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FEATURE ARTICLE

Tetraphenylethene: a versatile AIE building block for the construction of efficient luminescent materials for organic light-emitting diodes

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Luminescent materials with efficient solid-state emissions are important for the advancement of optoelectronics. Recently, a new class of propeller-like luminogenic molecules with aggregation-induced emission (AIE) characteristics has drawn increasing research interest. Among them, tetraphenylethene (TPE) is an archetypal luminogen with a simple molecule structure but shows a splendid AIE effect. Utilizing TPE as a building block, an effective strategy to create efficient solid-state emitters is developed. In this feature article, we review mainly our recent work on the construction of luminogenic materials from TPE and present their applications in organic light-emitting diodes. The applicability of the synthetic strategy and the utility of the resulting materials are demonstrated.

1. Introduction

The fabrication of organic light-emitting diodes (OLEDs) has drawn considerable research interest in the past two decades since Tang and VanSlyke succeeded in the construction of the first electroluminescence (EL) device by vapor deposition.[1] Thanks to the research efforts contributed by the scientists, OLEDs with various emission colors in high efficiencies have been fabricated and utilized in full-color flat panel displays and solid-state white lighting.[2] To achieve a substantial breakthrough, development of stable and efficient organic materials with various optical and electronic properties, as well as fabrication technology, is particularly important. Whereas many luminophors exhibit strong photoluminescence (PL) in dilute solutions, their light emissions are often weakened or even completely quenched in concentrated solutions or in the solid state.[3] Because the luminogenic molecules are located in the immediate vicinity under these circumstances, the aromatic rings of the neighboring fluorophors, especially those with disc-like shapes, experience strong π–π stacking interactions, which promote the formation of species that are detrimental to the light emission. The excited states of the aggregates often decay *via* nonradiative relaxation pathways, which are notoriously known

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Jacky W. Y. Lam

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as aggregation-caused quenching (ACQ) of light emission in the condensed phase.[4] The ACQ effect has prevented many leading luminogens identified by the laboratory solution-screening process from finding real-world applications in an engineering robust form. Closely related to the ACQ effect is the crystallization of dye molecules in the solid state, which normally shifts the luminescence spectra of the dyes to the red region, weakens their emissions and decreases their fluorescence quantum yields (Φ_F). Scientists have worked hard to fabricate amorphous films in the construction of light-emitting diodes, although crystalline films are known to exhibit higher charge mobilities.

To mitigate the ACQ effect, various chemical, physical and engineering approaches and processes have been proposed. Attaching bulky cyclics, adopting rigid and highly branched conformations, encapsulation by amphiphilic surfactants and doping in transparent polymers are commonly used methods to impede the aggregate formation.[5] These approaches, however, have met with limited success and are often accompanied with severe side effects. For example, the sterically bulky pendant groups can twist the conformations of the chromophoric units and disastrously jeopardize the electronic conjugations of the luminogens. The electronic effect of the saturated surfactants and non-conjugated polymers can dilute the luminophor density and barricade the charge transport in EL devices. In many cases, aggregation is suppressed only partially or temporarily. The difficulty lies in the fact that aggregate formation is inherent when luminogenic molecules are located in close vicinity in the condensed phase.

In 2001, Tang and co-workers observed a phenomenon of aggregation-induced emission (AIE) that is exactly opposite to the ACQ effect.[6] Instead of quenching, aggregate formation boosted the Φ_F values of silole molecules up to unity, turning them from faint fluorophores to strong emitters.[7] What is the cause for the AIE effect? We consider a number of possible mechanistic pathways, including the conformation planarization, twisted intramolecular charge transfer and *J*-aggregate formation. None of them, however, is fully supported by the experimental results and theoretical calculations. Fundamental physics teaches us that any molecular motion consumes energy. In the solution state, the active intramolecular rotations (IMR), which are also known as the low-frequency modes of the reorganization energy, of the molecules serve as a relaxation channel for the excited state to decay, whereas in the aggregated state, the IMR process are restricted, which blocks the nonradiative decay pathway and populates the radiative excitons.[8,9] Since then, many research groups have worked on the design and synthesis of AIE luminogens and various tailored AIE molecules with fine-tuned emission colors and desired functions have been developed.[10] They have explained the AIE effects of their systems using our mechanism, and details can be found in our recently published review.[7g]

