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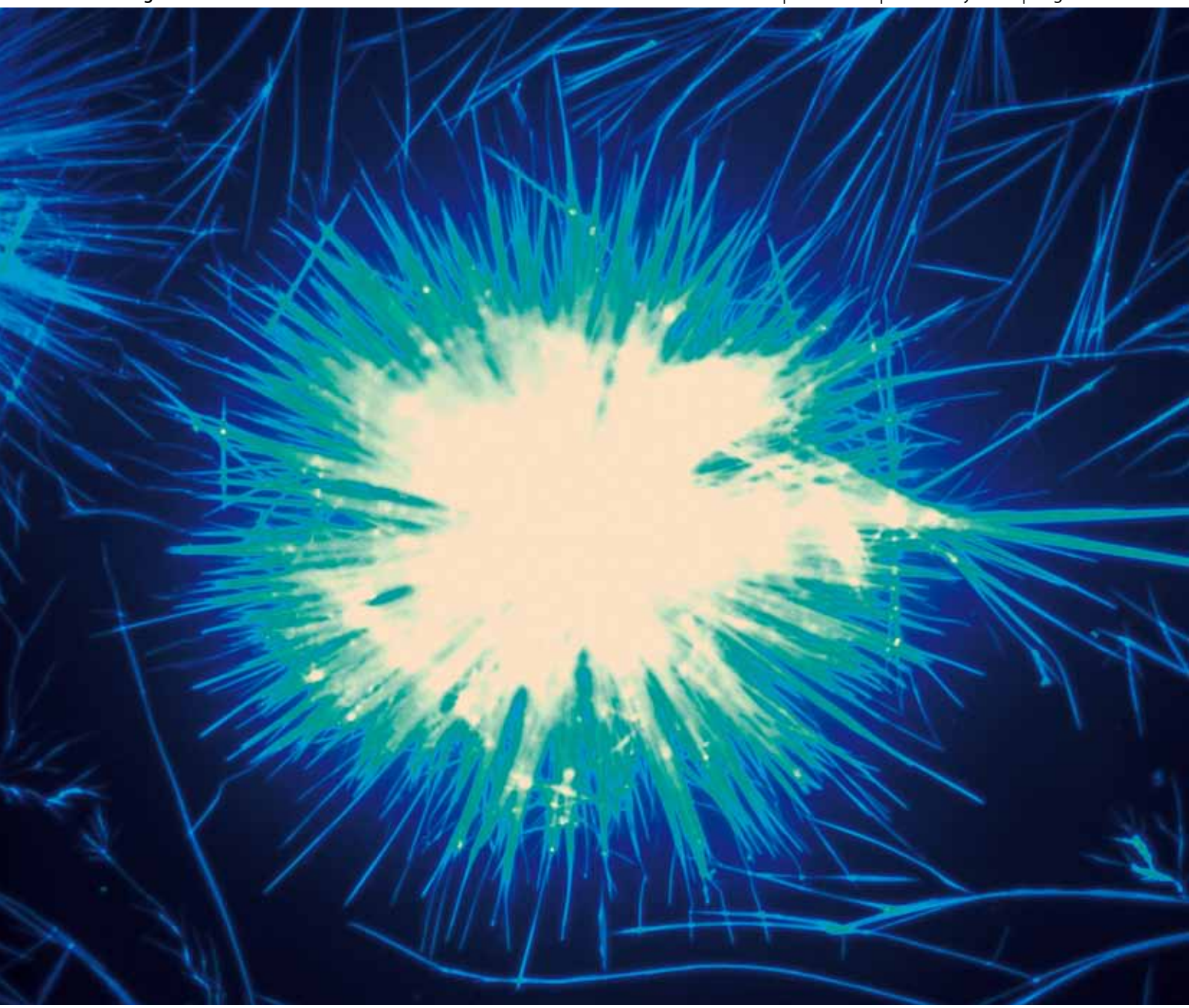

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Aggregation-induced emission, self-assembly, and electroluminescence of 4,4′-bis(1,2,2-triphenylvinyl)biphenyl†

