

Cite this: *Chem. Commun.*, 2012, **48**, 11671–11673

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COMMUNICATION

Tetraphenylethene modified perylene bisimide: effect of the number of substituents on AIE performance†

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Received 21st August 2012, Accepted 9th October 2012

DOI: 10.1039/c2cc36060h

Perylene bisimide derivatives substituted with one and two tetraphenylethene moieties at 1 and 1,7-positions show distinct optical properties. The former displays characteristic emission features of perylene bisimides in solution and red emission in the aggregate state, while the latter is nonemissive in solution but highly red-emissive in the aggregate state.

Organic luminophores with aggregation-induced emission (AIE) property have attracted great research efforts, because AIE opens an avenue to turning away from the aggregation-caused quenching (ACQ) effect and deriving luminescent materials with high quantum efficiency in the solid state.¹ For example, tetraphenylethene (TPE, Chart 1) is a representative AIE-active luminophore, and TPE-derivatives have been widely used as fluorescent probes for the detection of ions, biomolecules and explosives.^{1,2} More recently, we found that TPE could be used as a modifier to turn an ACQ luminophore to an AIE one. This strategy has proved to be workable for a series of classical ACQ luminophores such as naphthalene, anthracene, phenanthracene,

pyrene, triphenylamine, and carbazole by attaching TPE moieties to the luminophores.³ For example, the modification of triphenylamine and *N,N',N'',N'''*-tetraphenylbiphenyl-4,4'-diamine with three and four TPE units resulted in two novel AIE luminogens. The fluorescence (FL) quantum yields of their films ($\Phi_{F, \text{film}}$) are 91.6% and 100%, while their FL quantum yields in dilute solutions ($\Phi_{F, \text{solut}}$) are only 0.42% and 0.55%, respectively.^{3d}

These successes triggered our interest in converting larger conjugated systems from ACQ to AIE luminophores. Perylene bisimides (PBIs, Chart 1) are one class of the most investigated organic dyes that have found promising application as an active component in organic light harvesting systems, fluorescent emitters and biosensors.⁴ PBIs have near-unity fluorescence quantum yield in dilute solutions, but their aggregates or solids display drastic fluorescence quenching due to the attractive dipole-dipole interactions and/or effective intermolecular π - π stacking.⁵ Thus the conversion of PBIs from ACQ to AIE materials is of great significance. Recently, we have shown that the decoration of two TPE moieties at 1,6- or 1,7-positions on the perylene core can make the PBI derivatives be AIE active, and the highly efficient red emission in solid states and the formation of ordered microstructures have been investigated.⁶ However, there are still a few important issues should be figured out. For smaller conjugated systems, it is enough to convert the emission behavior from ACQ to AIE by attaching one TPE unit to the core. But for larger conjugated systems (e.g. PBI and rubrene), is one TPE unit enough to achieve the same conversion? In addition, the effect of substitution position is also an important factor relevant to the conversion process. Moreover, the TPE unit(s) can be directly attached onto the perylene core *via* a single bond, or indirectly *via* a spacer. It is necessary to evaluate the effect of the linking mode on the conversion process. Herein, we demonstrate our results by a comparative investigation on the fluorescence properties of non-, mono- and di-TPE-substituted PBIs (Chart 1).

The synthetic routes to DBuTPEPBI and DBuDTPEPBI are shown in Scheme S1 (ESI†). The detailed procedures for the syntheses and the characterization data are described in ESI.† In dilute dichloromethane (DCM) solution (10^{-6} M), the FL spectrum of the non-TPE substituted PBI (DBuBrPBI) has an emission peak at 538 nm with a shoulder at around 577 nm (Fig. S3, ESI†). This is the typical feature of *N,N'*-substituted PBIs. $\Phi_{F, \text{solut}}$ is calculated to be 95.2%. While its solid film has very weak fluorescence (Fig. 2A and S4 (ESI†)). The concentration dependent fluorescent behaviors

