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High efficiency luminescent liquid crystal: aggregation-induced emission strategy and biaxially oriented mesomorphic structure†

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Rational combination of aggregation-induced emission active luminogens and mesogens generates high solid-state efficiency luminescent liquid crystals, thus resolving the problem of aggregation-caused quenching normally occurs in the fabrication of luminescent mesomorphic films.

There have been growing interests in luminescent liquid crystals (LCs) in the past decades.^{1–5} The combination of intrinsic light-emitting ability and unique supramolecular organization and self-healing features within a liquid crystalline phase is of fundamental interest for such applications as anisotropic light-emitting diodes,^{2,6} polarized organic lasers,⁷ information storage, sensors, and one-dimensional semiconductors.⁸ Particularly, their capability of emitting linear or circular polarized light when aligned can be utilized in the construction of bright, more efficient emissive liquid crystal displays (LCDs).^{16,17} This would obviate the use of dichroic sheet polarizers and absorbing color filters in the LC cell and thus enhance the power efficiency of LCDs.^{1f} Moreover, such approaches can simplify the device design and substantially increase the device brightness, contrast, efficiency, and viewing angle.¹⁰

Despite the promising prospects of luminescent LCs, their synthesis is still challenging.¹¹ Firstly, it is not easy to incorporate emissive functional groups in LCs while retaining mesogenic properties;^{11,12} Moreover, many molecular emitters, which are highly emissive in solution, are dim in the solid-state when aggregates are formed, exhibiting typical aggregation caused quenching (ACQ) effects.^{13–15} However, in the mesophases, molecular aggregation or self organization is an intrinsic natural process. Particularly, the

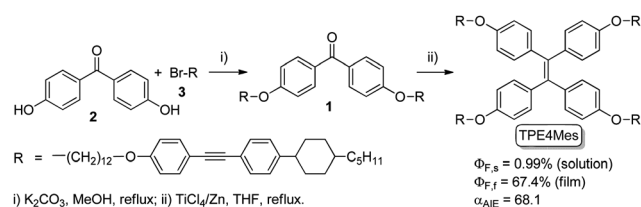
disc-like chromophoric mesogens are orderly packed and experience strong intermolecular interactions, which often quench their light emissions due to the formation of detrimental species.^{16,17} Various molecular strategies are used to maintain exciton emission in the solid state and to avoid the quenching configurations.^{18,19} Nevertheless, the light emission is often enhanced at the expense of ordered molecular packing, thus making the synthesis of mesomorphic materials with efficient light emissions a daunting task.

Recently, a novel phenomenon of aggregation-induced emission (AIE) was discovered.^{20–22} Instead of quenching commonly observed in “conventional” luminophores, aggregation has enhanced their light emissions, turning them from weak fluorophores into strong emitters. Introduction of AIE-active dyes into LCs may solve the above problem.

To testify the conjecture, in this communication, we present our effort on the creation of AIE-active liquid crystals (AIE-LC). A typical AIE-active dye, tetraphenylethylene (TPE) is employed as a luminogen due to its facile synthesis, high solid-state efficiency ($\Phi_{F,f}$), and versatile functionalization approaches.^{20c,21a} Through rational molecular design, we succeeded in creating an AIE-LC that is completely free of ACQ effect and whose $\Phi_{F,f}$ can be as high as $67.4 \pm 5\%$ (measured using an integrating sphere).

Unlike traditional approaches, the new strategy doesn't try to avoid aggregation of chromophores but in fact encourages it. Different from conventional luminescent LC systems, where contradictory requirements are expected towards high emission quantum yields (avoiding aggregation) and mesophases formation (ordered molecular packing), the new one synergistically and cooperatively generates efficient luminescent LCs through aggregation and ordered packing of AIE units and peripheral mesogens.

The target molecule TPE4Mes consisting of a TPE core and four peripheral mesogenic substituents was prepared according to the synthetic route shown in Scheme 1. Briefly, **3** was prepared as a key



Scheme 1 Synthetic route to compound TPE4Mes.

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intermediate in high yield through multistep reactions (Scheme S1), followed by nucleophilic substitution with 4,4'-dihydroxylbenzophenone (**2**) to yield **1**. Subsequent McMurry coupling of **1** gave TPE4Mes in moderate yield (65.1 %). All the reaction intermediates and final product were characterized spectroscopically with satisfactory data obtained (see ESI for detail).

