

Creation of highly efficient solid emitter by decorating pyrene core with AIE-active tetraphenylethene peripheries†

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Turning “stone” into “gold”: pyrene, a faint fluorophore in the solid state, is transformed into a bright emitter by decorating it with tetraphenylethene units; the new luminogen is thermally and morphologically stable and its light-emitting diode shows excellent performance, with external quantum efficiency and current efficiency up to 4.95% and 12.3 cd A⁻¹, respectively.

Researchers are actively searching for efficient solid emitters, for they are essential materials for the fabrication of practically useful organic light-emitting diodes (OLEDs).¹ Emissions of traditional fluorophores, however, are often quenched when their molecules are aggregated in the solid state. Pyrene (Py) is a “classic” example of such a fluorophore, whose film emission is weakened by the notorious effect of aggregation-caused quenching (ACQ).² Many research groups have attempted to enhance the emission of Py in the solid state by modifying its molecular structure. Four phenyl (Ph) rings, for example, have been attached to a Py core, but the resultant 1,3,6,8-tetraphenylpyrene (TPPy) showed poor OLED performance: its maximum external quantum efficiency (η_{ext}) was as low as 0.5%, although its solution gave a fluorescence quantum yield (Φ_{F}) as high as ~90%.²

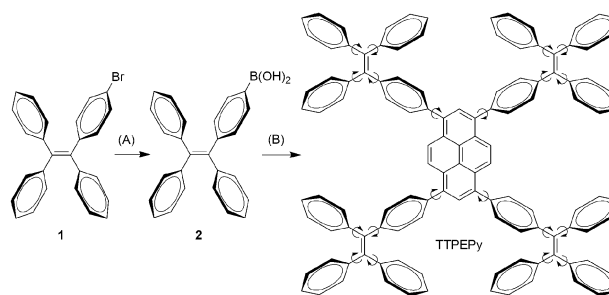
Attaching methylated Ph groups to a Py core as peripherals or hooking up two Py rings by a substituted Ph spacer furnished Py derivatives with twisted conformations.² These molecules were found to serve as excellent light emitters and hole transporters in electroluminescence (EL) devices, with the best performance achieved with 1-[2,5-dimethyl-4-(1-pyrenyl)-phenyl]pyrene. The emission colours of the films of the Py derivatives, however, were all red shifted from those of their solutions, with $\Delta\lambda_{\text{em}}$ up to 52 nm. Furthermore, the highest current efficiency (η_{C}) was a moderate 5.2 cd A⁻¹, thus leaving much room for further improvement.²

Triphenylamine (TPA) is another typical example of an ACQ dye. We have recently succeeded in synthesizing TPA

derivatives with Φ_{F} up to 100% in the solid state by decorating TPA cores with multiple tetraphenylethene (TPE) units as peripherals.³ TPE is a representative example of a luminogen that shows an unusual effect of aggregation-induced emission (AIE):⁴⁻⁶ its molecules are non-emissive when dissolved in a good solvent but become highly luminescent when aggregated in a poor solvent. The AIE effect of TPE is rationalized to be caused by the restriction to its intramolecular rotations (RIR). In the solution state, the active rotations of its multiple Ph blades non-radiatively deactivate its excitons. In the aggregate state, however, the RIR process effectively blocks the non-radiative channel and hence makes TPE highly emissive.⁵

Our success in the development of highly efficient TPA-based solid fluorogens prompted us to apply the same strategy to the Py system. Because Py is the best-known ACQ fluorophore, we are intrigued to learn how its photoluminescence (PL) in the solution and solid states will vary with peripheral attachment of multiple TPE units. If the solution PL of the resultant TPE-Py adduct becomes weaker, it will offer additional evidence to verify that intramolecular rotations of aromatic rings are indeed responsible for PL quenching.⁵ Moreover, if the TPE-Py adduct is an efficient solid emitter, it will prove that molecularly melting ACQ and AIE units is a general strategy for solving the thorny ACQ problem.