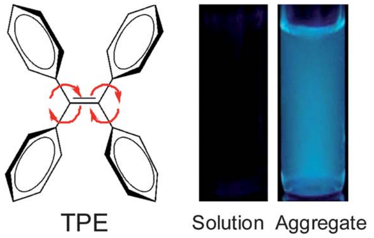

Fig. 1 (Left) Chemical structure of TPE. (Right) Photographs of a solution and a suspension of TPE in pure THF and a THF–water mixture containing 90% volume fraction of water taken under illumination of a UV lamp.

Ben Zhong Tang

Ben Zhong Tang received his Ph.D. degree from Kyoto University in 1988. He conducted his postdoctoral work at University of Toronto and worked as a senior scientist in Neos Co., Ltd. He joined HKUST in 1994 and was promoted to Chair Professor in 2008. He is interested in the creation of new molecules with novel structures and unique properties. He received a Natural Science Award from Chinese Government in 2007 and was elected to Chinese Academy of Sciences in 2009. He is serving as News Contributor to Noteworthy Chemistry (ACS), Editor-in-Chief of Polymer Chemistry Series (RSC) and Editor of Polymer Bulletin (Springer).

Amongst various luminogens, tetraphenylethene (TPE) possesses a simple molecular structure but shows a splendid AIE effect (Fig. 1).[7f,11] As shown in its crystalline lattice, its four phenyl rings are twisted out of the central alkene plane by ∼50° (Fig. 2A). Such propeller-like conformation effectively prevents direct π–π stacking interactions that tend to induce nonradiative recombination and red-shift as observed in normal crystals. Multiple C–H$\cdots\pi$ hydrogen bonds are formed between the hydrogen atoms of phenyl rings of one TPE molecule and the π electrons of the phenyl rings of the adjacent molecule (Fig. 2B). These intermolecular hydrogen bonds can further lock and stiffen the molecular conformation. All these collective effects make TPE highly emissive in the aggregated state. TPE is a very attractive and useful molecule as it can be facilely introduced to many ACQ chromophores, generating new luminogens with AIE or aggregation-enhanced emission (AEE) characteristics and

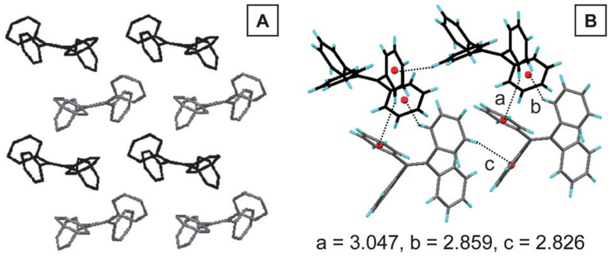

Fig. 2 (A) Molecular packing pattern and (B) C–H$\cdots\pi$ hydrogen bonds with indicated distances (Å) between adjacent molecules of TPE in the crystalline state. Reproduced with permission from ref. 7*d*. Copyright (2011) The Royal Society of Chemistry.

high emission efficiency in the aggregated state for the fabrication of efficient non-doped OLEDs. Such a finding has demonstrated an alternative strategy to solve the ACQ problem of conventional luminophors and paved a new path for researchers to design and synthesize efficient luminogenic materials.