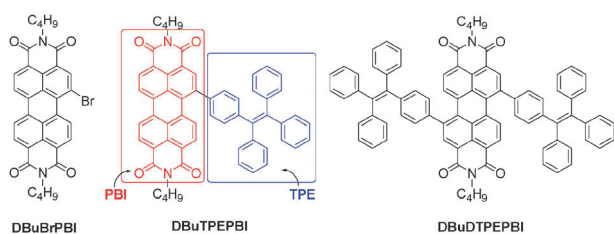


Chart 1 Molecular structures of the non-, mono- and di-TPE substituted perylene bisimides.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2cc36060h

of mono-TPE substituted PBI (DBuTPEPBI) are shown in Fig. 1, the FL spectrum recorded for its dilute DCM solution (10^{-6} M) shows a peak at 537 nm with a shoulder at around 574 nm, which is similar to that of its precursor DBuBrPBI. When concentration is increased to 10^{-5} M, the shoulder becomes more pronounced. And as it is increased to 10^{-4} M, the emission peak shifts to 590 nm. For its powder sample, the emission peak red-shifts further to 682 nm. The $\Phi_{F,solut}$ of DBuTPEPBI in DCM is measured to be 2.2%. The solid sample emits bright red light (Fig. 2B). Noticeably, the di-TPE substituted PBI (DBuDTPEPBI) shows quite distinct fluorescent behavior from both DBuBrPBI and DBuTPEPBI. In DCM solutions with different concentrations (10^{-6} – 10^{-4} M), only FL signals in the noise level were detected. $\Phi_{F,solut}$ is merely 0.07%. For DBuDTPEPBI cast film, the emission is still efficient (Fig. 2C) and the emission peak appears at 706 nm (Fig. S5, ESI[†]).

The comparison of the three PBI derivatives discloses significant information. Firstly, they take more and more planar configuration in an order of DBuBrPBI, DBuTPEPBI and DBuDTPEPBI. For DBuBrPBI, the perylene core takes the most distorted configuration due to the steric repulsion between the Br and H atoms on positions 1 and 12 (Fig. 2A). Although TPE is a conjugated moiety, the optimized molecular geography indicates that the phenyl groups at 1 or 1,7-positions are perpendicular to the perylene core (Fig. 2B and C). Meanwhile, the C atom is smaller than Br in size. As a result, the perylene core has a more planar configuration. The corresponding dihedral angles decrease from 21.09° for DBuBrPBI to 18.64° for DBuTPEPBI and 12.87° for DBuDTPEPBI. As a result, there is only partial electronic conjugation between the TPE moieties and the PBI core (Fig. S6, ESI[†]). This is also reflected by the absorption spectra of DBuBrPBI, DBuTPEPBI and DBuDTPEPBI, which show absorption peaks at 522, 533 and 567 nm (Fig. S7–S9, ESI[†]), respectively.

The second significant information is the evolution of the FL quantum yield of their aggregates. In dilute DCM solution, $\Phi_{F,solut}$ for DBuBrPBI and DBuDTPEPBI is 95.2% and 0.07%, respectively, which are the highest and the lowest one among the three compounds. As revealed by the optimized molecular geometry, the phenyl rings of the TPE moieties are in a propeller shape. In good solvents, they undergo active intramolecular rotations and consume the excitation energy, which leads to the vanishing of the fluorescence. Similar phenomenon has been observed in other TPE modified conventional planar luminophores.³ It is interesting that DBuTPEPBI has a $\Phi_{F,solut}$ of 2.2% in DCM solution, which is much lower than that of its precursor but much higher than that of the disubstituted counterpart DBuDTPEPBI. According to the restricted

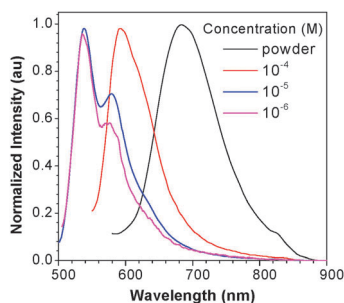


Fig. 1 Normalized fluorescence (FL) spectra of DBuTPEPBI cast film and in DCM solution with different concentrations ($\lambda_{ex} = 479$ nm).