TPE4Mes shows almost identical absorption profile to that of **3** with two peaks at 295 and 313 nm (Fig. S1),[†] indicating the overlapped absorptions of TPE core and peripheral groups. The absence of obvious electronic transitions beyond 330 nm strongly suggests the highly twisted TPE configurations herein. When illuminated with a UV lamp, its THF solution does not emit any observable light but strong light is generated from its solid powders and films, indicating aggregation has turned on its light emission processes. To verify the visual observation, photoluminescence (PL) spectra of TPE4Mes in THF and THF/water mixtures were measured. Water is used because it is a non-solvent of TPE4Mes: the luminogen molecules will aggregate in the aqueous mixtures with high water fractions (f_w). As shown in Fig. 1, weak PL signals are recorded at $f_w \leq 20$ % because the TPE4Mes molecules are genuinely dissolved in these mixtures. The PL intensity starts to rise at $f_w > 20$ %, at which point the solvating power of the mixture is worsened to such an extent that the luminogenic molecules start to aggregate.

Normally, TPE derivatives emit sky blue light with the maxima at 470~485 nm in the aggregated state.^{20c,21a,23} However, upon aggregation, TPE4Mes nanosuspensions exhibit a peak and a broad shoulder emissions at 380 and 450 nm, respectively. According to previous results,^{20c,21a,23} as well as the short absorption range of TPE4Mes, the shoulder emission at 450 nm can be ascribed to the TPE units. Thus it is speculated that the peak emission is corresponded to the tolane moieties. Additional comparison of PL measurement of **3** was conducted to verify this. When excited in 10/90 THF/water mixture, **3** gives an emission peak at 360 nm. Considering that inter- and/or intramolecular interactions of tolane units in TPE4Mes may result in bathochromic shift of the emission, the peak at 380 nm thus can be assigned to the tolane emission. Additionally, similar trends are observed in the peak intensities (first increase to maxima, then decrease) at 360 and 380 nm for **3** and TPE4Mes in aqueous mixtures, thus duly suggesting the above attribution (Figs. S2 and 1B). To evaluate the contributions from both emitting units, the PL spectrum of TPE4Mes in 10/90 THF/water was fitted into two separate divisions with maxima at 380 and

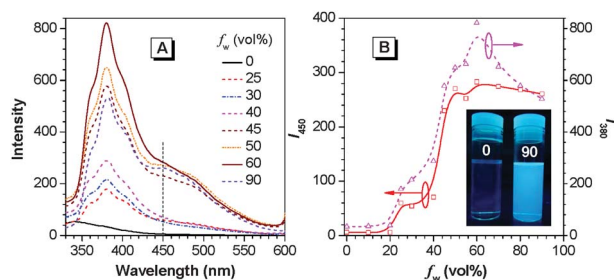


Fig. 1 (A) PL spectra of TPE4Mes in THF and THF/water mixtures; (B) plots of the emission intensities at 450 and 380 nm versus water fractions (f_w) for TPE4Mes in THF and THF/water mixtures. Concentration = 4 μ M. Excitation wavelength = 310 nm. The inset graph is TPE4Mes in THF and 10/90 THF/water mixture taken under UV illumination.

450 nm, respectively. Integration of such two parts gives the emission proportion for tolane and TPE of $\sim 1 : 1.68$ (or $0.37 : 0.63$, Fig. S3), indicating the major contribution of TPE units. Meanwhile, the much bluer emission of TPE core proves that it is more twisted and thus less conjugated when compared to its cousin counterparts,^{20c,21a,23} which is consistent with the UV result.

From the molecular solution in THF to the nanosuspension in 90 % aqueous mixture, the PL intensities of TPE4Mes at 380 and 450 nm are increased by ~ 16 and 42 times (Fig. 1B), respectively. Evidently, TPE4Mes is AIE active, which also can be seen from the vivid contrast of the insert photo in Fig. 1B. Comparison of the Φ_F values of TPE4Mes in the solution and solid state further validates their AIE activity. While the $\Phi_{F,s}$ value of TPE4Mes in THF is as low as 0.99 %, that of its solid film is boosted to 67.4 % upon aggregate formation, resulting in an AIE factor ($\alpha_{AIE} = \Phi_{F,t}/\Phi_{F,s}$) as high as 68.1. To the best of our knowledge, such high efficiency is the record value among those reported for luminescent LCs in the solid state.³

It is worthy of noticing that compound **3** is also AIE-active (Fig. S2). The phenyl rings in the TPE core and tolane substituents undergo active intramolecular rotations in the solutions, which effectively quench the light emissions of TPE4Mes and **3**. However, in the aggregates, their intramolecular rotations are physically constrained in the condensed phase, thus lighting up their emissions.^{20,21}

Before checking whether TPE4Mes is mesomorphic, a TGA measurement was conducted to evaluate its thermal stability. The result shows that it is highly thermally stable, with an onset decomposition temperature as high as 274 $^{\circ}$ C (Fig. S4). We then proceeded to study its mesomorphic properties. The thermotropic behavior of TPE4Mes has been investigated by means of differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Additional characterizations of the mesophases and the determination of the structural parameters have been performed by wide X-ray diffraction (WAXD).