New concepts lead to new applications. In principle, the AIE effect can be utilized to do useful work wherever the process of restriction of intramolecular rotations (RIR) is involved. Many laboratories have worked on the exploration of biological applications of the AIE effect, while others have devoted much effort on its utilities in optoelectronic and sensory systems. To avoid reduplicate description in this feature article, we focus on the utilization of TPE as a building block for the design and construction of functional materials for OLEDs. Readers who are interested in the AIE mechanism and the high-technical applications of other AIE systems can refer to previously published papers.[7c–g] Here, we review mainly our recent works in the creation of TPE-based luminogens and present their PL and EL properties. It is demonstrated that TPE is a versatile building block for the construction of efficient solid-state light emitters for OLED applications.

2. Classification of TPE-based luminogens

Since structure determines property, better understanding the structure–property relationship can guide the rational design of AIE luminogens through molecular engineering endeavors in the future. Thus, in the following discussion, we will elaborate on typical AIE luminogens constructed from TPE according to their molecular structures. TPE is a promising building block for the construction of luminescent materials, due to its simple but stable chemical structure. Pristine TPE, and its derivatives with topological structures, can be easily synthesized by the McMurry coupling reaction. By facile chemical modifications, a series of intermediates, such as 1-(4-bromophenyl)-1,2,2-triphenylethylene, 1,2-bis(4-bromophenyl)-1,2-diphenylethene, 4-(1,2,2-triphenylvinyl)phenylboronic acid, *etc.*, can be generated from TPE in high yields. Attachment of TPE to pure hydrocarbons and heterocyclic rings can be achieved easily by simple organic reactions, such as Suzuki coupling. The resulting pure hydrocarbon AIE luminogens provide models for the study of the structure–property relationship. The incorporation of heteroatoms can induce electronic effects, which will diversify the photophysical properties, tune the emission colors and endow the luminogens with a good charge-transporting property for the fabrication of efficient OLEDs with simple device structures.

2.1 Luminogens with topological structure

TPE shows almost no PL signal in dilute acetonitrile solution, revealing that it is practically non-luminescent when molecularly dissolved in good solvents. However, when a large amount of water, a non-solvent for TPE, is added into the acetonitrile solution, intense emission is observed under identical conditions. The Φ_F value of TPE in acetonitrile solution is 0.24%, while it is enhanced greatly to 49% when fabricated as a thin solid film.[12] Based on TPE, a series of linear and starburst luminogens with AIE effects are synthesized (Chart 1). For example, BTPE is a dimer of TPE and is prepared by connecting two TPE units through a covalent single bond. In solution it shows an even lower Φ_F value (~0%). In the amorphous thin film and solid state, however, it emits much more efficiently with Φ_F values of 92 and 100%, respectively.[13] A similar AIE effect is also observed from other TPE-based starburst luminogens. They emit bluer lights than their linear counterparts due to their highly twisted molecular conformations, which undermines their conjugation. For example, the emission maximum of BTPTPE aggregates is located at 460 nm, which is much shorter than those of BTPE and TPTPE (~485 nm). Some TPE-based topological luminogens are also found to be AIE-active.[14] These luminogens show slightly higher emission efficiencies than TPE and BTPE in solution due to their sterically congested molecular conformations, which hamper the IMR process to some extent.

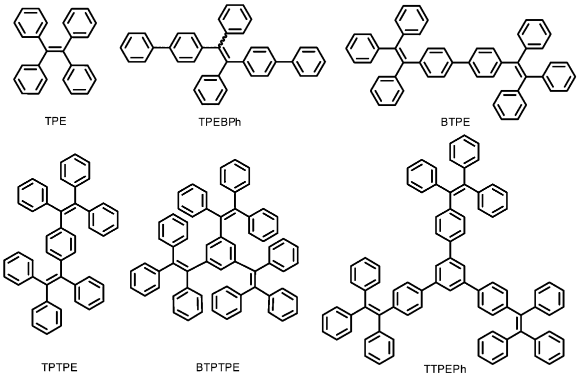

Chart 1 Examples of TPE-based AIE luminogens with topological structures.