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***Two is better than one*: a luminogen comprised of *two* units of tetraphenylethene (BTPE) emits more efficiently than that with *one* tetraphenylethene unit in the solid state; self-assembly of the BTPE molecules affords crystalline microfibers that fluoresce in 100% efficiency, giving the largest effect of aggregation-induced emission ($\alpha_{AIE} \rightarrow \infty$); BTPE-based electroluminescence devices emit in current efficiency up to ~7.3 cd/A.**

Generation of new luminogens that efficiently emit in the solid state is of great value. Luminogenic molecules are commonly used as solid materials in the real-world applications but many of the "conventional" luminophores suffer from the notorious effect of aggregation-caused quenching in the condensed phase.[1] We have recently observed an exactly opposite effect—aggregation-induced emission (AIE):[2] molecules non-emissive in the solution state are induced to emit by aggregate formation. Tetraphenylethene (TPE; Chart 1) is an archetypal AIE luminogen: its fluorescence quantum yield (Φ_F) in acetonitrile is 0.24%, which is increased to 14.63% when the TPE molecules are aggregated in an acetonitrile/water mixture with 90 vol% of water.[3] The AIE effect can be quantified by the extent of emission enhancement (α_{AIE}), as defined below:

$$\alpha_{AIE} = \frac{\Phi_{F,A}}{\Phi_{F,S}} \quad (1)$$

where $\Phi_{F,A}$ and $\Phi_{F,S}$ are the quantum yields in the aggregate and solution states, respectively. From eqn (1), the α_{AIE} value for TPE is calculated to be 60.96.

The AIE effect is rationalized to be caused by the restriction to the intramolecular rotation (IMR) process of the luminogen.[2,4] In the case of TPE, its four phenyl rings undergo an active IMR process in the solution state that quenches its emission. In the aggregate state, the IMR process is impeded, which blocks the non-radiative decay channel and hence makes TPE emissive.[3] According to this mechanism, it is envisaged that a luminogen molecule containing more rotor units should show more distinct AIE effect or higher α_{AIE} value. This is proved to be true by our previous studies.[2] For example, when two more phenyl rotors are incorporated into the TPE structure, the resultant DPBPPE is virtually non-luminescent in the solution ($\Phi_{F,S}$ = 0.037% in acetonitrile) but highly emissive as aggregates ($\Phi_{F,A}$ = 50% in the 90% acetonitrile/water mixture), displaying a remarkable AIE effect, as evidenced by its very high α_{AIE} value (1351.35; Chart 1).[3]

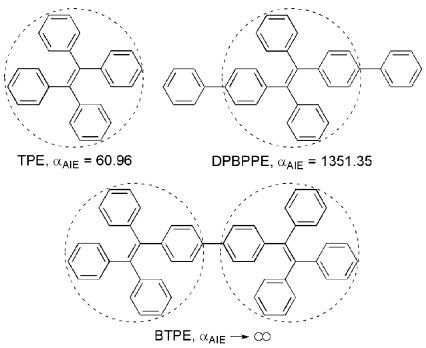

Chart 1 Chemical structures and aggregation-induced emission effects (α_{AIE}) of tetraphenylethene (TPE) and its derivatives 1,2-diphenyl-1,2-bis(4-phenylphenyl)ethene (DPBPPE) and 4,4′-bis(1,2,2-triphenylvinyl)biphenyl (BTPE). The TPE units are marked with dotted cycles.

What kind of AIE effect will we observe if we merge two TPE units into one molecule (BTPE; Chart 1)? Will BTPE give an even higher α_{AIE} value? Intrigued by these questions, in this work, we investigated the photophysical properties of BTPE in the solution and aggregate states. BTPE was prepared by the synthetic route shown in Scheme 1 (**4** was not formed). The purified compound was characterized by spectroscopic methods, from which satisfactory analyses data were obtained (ESI).† A literature search reveals that BTPE had been prepared from the reaction of diphenylmethyl lithium with 4,4-bisbenoylbiphenyl.[5] Its redox activity was studied but its photophysical properties are virtually unknown.

