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## Locking the phenyl rings of tetraphenylethene step by step: understanding the mechanism of aggregation-induced emission†

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**Stepwise locking of phenyl rings of tetraphenylethene increases the emission efficiency of luminogen solutions gradually, thus verifying the restriction of intramolecular rotation (RIR) mechanism of the aggregation induced emission phenomenon. The emission of the luminogen with one “O” bridge could be tuned reversibly in solid state through repeated heating and grinding.**

Many efforts have been devoted to the development of efficient solid-state luminogens due to their practical applications.<sup>1</sup> However, emissions of many panel-shaped luminogens are weakened or even quenched in the aggregates due to the formation of detrimental species such as excimers and exciplexes.<sup>2</sup> To mitigate the aggregation-caused quenching (ACQ) effect, various approaches have been developed to hamper the chromophore aggregation, but only limited success has been achieved because luminophoric molecules tend to form aggregates in concentrated solutions or solid state.<sup>3</sup>

Instead of working against the natural process of chromophore aggregation, we have recently discovered that a group of propeller-shaped luminogens which are nonemissive in dilute solutions emit efficiently upon aggregation. This phenomenon is coined as aggregation-induced emission (AIE), which is exactly opposite to the ACQ effect.<sup>4</sup>

The emission intensities of AIE luminogens increased upon restriction of intramolecular rotation (RIR) through increasing the viscosity of solvent, lowering the temperature, or applying

high pressure and so on.<sup>4b</sup> Thus RIR in the aggregates is identified as a main cause for the AIE effect.<sup>5</sup> Many new AIE luminogens have been developed based on the RIR mechanism, and applied as functional materials, especially as chemosensors, bioprobes and solid-state emitters.<sup>4b</sup>

In addition to those external control experiments, we prepared model compounds and exercised an internal control on their emissions. When the steric hindering groups were introduced into the phenyl rings at 3 and 4 positions of hexaphenylsilole (**1**, HPS),<sup>6</sup> the emission of the new luminogen (**1a**) was turned on due to the greatly enhanced steric hindrance. Locking of some phenyl rings in the AIE molecules **2** and **3** afforded two highly emissive luminogens (**2a**, **3a**) in solution,<sup>7</sup> thus further verifying the RIR mechanism of the AIE phenomenon. While both **2a** and **3a** exhibited ACQ behaviour due to the panel part in their molecules (Chart 1).

Many AIE luminogens have more than four phenyl rings, while the detailed relation between the number of restricted phenyl rings and photophysical properties of AIE molecules has seldom been reported, which may further disclose the RIR mechanism of the AIE effect and may also help to explore the elaborate application of AIE luminogens. We also wonder whether it is possible to obtain a luminogen which exhibit a similar PL spectrum and fluorescence quantum yield ( $\Phi_F$ ) in both solution and crystalline states through locking the phenyl rings of the AIE molecule but keeping its twisted conformation.

Here we locked phenyl rings of a popular AIE luminogen, tetraphenylethene (TPE), with the “O” bridge step by step, and  $\Phi_F$  of molecules increased with the number of locked phenyl rings. The emission spectrum and  $\Phi_F$  of 2OTPE solution fitted

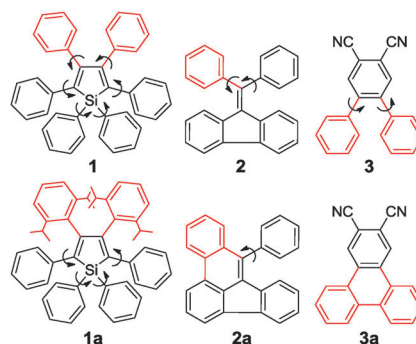
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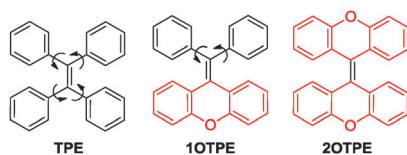
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† Electronic supplementary information (ESI) available: Experimental procedures, crystal structure of 1OTPE and 2OTPE, characterization data and UV and PL spectra for three luminogens, DSC thermograms and powder XRD patterns of 1OTPE in different aggregation states. CCDC 893966 and 893967. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc35641d



**Chart 1** Examples of AIE luminophores and their analogues with restricted phenyl rings.



**Chart 2** Structures of the TPE and its derivatives with the “O” bridge.

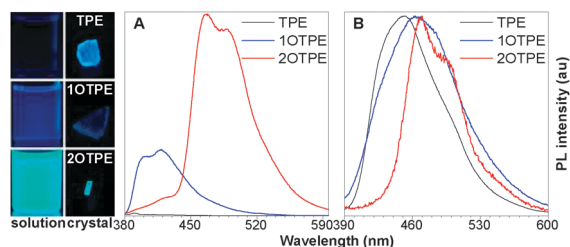
well with those of its crystal due to the fully locked phenyl rings and twisted conformation. The emission of 1OTPE can be tuned reversibly between yellow-greenish and blue in solid state through a grinding–heating process.