TPE shows a deep blue EL emission peak at 445 nm, which is close to the PL of its crystals. The device performances, however, are inferior with maximum luminance (L_{max}), current efficiency ($\eta_{C,max}$) and external quantum efficiency ($\eta_{ext,max}$) of merely 1800 cd m^{-2} 0.45 cd A^{-1} and 0.4%, respectively. When two more phenyl rings are attached to TPE, the resulting luminogen TPEBPh shows improved EL property. The OLED of TPEBPh with a configuration of ITO/NPB (50 nm)/TPEBPh (30 nm)/BCP (20 nm)/Alq$_3$ (10 nm)/LiF (1 nm)/Al (150 nm) emits a blue EL at 476 nm with a L_{max} of 10 680 cd m^{-2}, a $\eta_{C,max}$ of 5.15 cd A^{-1} and a $\eta_{ext,max}$ of 2.56%. TPTPE shows slightly better device performances than TPEBPh. An OLED based on TPTPE exhibits a sky blue EL at 488 nm with L_{max}, $\eta_{C,max}$ and $\eta_{ext,max}$ of 10 800 cd m^{-2} 5.8 cd A^{-1} and 2.7%, respectively. Compared with TPTPE, the starburst BTPTPE emits a bluer EL (448 nm). Inferior EL efficiencies (2.8 cd A^{-1} and 1.6%) are attained in the OLED of BTPTPE,[14a] probably due to its low molecular conjugation caused by the severe steric congestion between the triphenylvinyl substituents. Among the luminogens, BTPE shows the best device performance. The BTPE-based device [ITO/NPB (60 nm)/BTPE (20 nm)/TPBi (10 nm)/Alq$_3$ (30 nm)/LiF (1 nm)/Al (100 nm)] is turned on at low bias (~4 V) and radiates brilliantly at 488 nm with a L_{max} of 11 180 cd m^{-2}, a $\eta_{C,max}$ of 7.26 cd A^{-1} and a $\eta_{ext,max}$ of 3.17%.[13] Clearly, BTPE is a promising solid-state emitter for OLEDs.

Light extraction from OLEDs is an important issue for practical application, as only ~20% of the internally generated photons escape from the device and the remaining are lost at the air–glass and ITO–glass interface due to the total internal reflection effect. To address this problem, scattering the waveguide light by using a diffuser film is a simple and effective approach. We find that nano-structured material made of TPE is promising as a scattering medium for extracting waveguide light from the substrate.[15a] TPE can facilely form crystalline nanoparticles by vacuum sublimation of its powder. The as-deposited TPE film consisting of nanoparticles (Fig. 3a) scatters light effectively, based on which a 28% efficiency improvement for blue OLEDs is achieved. The introduction of TPE nanoparticles into the color conversion layer leads to an efficiency enhancement of 33% for blue-to-white photon conversion in a top-emitting white OLED (Fig. 3c).

BTPE is the first AIE luminogen that shows an intriguing self-assembly capability and can form crystalline nanofibers in THF–ethanol mixture with a high PL efficiency up to unity.[13] Further research demonstrates that BTPE can be easily grown into various nano-structured materials by post-annealing of its vacuum-sublimed thin film, depositing its molecules on heated glass/Au substrate or evaporating its chloroform solution. The self-assembled crystalline BTPE nanowires and nanotubes (Fig. 3b) show enhanced and blue-shifted PL, lower wettability and a stronger light scattering ability in comparison with those of BTPE amorphous film. The BTPE nanowires can also serve as an efficient scattering media for OLEDs. By depositing the BTPE nanowires on the backside of the glass substrate as a scattering medium for the $Ir(ppy)_3$-based OLED, the efficiency at a driving current of 1 mA cm^{-2} is boosted from 78.2 to 102.8 cd A^{-1}, showing a 31.5% enhancement (Fig. 3d).[15b] These results reveal that BTPE nanowires have potential for application in nano-optoelectronic devices, self-cleaning surfaces or brightness enhancement films.