Fig. S1 (ESI†) shows the absorption spectrum of BTPE in THF, along with those of DPBPPE and TPE solutions.[3] BTPE shows an absorption peak at 340 nm, which is 10 nm and 30 nm red-shifted from the absorption peaks of DPBPPE and TPE, respectively. The molar absorptivity increases in the order of TPE → DPBBPE → BTPE. These spectral data

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† Electronic supplementary information (ESI) available: Experimental procedures and characterisation data for the synthesis of BTPE, absorption spectrum of its THF solution, ED pattern of its amorphous and crystalline aggregates formed in aqueous mixtures, XRD pattern of its microfibers, and plots of current density *vs.* voltage and external quantum efficiency *vs.* current density of its EL devices. See DOI: 10.1039/b915271g

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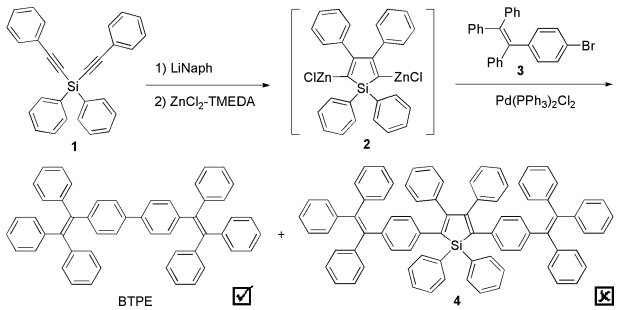

Scheme 1 Synthetic route to BTPE. Naph = 1-naphthalenyl; TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

imply that the TPE derivative carrying more phenyl rings is statistically more π-conjugated in the ground state.

Emission spectrum of the THF solution of BTPE is a flat line parallel to the abscissa (Fig. 1A), manifesting that BTPE is non-fluorescent when it is molecularly dissolved as an isolated species in a good solvent. Although attempts have been made to optimize the measurement conditions, a spectrum with a discernable peak cannot be obtained, corroborating that the emission efficiency of BTPE is intrinsically low and approaches to nil ($\Phi_{F,S} \rightarrow 0$). However, in the THF/water mixtures with high fractions of water ($f_w \geq 70\%$), BTPE gives emission spectra with clear peaks. Since water is a non-solvent of BTPE, its molecules must have aggregated in the aqueous mixtures with high f_w ratios. The emission of BTPE is thus induced by aggregation, confirming its anticipated AIE activity.

BTPE contains many freely rotatable phenyl rings. In the dilute solution, the multiple aromatic rings in an isolated BTPE molecule can undergo an active IMR process with little restraint. Collectively, these multiple molecular motions quickly consume the photonic energy in the excited state. The swift dissipation of the photonic energy as thermal energy effectively deactivates the excitons of BTPE, accounting for the virtual nullity of its $\Phi_{F,S}$ value. In the aggregates, the IMR process is restricted and the non-radiative relaxation pathway is blocked, which changes BTPE to a strong emitter. With an increase in the water content in the THF/water mixture, the aggregates become more compact and the limit to the IMR process becomes severer. As a result, the AIE effect is further enhanced and BTPE becomes even more emissive (Fig. 1A).

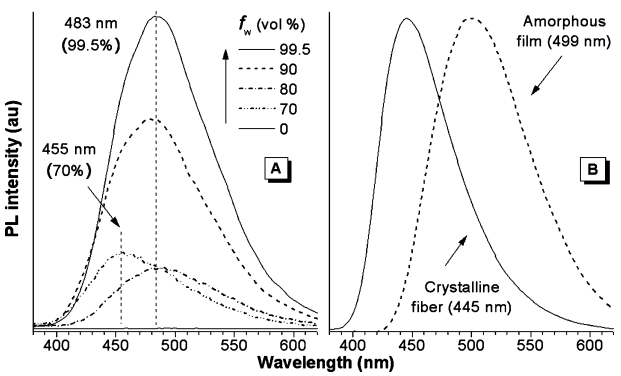

Fig. 1 Emission spectra of (A) THF solution of BTPE (10 μM) and its aggregates suspended in THF/water mixtures with different fractions of water (f_w 70–99.5 vol%) and (B) its amorphous film and crystalline fibre in the solid state.