With these considerations in mind, we elaborated a synthetic scheme for making the TPE-Py adduct (Scheme 1). Boronation of brominated TPE **1** gave **2** whose coupling with 1,3,6,8-tetrabromopyrene furnished 1,3,6,8-tetrakis[4-(1,2,2-triphenylvinyl)phenyl]pyrene (TTPEPy). The structure of TTPEPy was characterized by mass spectroscopy (ESI, Fig. S1)† and elemental analysis. Its powder was crystalline, as revealed by its X-ray diffractogram (ESI, Fig. S2)†. Its molecular conformation was optimized by a semiempirical PM3 method,



Scheme 1 Synthesis of TTPEPy, a tetrakis(tetraphenylethene) (TPE)-substituted pyrene (Py); reagents: (A) (a) *n*-BuLi, (b) B(OMe)₃, (c) HCl; (B) 1,3,6,8-tetrabromopyrene, Pd(PPh₃)₄, K₂CO₃.

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† Electronic supplementary information (ESI) available: Experimental procedures and characterization data for the synthesis of TTPEPy, XRD diffractogram of its crystalline powder, absorption and PL spectra of its THF solutions with different concentrations, and temperature-dependent PL spectra and decay curves of its THF solution, crystalline powder and amorphous film. See DOI: 10.1039/b921451h

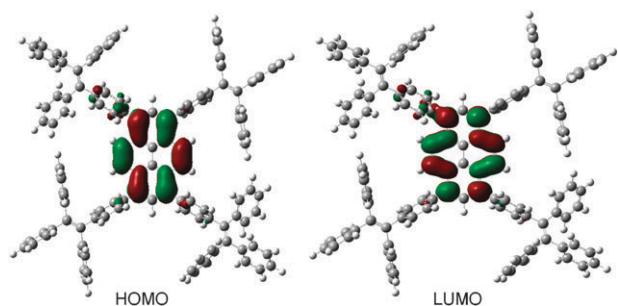


Fig. 1 Molecular orbital amplitude plots of HOMO and LUMO energy levels of TTPEPy calculated by semiempirical PM3 method.

in which the Ph rings of TPE units were arranged in a propeller-like shape. Fig. 1 shows the molecular orbital amplitude plots of the HOMO and LUMO energy levels of TTPEPy, which are clearly dominated by the orbitals from the central Py ring. The Ph rings directly linked to the Py ring at 1,3,6,8-positions make some contributions to the HOMO and LUMO energy levels, while the other Ph rings make no contributions at all. This suggests that the emission of TTPEPy is from the excited state of its TPPy core.

TTPEPy shows an absorption maximum at 398 nm (Fig. 2a). From the onset of the absorption spectrum, its energy band gap is calculated to be 2.8 eV. The PL spectrum of its solution peaks at 462 nm. Using 9,10-diphenylanthracene as standard, the Φ_F of TTPEPy is estimated to be 9.5%, which is much lower than that of TPPy ($\sim 90\%$).² The structural difference between TTPEPy and TPPy is that the former and latter carry four TPE and Ph peripheral units, respectively. Evidently, the active intramolecular rotations of the multiple TPE blades around the Py stator have largely

deactivated the excitons of TTPEPy, rendering it weakly luminescent in the solution.⁵

Gradually thickening the TTPEPy solution (from 0.1 to 10 μM) monotonically increases its absorption and emission intensities but hardly affects its spectral profiles and peak positions (ESI, Fig. S3)†. Cooling its solution (from 298 to 77 K) dramatically boosts its PL intensity but exerts little effect on its spectral position (ESI, Fig. S4)†. The singlet excited state of TTPEPy rapidly decays in a single-exponential fashion with a lifetime as short as 0.25 ns at 300 K in THF. With a progressive decrease in temperature, the lifetime gradually lengthens and finally reaches 1.29 ns at 77 K (ESI, Fig. S5a)†. This indicates that the intramolecular rotations of the TPE blades have been greatly restricted at the cryogenic temperature and that the accompanying RIR process has helped enhance the PL of the frozen TTPEPy solution.

Addition of a large amount of water ($f_w \geq 60\%$) into the THF solution of TTPEPy causes its molecules to aggregate, due to the immiscibility of the hydrophobic luminogen with the hydrophilic medium. The aggregate formation activates the RIR process and boosts the light emission (Fig. 2b). TTPEPy is thus a luminogen that exhibits an aggregation-induced emission enhancement (AIEE) effect.^{7,8} It is AIEE active because the strong emission of its TPPy core in the solution is not completely quenched by intramolecular rotations of its TPE blades.⁷ This is different from its AIE-active TPE parent, whose PL in the solution is totally extinguished by the rotations of its Ph rotors.