The three compounds were prepared conveniently by McMurry coupling and the detailed synthetic route and characterization are described in the ESI† (Chart 2).

TPE is nearly nonemissive when molecularly dissolved in solution. However, the solution of 1OTPE emits deep blue light, and solution of 2OTPE emits strong sky blue light (Fig. 1). The PL intensity of the luminogens increased promptly with increase of the number of locked phenyl rings. The  $\Phi_F$  of the TPE is nearly zero and cannot be detected by the integrated sphere. While the  $\Phi_F$  of 1OTPE and 2OTPE are 4.6% and 30.1% respectively, indicating that the  $\Phi_F$  increases greatly with the number of locked phenyl rings in the TPE molecules, fitting well with their photos and PL spectra.

When TPE molecules are dissolved as isolated species in solution less restriction is imposed on their intramolecular rotation. The intramolecular rotation of phenyl rings in TPE molecules may induce the efficient nonradiative annihilation process, thus TPE solution is nearly nonemissive. While if the rotation of phenyl rings in the TPE molecule is restricted, the emission of the molecule may be turned on due to blocking of the nonradiative annihilation process. Two phenyl rings of 1OTPE are locked by one “O” bridge, thus the nonradiative process caused by intramolecular rotation of phenyl rings may be blocked. And the increase of  $\Phi_F$  from 0% (TPE) to 4.6% (1OTPE) validated our hypothesis. As we expected, the  $\Phi_F$  of 2OTPE, all phenyl rings of which are locked with two “O” bridges, boosts to 30.1% due to further blocking of the nonradiative pathway caused by intramolecular rotation. Then we can see that the  $\Phi_F$  can be gradually increased by restriction of intramolecular rotation step by step, hence verifying that RIR in the aggregates is a main cause for the AIE effect.

The emission colors of luminogens depend on the chemical structures and conformation of their molecules. The energy band gaps of TPE, 1OTPE and 2OTPE are 4.116, 4.165, 3.736 eV,



**Fig. 1** (left panel) Photos of THF solutions and crystals of luminogens. (A, B) PL spectra of (A) THF solutions and (B) crystals of luminogens. Photos are taken under UV illumination. Excitation wavelength: 350 nm, concentration: 10  $\mu$ M.

**Table 1** Optical properties of TPE, 1OTPE and 2OTPE

Sample	$\lambda_{em}^a$ [nm]		Fluorescence decay of solution			Fluorescence decay of crystal					
	$(\Phi_F^b [\%])$		$A_1/A_2^d$	$\tau_1$ (ns)	$\tau_2$ (ns)	$A_1/A_2$	$\tau_1$ (ns)	$\tau_2$ (ns)	$\langle\tau\rangle^e$ (ns)		
TPE	nd	(nd)	453	(24.6)	nd	nd	nd	48/52	1.7	6.1	3.988
1OTPE	401	(4.6)	458	(8.0)	1/0	3.76	—	24/76	1.1	5.7	4.596
2OTPE	466	(30.1)	467	(30.8)	1/0	5.14	—	100/0	7.57	—	7.57

<sup>a</sup>  $\lambda_{em}$  = emission maximum. <sup>b</sup>  $\Phi_F$  = fluorescence quantum yield determined using a calibrated integrating sphere. <sup>c</sup> Measured in THF. <sup>d</sup> Fraction ( $A_i$ , %) and lifetime ( $\tau_i$ , ns) of shorter (1) or longer lived species (2). <sup>e</sup> The mean lifetime  $\langle\tau\rangle$  was calculated according to equation  $\langle\tau\rangle = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$ .

respectively, nicely correlating with their different emission colors and PL spectra in solutions (Fig. S2, ESI†).

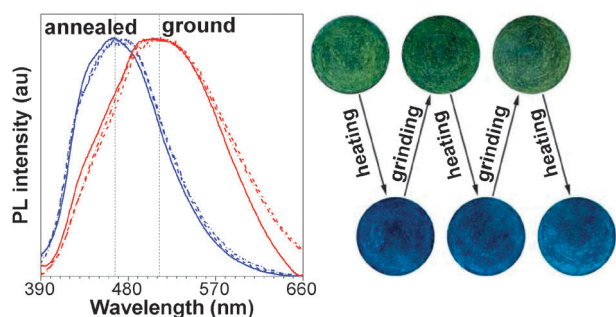
In addition to the steady-state spectra measurements, time-resolved PL spectra can provide information on the excited states of fluorogens. We measured the time-resolved PL spectra of the three luminogens and dynamic parameters are summarized in Table 1. The excited state of TPE in solution deactivated too fast to be measured with our equipment (the limit is 0.1 ns) which coincides with some reported TPE derivatives.