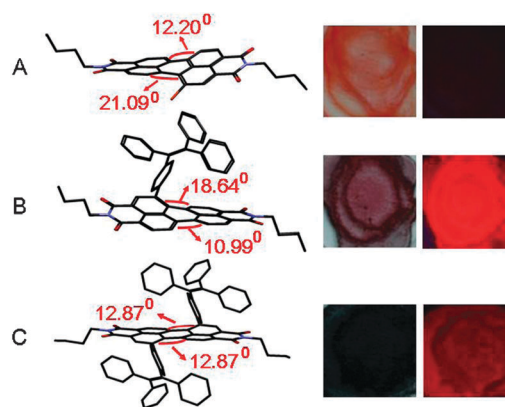


Fig. 2 (A), (B) and (C) show the optimal structures of DBuBrPBI, DBuTPEPBI, and DBuDTPEPBI calculated by the semi-empirical AM1 method. The photographs display the solution cast films of DBuBrPBI (A), DBuTPEPBI (B) and DBuDTPEPBI (C) taken under day light (left column) and 365 nm UV light (right column).

intramolecular rotation mechanism for the AIE phenomenon,¹ for molecule DBuDTPEPBI, the rotations of phenyl groups in two TPE moieties dissipate the excitation energy thereby rendering it with weak emission. For molecule DBuTPEPBI, which has only one TPE moiety attaching onto the PBI core, the number of freely rotary phenyl groups is the half of that in DBuDTPEPBI. Thus the intramolecular rotations cannot completely dissipate the excitation energy. As a result, DBuTPEPBI shows subdued but characteristic emission of the PBI moiety in solution.

The third is that the emission of their solid films. DBuBrPBI emits very weak red light (Fig. 2A). Compared with the strong emission of its DCM solution, the drastic FL quenching of DBuBrPBI is due to the effective intermolecular π - π stacking.⁷ However, the cast films of DBuTPEPBI and DBuDTPEPBI emit effective red light upon illumination of UV light (see photographs in Fig. 2B and C). Based on the RIR mechanism,¹ the rotations of the phenyls around the perylene core are restricted in the solid state, and the channel of consuming the excitation energy is switched out. Meanwhile, the bulky TPE moieties impair the intermolecular π - π stacking. Thus, the increased FL intensity in solid films over that in solutions was observed.

The solid state fluorescent behaviors indicate that precursors and the TPE-modified PBIs are typical ACQ and AIE molecules, respectively. Using a common method,^{2,3,6} we investigated the AIE behaviours of DBuTPEPBI and DBuDTPEPBI in hexane/DCM mixtures with different volume percentage of hexane (f_h). As shown in Fig. 3A, when $f_h \leq 60\%$, the FL spectra of DBuTPEPBI display the PBI's characteristic green band peaked at 537 nm with a shoulder at 574 nm. When f_h increases from 60% to 80%, the intensity of the red emission band peaked at 638 nm is enhanced. At $f_h = 90\%$, the red band becomes dominant; while the green band still exists. The green and red bands are assigned to the free and aggregated DBuTPEPBI molecules, respectively. In the whole process, the absorption features have little changes with the variation in f_h values (Fig. S8, ESI[†]).

The FL spectra of the disubstituted counterpart of DBuDTPEPBI demonstrate different features from that of DBuTPEPBI in hexane/DCM mixtures. When $f_h \leq 40\%$, no peak can be detected. However, a peak at 645 nm can be observed when f_h is increased. This deep-red band is assigned to the emission from