The crystalline powder of TTPEPy emits at 465 nm (Fig. 2d), which is very close to the PL peak of its solution, implying that the PL is from its monomeric species. The PL of its amorphous film peaks at 483 nm, which is red-shifted from that of its crystalline powder. Such a phenomenon has often been observed in the AIE(E) systems, because of the conformational twisting of the luminogens in the crystalline lattices.⁶ The emissions in both crystalline and amorphous states are enhanced when the temperature is decreased (ESI, Fig. S6)†. Compared to its solution at 300 K, the crystal of TTPEPy shows a much longer lifetime (1.26 ns), which is only slightly lengthened with decreasing temperature (ESI, Fig. S5b)†. This suggests that the conformations of the TTPEPy molecules have been largely locked in the crystalline lattices. The Φ_F value of the TTPEPy film is 70%, as measured by an integrating sphere, which is much higher than those of its tetraarylpyrene cousins (normally 24–44%),^{2,9} thanks to the RIR process in the TTPEPy aggregates.

TTPEPy is thermally stable: its temperatures for glass transition (T_g) and thermal degradation (T_d) are 204 and 485 $^\circ\text{C}$, respectively (Fig. 2c), as revealed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements. Although the molecular weight of TTPEPy is relatively high, its excellent stability enables it to be sublimed for film deposition at $3\text{--}7 \times 10^7$ Torr and ~ 200 $^\circ\text{C}$ without decomposing. With the aid of cyclic voltammetry, its HOMO energy is derived from the onset potential of oxidation to be 5.4 eV, subtracting the optical band gap energy from which gives a LUMO energy of 2.6 eV.

High PL efficiency often promises excellent EL performance. Indeed, TTPEPy works as a fabulous EL emitter. The

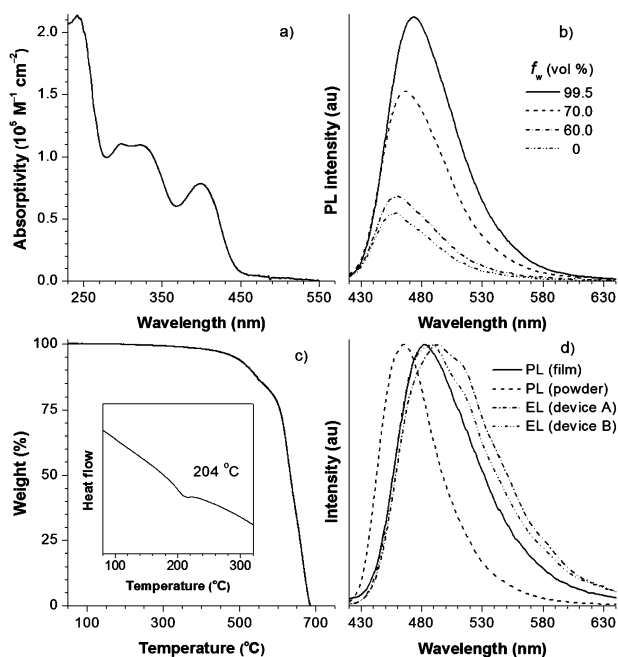


Fig. 2 (a) Absorption spectrum of TTPEPy in THF. (b) PL spectra of TTPEPy in THF–water mixtures with different fractions of water (f_w); $c = 1 \mu\text{M}$, $\lambda_{\text{ex}} = 350 \text{ nm}$. (c) TGA and DSC thermograms of TTPEPy. (d) PL spectra of amorphous film and crystalline powder of TTPEPy and its EL spectra.

Table 1 EL performances of TTPEPy and Alq₃^a

| Device | $\lambda_{\text{em}}/\text{nm}$ | V_{on}/V | $L_{\text{max}}/\text{cd m}^{-2}$ | $\eta_{\text{C}}/\text{cd A}^{-1}$ | $\eta_{\text{P}}/\text{lm W}^{-1}$ | $\eta_{\text{ext}}/\%$ |
|--------|---------------------------------|--------------------------|-----------------------------------|------------------------------------|------------------------------------|------------------------|
| A | 492 | 4.7 | 18 000 | 10.6 | 5.0 | 4.04 |
| B | 488 | 3.6 | 36 300 | 12.3 | 7.0 | 4.95 |
| C | 520 | 3.5 | 27 600 | 5.3 | 2.7 | 1.60 |

^a Configuration for device A: ITO/NPB (60 nm)/TTPEPy (40 nm)/TPBI (20 nm)/LiF (1 nm)/Al (100 nm); for device B: same as device A, except for the thickness of the TTPEPy layer (26 nm); for device C: ITO/NPB (60 nm)/Alq₃ (40 nm)/TPBI (20 nm)/LiF (1 nm)/Al (100 nm). Abbreviations: V_{on} = turn-on voltage, L_{max} = maximum luminance, η_{P} = power efficiency (@ 100 cd m⁻²), η_{C} = current efficiency (@ 100 cd m⁻²), and η_{ext} = maximum external quantum efficiency.