Closer check of the emission spectrum of BTPE in the aqueous mixtures reveals that the emission maximum is bathochromically shifted from 450 nm to 484 nm when f_w becomes higher than 70%. This is probably due to a change in the morphology of the BTPE aggregates. In a mixture with a lower f_w ratio (~70%), the BTPE molecules may slowly cluster together in an ordered fashion to form "bluer" crystalline aggregates. On the other hand, in a mixture with a higher f_w ratio ($\geq$ 80%), the BTPE molecules may abruptly heap up in a random way to form "redder" amorphous aggregates. This hypothesis is proved by the electron diffraction (ED) patterns of the aggregates: whilst clear diffraction spots are seen in the ED pattern of the aggregates formed in a mixture with f_w = 70%, the aggregates formed in a mixture with f_w = 80% gives only a diffuse halo (ESI,† Fig. S2).

To validate that the crystalline aggregates emit bluer light than the amorphous ones, we prepared crystalline fibres of BTPE by slow evaporation of its THF/ethanol solution and an amorphous film of BTPE by spin-coating its THF solution onto a quartz plate. The crystalline nature of the fibres is verified by the sharp Bragg reflection peaks in their X-ray diffraction patterns (ESI,† Fig. S3). Upon excitation, the crystalline fibres and amorphous film emit blue and green lights of 445 nm and 499 nm (Fig. 1B) in quantum yields of 100% and 92% (measured with an integrating sphere), respectively. Thus, the luminogen crystallization does not only blue-shift emission colour but also increases emission efficiency. The Φ_F value of unity indicates that the IMR process is completely inhibited when the BTPE molecules are packed in the crystalline lattices. Among the AIE luminogens we have developed so far,[2,6] BTPE shows the strongest AIE effect. This is evidenced by its two extreme Φ_F values: nullity and unity in the solution and crystalline states, respectively, which results in an infinitely large α_{AIE} value, according to eqn (1).

BTPE is capable of self-assembling. Its molecules pack in one-dimensional fashion to give crystalline microfibres when a solution of BTPE containing a poor solvent (*e.g.*, ethanol) in a Petri dish is slowly evaporated. Panels A and B of Fig. 2 show SEM images of the microfibres, which are several hundred microns in length and several microns in diameter. Most of the microfibres are smooth in surface, suggestive of a uniform arrangement of the luminogenic molecules. The fibres can also grow on a quartz plate when the plate is immersed into the dye solution. After solvent evaporation, fibres as long as several millimetres are readily formed, which can be observed even with naked eyes. The fibres can further assemble into thicker rods, as exemplified by the optical image shown in Fig. 2C. Panels D–F of Fig. 2 show fluorescence images of the wires of BTPE with different sizes. The microwires are highly luminescent, emitting intense blue light upon photoexcitation. The Φ_F value of the microwires is much higher than those of the organic nanowires reported by other groups (11–32%),[7] which may find high-tech applications in the fabrication of miniature electronic and photonic devices.

Crystallization often red-shifts emission colour and decreases emission efficiency, but why are opposite effects observed in the BTPE system? During the crystallization process, the molecules of BTPE may have conformationally adjusted themselves by twisting their phenyl rings to fit into

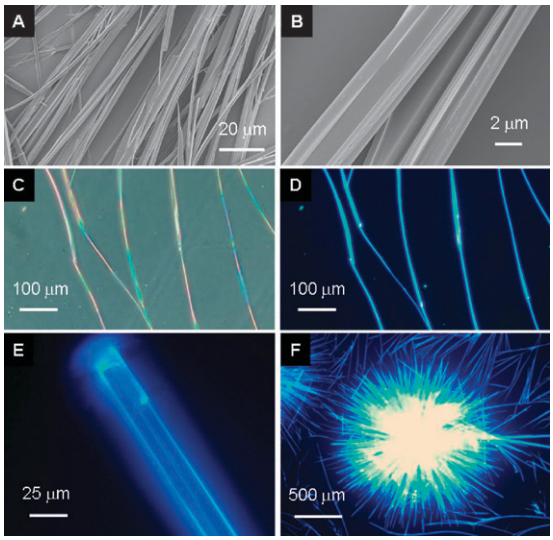

Fig. 2 (A, B) SEM, (C) optical and (D–F) fluorescent images of the microfibers of BTPE obtained by slow evaporation of its THF/ethanol solutions on (A, B) copper grids and (C–F) quartz plates.