POM microphotographs of the textures for TPE4Mes are recorded in the heating-cooling cycles. When it is cooled from its isotropic state to 190 $^{\circ}$ C, fan-shaped texture emerges from the homotropic

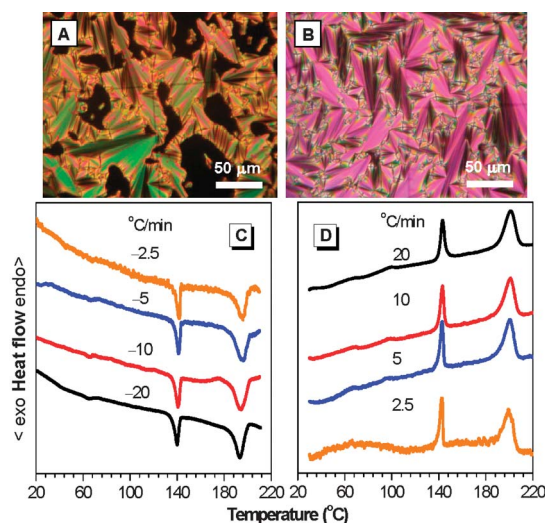


Fig. 2 POM images recorded on cooling TPE4Mes to (A) 190 and (B) 100 $^{\circ}$ C from its isotropic state and DSC thermograms of TPE4Mes during (C) cooling and (D) subsequent heating cycles at different scan rates.

dark background, forming an anisotropic mesomorphic texture (Fig. 2A). This indicates that TPE4Mes is liquid crystalline. Together with its luminescent behaviors, it can be concluded that TPE4Mes is an AIE-LC, thus proving the feasibility of such new strategy towards high efficiency mesomorphic compounds. Moreover, with further cooling from the mesomorphic phase to 100 °C, TPE4Mes does not crystallize but transforms to a more ordered mesophase (Fig. 2B). DSC traces of TPE4Mes reveal two first-order phase transitions upon cooling and heating (Fig. 2C and 2D). Two exothermic peaks at 194.2 (transition enthalpy $\Delta H = -26.14$ kJ mol⁻¹) and 140.8 °C ($\Delta H = -10.29$ kJ mol⁻¹) are observed at a cooling rate of 10 °C min⁻¹, whereas two endothermic peaks are recorded at 143.1 ($\Delta H = 10.18$ kJ mol⁻¹) and 201.0 °C ($\Delta H = 22.31$ kJ mol⁻¹) during the subsequent heating process. Meanwhile, the onset transition temperatures during cooling and heating processes are rather close, and the exothermic transition peaks are cooling rate independent, indicating such transitions approach to thermodynamic equilibrium, usually LC transitions.²⁴ Clearly, the transitions at higher and lower temperatures are associated to the isotropic-LC and LC-LC mutual transitions, respectively.

To get insights into the transitions and to clarify the nature of the mesophases, one- and two-dimensional (1D and 2D) WAXD experiments were carried out. Fig. 3A shows a set of 1D WAXD patterns for TPE4Mes recorded at various temperatures upon cooling. The WAXD pattern displays two amorphous halos at low and high 2θ regions of $\sim 5^\circ$ and $\sim 18^\circ$ at 200 °C, suggesting its isotropic nature. With the temperature decreased to 155 °C, while the amorphous halo slightly shifts to higher 2θ region of 19° , two new reflections at 2θ of 1.95 and 3.91° appear. The q ratio ($q = 4\pi\sin\theta/\lambda$) of 1 : 2 for such two new diffractions clearly indicates a layered structure is formed. Further cooling to 100 °C, the low angular reflections keep intact, whereas a fresh diffraction which can be fitted into an amorphous halo at 19° and an intense sharp reflection at 19.7° emerges. At much lower temperature of 30 °C, though TPE4Mes is solidified, typical mesomorphic 1D WAXD profile similar to that at 100 °C is observed, indicating that TPE4Mes is a LC glass at low temperature. Meanwhile, the sharp diffractions at high