TTPEPy-based multilayer OLEDs emit a strong sky blue light (Fig. 2d). The EL spectrum of TTPEPy is similar to the PL spectrum of its film and changes little with the device configuration (see footnote of Table 1 for detailed device structure). Device A is turned on at a low voltage and displays a maximum luminance (L_{max}) of 18 000 cd m⁻² (Fig. 3a). The maximum η_{C} , η_{P} and η_{ext} attained by the EL device are all impressively high. Even better EL performances are achieved by device B. It shows a lower V_{on} (3.6 V) but a higher L_{max} (36 300 cd m⁻²). Its η_{ext} is 4.95% at 6 V, closely approaching the theoretical limit for a singlet OLED (5%).¹ The device efficiency of TTPEPy is about one order of magnitude higher than that of its TPPy counterpart,² clearly demonstrating the positive and negative effects of AIE and ACQ, respectively, on the device performance.

The OLEDs fabricated from TTPEPy perform much better than that from Alq₃, a widely used EL emitter (Table 1). Compared with the Py derivatives previously prepared by other groups,¹⁰ TTPEPy exhibits superior properties, such as

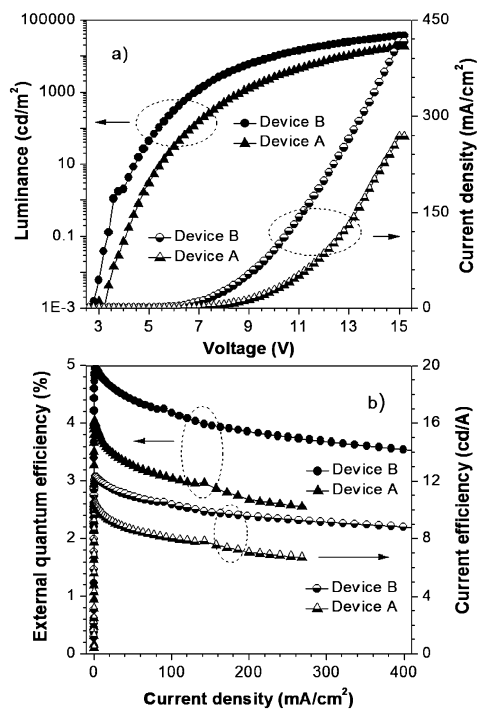


Fig. 3 (a) Changes in luminance and current density with applied biases. (b) Plots of external quantum efficiency and current efficiency versus current density in multilayer EL devices of TTPEPy.

high thermal stability, excellent PL efficiency, and outstanding EL performance. Whereas most Py derivatives are weak emitters in the solid state due to the ACQ effect, the TPE units in TTPEPy strongly suppress excimer formation and greatly promote solid-state luminescence *via* the RIR process. Clearly, using AIE units to modify a planar ACQ chromophore is an and effective approach to efficient solid emitters.

In summary, attaching TPE units to a Py core as peripheral ornaments endows the resultant TTPEPy with a novel AIEE effect, efficient solid PL ($\Phi_{\text{F}} = 70\%$), and excellent thermal stability ($T_{\text{d}} = 485\text{ }^{\circ}\text{C}$). The AIEE effect enables TTPEPy to work as a solid emitter for the construction of efficient OLEDs, with η_{C} , η_{P} and η_{ext} up to 12.3 cd A⁻¹, 7.5 lm W⁻¹ and 4.95%, respectively. This study unambiguously proves that intramolecular rotation is an energy-dissipating path for non-radiatively annihilating the excitons of a luminogen. The results for TTPEPy accomplished in this work, together with those for the TPA-based luminogens achieved in our previous study,³ verify that functionalizing an ACQ chromophore with AIE units is a general and versatile strategy for eliminating the ACQ effect and for creating efficient solid emitters with AIE(E) activity.

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