the crystalline lattices.[8] Because there is no such constraint in the amorphous film, the BTPE molecules may have adopted a more planar conformation and hence emit a redder light. The propeller-like molecular structures of the BTPE luminogens hamper the intermolecular interactions that cause non-radiative relaxations and red-shifts in the fluorescence processes.

The highly efficient photoluminescence of BTPE aggregates in the solid state prompted us to study its electroluminescence (EL). Multilayer light-emitting diodes with configurations of ITO/NPB (60 nm)/BTPE (x)/TPBi (10 nm)/Alq_3 (y)/LiF (1 nm)/Al (100 nm) are fabricated, where x = 20 nm, y = 30 nm for device I and x = 40 nm, y = 10 nm for device II.[2,3,9]

Both the EL devices emit a sky blue light of 488 nm (Fig. 3), a colour between those of the lights emitted by the amorphous film and crystalline fibres of BTPE, suggesting that the BTPE layers in the EL devices contain both amorphous and crystalline aggregates. The devices do not only show identical emission spectra but also similar EL performances. The devices are turned on at low biases (down to ~4 V) and radiate brilliantly with luminance up to 11180 cd/m^2 at 15 V (Fig. 3A). Current efficiency and external quantum efficiency of device I reach to 7.26 cd/A and 3.17%, respectively, at a bias of 6 V (Fig. 3B and ESI,† Fig. S4). Although the device configuration is yet to be optimized, the excellent EL data clearly demonstrate the great potential of BTPE as a solid light-emitter in the construction of efficient EL devices.

In summary, a new AIE luminogen of BTPE is created in this work by melding two TPE units into one molecular structure. The active, multiple IMR process of BTPE completely annihilate its excitons in the solution state ($\Phi_{F,S} \rightarrow 0$), while the suppression of the IMR process by the crystalline lattices enables BTPE to emit efficiently in the aggregate state ($\Phi_{F,A}$ = 100%), which collectively endow BTPE with the highest AIE effect ($\alpha_{AIE} \rightarrow \infty$). Its facile self-assembling and excellent EL performance make it promising for an array of technological applications. Guided by the insights into the structure–property relationship gained in this study, we are

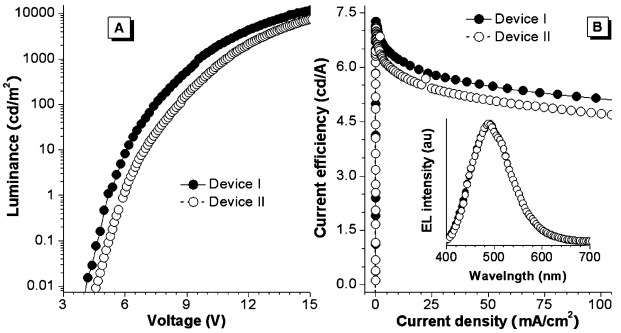

Fig. 3 Plots of (A) luminance *vs.* voltage and (B) current efficiency *vs.* current density in the BTPE-based multilayer light-emitting diodes with device configuration of ITO/NPB/BTPE/TPBi/Alq_3/LiF/Al. Inset in panel B: electroluminescence spectra. The (BTPE, Alq_3) layers in devices I and II are (20 nm, 30 nm) and (40 nm, 10 nm) in thickness, respectively.

now designing and synthesizing new luminogens by combining different AIE units, for example, integrating TPE into the structure of silole (*e.g.*, **4**), another group of well-known AIE luminogen,[2,6] in an effort to develop new AIE systems with novel structures and unique properties.

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9 Abbreviations: ITO = indium tin oxide, NPB = *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbenzidine, TPBi = 1,3,5-tris-(*N*-phenylbenzimidazol-2-yl)benzene and Alq_3 = tris(8-hydroxy-quinolinolato)aluminium.

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