formed by the two phenyl planes experience great changes from  $S_0$  to  $S_1$ . This reveals that vibrational motions exist in PTZ or PXZ moieties, which will cause the nonradiative decay of the excited state. The vibration of PXZ and PTZ moieties as well as the rotation of phenyl rings in DPS can be restricted when these luminogens are situated in the condensed phase and therefore the nonradiative decay is blocked, which results in the AIE effect.

DFT calculations were further performed to predict the  $\Delta E_{ST}$  of these luminogens. The  $\Delta E_{ST}$  values of DBTO-PXZ, DPS-PXZ, DBTO-PTZ and DPS-PTZ are calculated to be 0.06, 0.10, 0.13 and 0.26 eV (Table 1), respectively. These  $\Delta E_{ST}$  values are relatively small, indicating that the RISC process can occur in these luminogens.<sup>5–7,11</sup> As shown in Fig. 6, the HOMO and LUMO distributions of these luminogens are clearly separated, owing to the large dihedral angles between the donor and acceptor planes. The HOMOs are mainly localized on the PXZ and PTZ moieties, whereas the LUMOs are mostly localized on the DBTO and DPS moieties. These distributions are consistent with the principle that the  $\Delta E_{ST}$  value of a molecule decreases as the overlap of the HOMO and LUMO wavefunction diminishes.<sup>12</sup> According to our observations, the lifetime of the delayed fluorescence shortens as the  $\Delta E_{ST}$  value decreases, which is attributed to a narrower singlet–triplet energy gap being more beneficial for upconversion from  $T_1$  state to  $S_1$  state.<sup>13</sup> A significantly larger  $\Delta E_{ST}$  value (within the range for which RISC occurs) makes the luminogens situate in the  $T_1$  state for a longer time, and the fluorescence is thus more apparently delayed.

In conclusion, a series of D–A luminogens, DPS-PXZ, DBTO-PXZ, DPS-PTZ and DBTO-PTZ, are facilely synthesized and characterized. Owing to the strong electron-donating ability of the PXZ moiety, DPS-PXZ and DBTO-PXZ exhibit clear absorption peaks associated with the ICT effect. These luminogens show AIE characteristics as a result of suppressed intramolecular vibrations and rotations. The twisted conformations of the luminogens are also helpful to inhibit strong intermolecular  $\pi$ – $\pi$  interactions and thus reduce nonradiative decay in the aggregated state. A large twisted angle between the donor and acceptor leads to efficient separation of HOMOs and LUMOs, which gives rise to small  $\Delta E_{ST}$  values and thus delayed fluorescence. These luminogens possessing the merits of AIE and

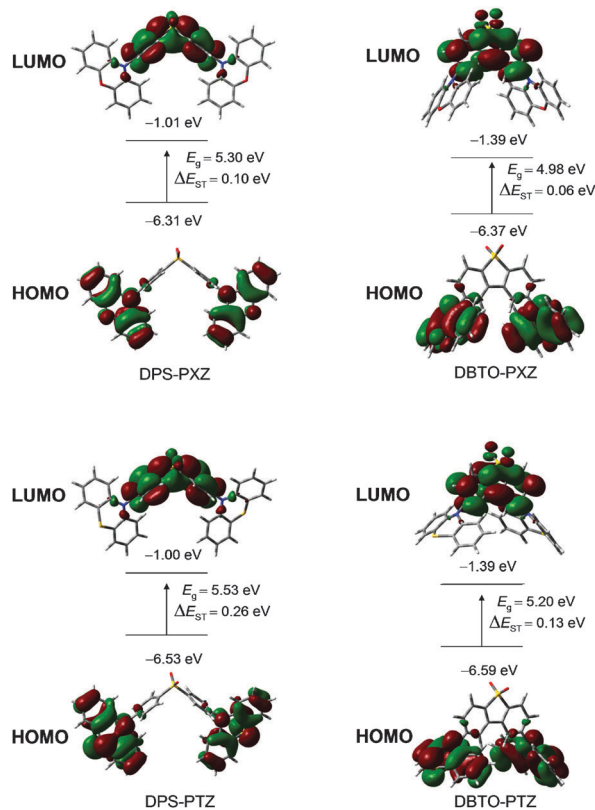


Fig. 6 Frontier-molecular-orbital distributions, energy levels and energy gaps ( $\Delta E_{ST}$ ) between singlet and triplet states for DPS-PXZ, DBTO-PXZ, DPS-PTZ and DBTO-PTZ characterized by DFT calculations in the ground state.

delayed fluorescence may simultaneously solve the problems of ACQ and low exciton utility of many fluorescent materials and may become promising candidates as light emitters for nondoped OLEDs.

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