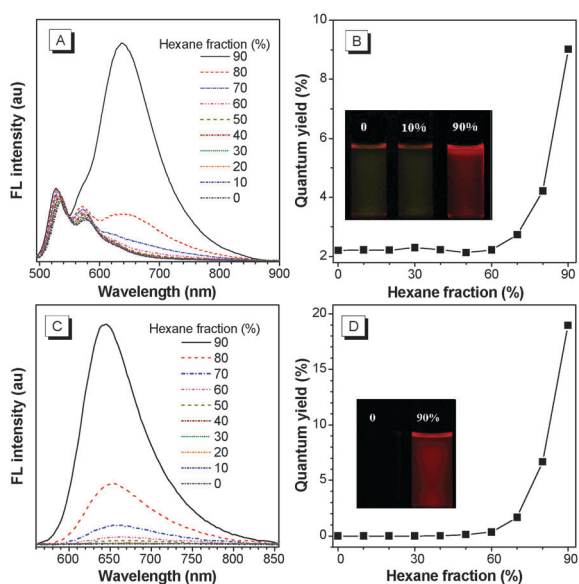


Fig. 3 FL spectra of DBuTPEPBI (A) and DBuDTPEPBI (C) in hexane/DCM mixtures with different f_h . Variation in quantum yield of DBuTPEPBI (B) and DBuDTPEPBI (D) with f_h in hexane/DCM mixtures ($\lambda_{\text{ex}} = 479$ and 453 nm, respectively). The insets of B and D show the photographs of the FL images (taken under 365 nm UV light) for the corresponding mixtures. Concentration: $10 \mu\text{M}$.

molecular aggregates. For DBuDTPEPBI, only this deep red band can be detected in hexane/DCM mixtures. At $f_h = 90\%$, the quantum yields of the aggregates ($\Phi_{\text{F,aggr}}$) of DBuTPEPBI and DBuDTPEPBI are 9.0% and 18.9% , respectively. In aggregates, the active intramolecular rotations of multiple phenyl rotors of TPE are restricted, which renders their aggregates with strong luminescence. Since hexane is non-solvent for both DBuTPEPBI and DBuDTPEPBI, the molecules must have aggregated when a large amount of hexane was added. The morphological observations provide direct evidence for the formation of aggregates. As shown in Fig. S10 and S11 (ESI[†]), the SEM images display that both DBuDTPEPBI and DBuTPEPBI can assemble into ordered microstructures such as fibers and belts with hundreds of microns in length and several microns in diameter, just as PBI dyes reported in the literature.^{4,7}

In summary, the comparative and controlled investigations on the fluorescent behaviors of non-, mono- and di-TPE substituted PBI derivatives have demonstrated the feasibility to convert the fluorescence performance of PBIs from ACQ to AIE. Unlike those small conjugated systems such as naphthalene, anthracene and so on, whose FL behavior can be completely converted from ACQ to AIE by modification with a single TPE moiety, the modification of the larger PBI core with one TPE moiety can only partially alter its FL property. The mono-TPE substituted PBI (DBuTPEPBI) in dilute solution shows the characteristic FL features with decreased $\Phi_{\text{F,solut}}$ (2.2%). Its aggregates formed in hexane/DCM mixture ($f_h = 90\%$) and the powder sample emit red fluorescence ($\lambda_{\text{em,solid}} = 682$ nm, $\lambda_{\text{em,aggr}} = 638$ nm, $\Phi_{\text{F,aggr}} = 9.0\%$). The di-TPE substituted PBI (DBuDTPEPBI) in dilute solution has very low $\Phi_{\text{F,solut}}$ (0.07%), but its aggregates formed in hexane/DCM mixture ($f_h = 90\%$) and the powder sample emit efficient red to near infrared FL

($\lambda_{\text{em,solid}} = 706$ nm, $\lambda_{\text{em,aggr}} = 645$ nm, $\Phi_{\text{F,aggr}} = 18.9\%$). The robusticity of the PBI core is also embodied by the observations that both DBuTPEPBI and DBuDTPEPBI can form ordered microstructures as revealed by the SEM images of the aggregates. The effects of the linking mode and substitution positions on the perylene core on the AIE performance are underway in our laboratory. These results will provide a useful criterion for deriving AIE molecules by rational modification of classical luminogens and construction of highly efficient luminescent solid materials.

This work was supported by the National Science Foundation of China and Zhejiang Province (51273175, 50573086 and Z4110056); the key project of the Ministry of Science and Technology of China (2009CB623605), the Research Grants Council of Hong Kong (603509, HKUST2/CRF/10, and 604711), the University Grants Committee of Hong Kong (AoE/P-03/08).

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