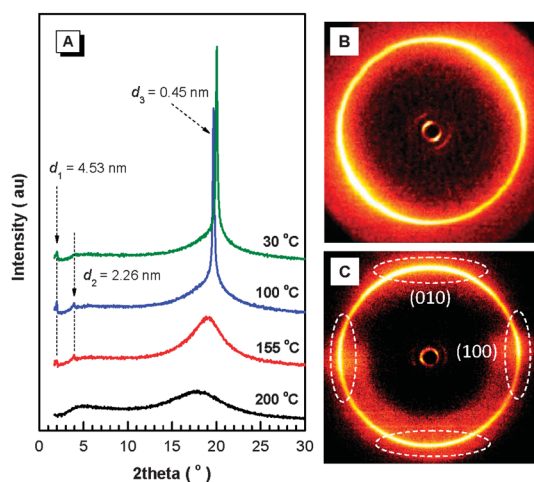


Fig. 3 (A) 1D WAXD powder patterns of TPE4Mes recorded at varying temperatures upon cooling and 2D WAXD patterns of its annealed film with the incident X-ray beam (B) perpendicular and (C) parallel to the film at room temperature.

angular region imply the presence of a long-range order on the sub-nanometre scale in the low temperature phase, whose correlation length is ~ 33 nm as estimated from the peak width using Scherrer equation (see ESI for detail).

It is also noted that the high enthalpy change (~ 26 kJ mol⁻¹) involved in the higher temperature transition (~ 190 °C) suggests an ordered mesophase, which is consistent with the POM observation. Such high enthalpy is caused by the effective packing and intermolecular interactions between TPE cores. However, the weak diffraction peaks recorded at 155 and 200 °C indicate that the TPE units can not be stacked as well as such planar aromatics as benzophenanthrenes.

Since 1D WAXD patterns lack dimensionality, 2D WAXD experiments were conducted on molecularly oriented film to identify the mesophase. It is reported that thermal annealing can be applied to align mono-domains of LCs,^{8,25} particularly for discotic molecules to form face-on alignment.^{8,25b} Therefore TPE4Mes was slowly cooled from its isotropic state to 140 °C, annealed overnight and then quenched to room temperature to prepare the molecularly oriented film. Fig. 3B and 3C illustrate the 2D WAXD patterns of the oriented film recorded with the incident X-ray beam perpendicular and parallel to it, respectively. Fig. 3B depicts a typical pattern of a smectic phase with the mesogens perpendicular to the smectic layer plane and a long-range order within the layer. The layer thickness (d spacing) derived from 2θ of 19.6° is 4.53 nm, which is comparable to the extended molecular length of TPE4Mes. Meanwhile, Fig. 3C clearly shows that the diffraction at 2θ of $\sim 20^\circ$ split into four arcs at the equator and meridian directions, respectively. Closer inspection of the pattern reveals that the four arcs can be fitted to two amorphous halos at 2θ of 19° in the meridian direction and four equal-spaced strong and narrow arcs at 2θ of 19.7° in both meridian and equator directions. The derived d spacings are 0.47 and 0.45 nm, which correspond to the intracolumnar distances between the face-on stacked TPE cores and the tetragonally packed peripheral mesogens, respectively.

The WAXD results clearly suggest a biaxial orientation arrangement of TPE4Mes at the low temperature mesophase, as schematically illustrated in Fig. 4A. While the twisted disc-like central TPE cores are packed together to generate face-on aligned columns,²⁶ the mesogenic peripheral substituents decoupled from the TPE cores by dodecyl spacers prefer to form tetragonally²⁷ stacked smectic building blocks orthogonal to the TPE columns. Meanwhile, top view of the

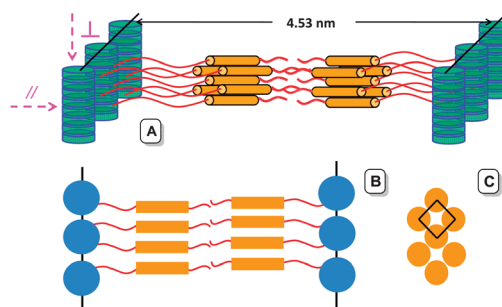


Fig. 4 Schematic illustration of the biaxially oriented packing model of TPE4Mes in the low temperature phase: (A) side view perpendicular to the side-chain mesogens, (B) top view, and (C) side view along the side-chain mesogens of the model.

structure and side view along the peripheral substituents are also outlined in Fig. 4B and 4C, respectively.

In summary, through rational combination of AIE-active TPE core and peripheral mesogens, an AIE-LC, namely TPE4Mes with high solid-state efficiency of $67.4 \pm 5\%$ and stable mesomorphic structure at low temperature (e.g. 30 °C) is successfully obtained. Though the TPE cores are strikingly twisted, they are still capable of columnar packing together in the liquid crystalline state; meanwhile, the peripheral mesogens can self-assemble into tetragonal smectic building blocks orthogonal to the TPE columns, giving the resulting TPE4Mes a unique biaxially oriented mesomorphic structure. Moreover, our new strategy overcomes the ACQ problem of conventional luminescent liquid crystals, thus paving the way for the fabrication of high efficiency luminescent mesomorphic compounds.

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