The introduction of the “O” bridge significantly alters the dynamics of the singlet excited states of TPE derivatives. The excited species of 1OTPE and 2OTPE in solution relax much more slowly with PL lifetime lengthened to 3.76 and 5.14 ns respectively. The lifetime increases promptly with the number of locked phenyl rings in molecules from TPE *via* 1OTPE to 2OTPE, which coincided well with the change of PL intensity and  $\Phi_F$ , further verifying the RIR mechanism of the AIE phenomenon.

The crystals of TPE are highly emissive with the  $\Phi_F$  increase from zero (in solution) to 24.6% and the average lifetime is lengthened to 3.9 ns, which is due to the block of the nonradiative pathway through restriction of rotation of phenyl rings in crystals. The  $\Phi_F$  of 1OTPE also increased from 4.6 to 8.0% when forming crystals. Thus TPE exhibits AIE activity and 1OTPE shows aggregation induced emission enhancement (AIEE) activity. However,  $\Phi_F$  of 2OTPE (30.1 to 30.9%) remained nearly unchanged when transforming from solution to crystals, exhibiting no AIE activity. The rotation of phenyl rings in 2OTPE is already locked by two “O” bridges, thus when forming crystals, the phenyl rings of 2OTPE cannot be restricted more tightly by intermolecular interaction, hence exhibiting no AIE activity. It is worth noting that PL spectrum and  $\Phi_F$  of 2OTPE solution fit well with those of 2OTPE crystals, which is seldom reported (Fig. S3, ESI†).

Some AIE luminogens transform into ACQ molecules when the phenyl rings are locked due to the close interaction of the panel parts of the molecules (Chart 1, **2a** and **3a**).<sup>7</sup> However, 1OTPE and 2OTPE do not exhibit such ACQ activity. Closer inspection of molecular conformations and packing patterns of 1OTPE and 2OTPE unveiled that molecules of both 1OTPE and 2OTPE take a twisted conformation, thus avoiding close packing which may quench the excited states (Fig. S4, ESI†).

Several AIE active luminogens have been reported to exhibit piezochromic luminescence. Grinding normally amorphizes



**Fig. 2** (left panel) Normalized PL spectra and (right panel) photos of 1OTPE in three repeating cycles of (red lines) grinding and (blue lines) annealing (170 °C, 25 min).

organic crystals. Crystals and amorphous solids of some AIE active luminogens exhibit different emissions due to different conformations of molecules in various aggregates. Therefore emissions of those AIE active luminogens will change upon grinding. Thus we checked whether the emissions of the three TPE derivatives could be modulated by a mechanical stimulus.<sup>8</sup>

Emission of 1OTPE crystals changed from bright blue to yellow-greenish ( $\Phi_F = 6.0\%$ ) upon grinding in a mortar (Fig. 2). And the emission reverted to blue ( $\Phi_F = 7.8\%$ ) upon heating. Thus the emission of 1OTPE could be tuned reversibly between blue and yellow-greenish through repeating heating and grinding. To unveil the mechanism of the mechanochromic emission of 1OTPE, powder X-ray diffraction (XRD) (Fig. S5, ESI†) and DSC measurements were carried out on the pristine blue crystals, the ground and annealed powder of 1OTPE.

The diffraction curves of both the original blue crystals and the annealed samples display many sharp and intense reflection peaks that coincide with each other, indicating their same crystalline orders and that ground solid can revert to the original crystalline state upon heating. Diffraction of the ground powder also exhibits some reflections that agree with those of the original crystal and annealed ground sample but does not have as many or as sharp peaks, hinting a not absolutely amorphous phase (Fig. S5, ESI†), which may be caused by the spontaneous recovery during grinding.

The DSC thermogram of ground 1OTPE shows a broad exothermic peak (at around 86 °C, Fig. S6, ESI†) before melting, which is absent in the DSC curves of both crystalline and annealed samples, indicating that the ground sample is in a metastable amorphous state and can crystallize promptly in the solid state upon heating. After crystallization, both the ground and annealed samples melt at a similar temperature to that of the pristine sample, suggesting that the ground sample can revert back to the original crystalline state. Thus the mechanochromic fluorescence of 1OTPE is ascribed to the transformation from a crystalline to an amorphous phase upon grinding.

However, the emissions of ground solids of TPE and 2OTPE are same as their crystals, that is, both TPE and 2OTPE exhibit no response to grinding. TPE crystallizes very

quickly, and we cannot obtain an amorphous solid of TPE through grinding or quenching of its melt, thus TPE is irresponsive to the mechanical stimulus. As all phenyl rings of 2OTPE are locked and the conformation of 2OTPE molecules kept unchanged in different aggregation states, 2OTPE does not exhibit mechanochromic fluorescence too.

In summary, emission intensity and  $\Phi_F$  of luminogens are increased with increasing number of locked phenyl rings in TPE molecules, thus the RIR mechanism of the AIE phenomenon was further verified. Emission of 1OTPE can be tuned reversibly between blue and yellow-greenish through repeating grinding and annealing. 2OTPE exhibits nearly same emission spectra and  $\Phi_F$  in both solution and crystal state, hinting a design strategy for such materials through a combination of highly rigid and twisted conformation.

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