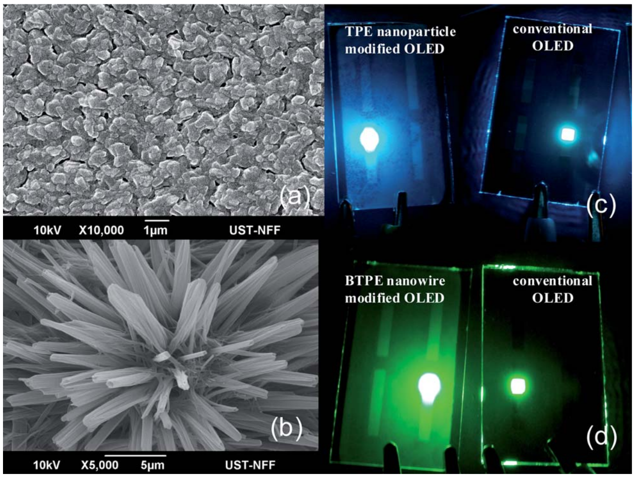

Fig. 3 Scanning electron microscopy images of (a) the 300 nm as-deposited TPE film formed at room temperature and (b) standing BTPE nanotubes fabricated by slow evaporation of its chloroform droplet in air. Photos of (c) blue and (d) green OLEDs with and without (c) TPE-scattering film and (d) BTPE-scattering medium. The TPE and BTPE modified OLEDs exhibit higher luminance and efficiency due to the efficient extraction of the substrate waveguide light. Reproduced with permission from ref. 15. Copyright (2012) The Royal Society of Chemistry and Copyright (2012) Elsevier.

2.2 Luminogens with polycyclic rings

As discussed in the introduction, conventional luminophors are generally disc-like shapes and constructed from flat planar aromatic rings. Since they are conjugated, they show intense emissions in solutions. However, in an aggregated or solid state, their molecules are stacked closely and experience strong intermolecular π–π interactions. Pyrene is one of such chromophores and shows excellent PL in solution. Many research groups have developed efficient solid-state light emitters from pyrene by modifying its molecular structure.[16] Four phenyl rings, for example, have been attached to a pyrene core. However, the resulting compound, named 1,3,6,8-tetraphenylpyrene, shows poor EL performance with a η_{ext} as low as 0.5%, although its Φ_{F} value in solution is as high as ~90%. Introduction of methylated phenyl rings as peripherals furnishes pyrene derivatives with twisted conformations, which relieve the PL bathochromic shift in the solid state. The Φ_{F} values (24–44%) of their films are close to those in dilute solutions. However, the device performances of these luminogens are still far from satisfactory with moderate $\eta_{\mathrm{C,max}}$ values of ~2.7 cd A^{-1}. Encapsulation of pyrene with large stiff dendrons can prevent close stacking of its molecules and keep the emission stable in both solution and film states. The EL efficiency (2.56 cd A^{-1}) of the solution-processed single-layer device is not so high,[17] leaving much room for further improvement.

Incorporation of a TPE unit at the periphery of pyrene affords luminogens (Chart 2)[18] with efficient PL in the solid state. For example, TPEPy is weakly luminescent in dilute solution but its fluorescence is turned on by solution thickening or aggregate formation.[7d] The Φ_{F} value of TPEPy in dilute THF solution is merely 0.34% and is much lower than that of pyrene (32%),[19] indicating that TPE works as an emission quencher in solution. In the solid state, however, TPEPy emits intensely, with a Φ_{F} value (100%) which is much higher than those of pyrene film (44%) and TPE film (49.2%) under the same conditions. Since TPE possesses a twisted conformation and is sterically demanding, it, in some sense, behaves similarly as bulky substituents to suppress π–π stacking interactions. On the other hand, it is AIE-active and electronically unsaturated, and its synergistic electronic interaction with the pyrene unit has turned the resulting adduct into an efficient solid-state emitter.

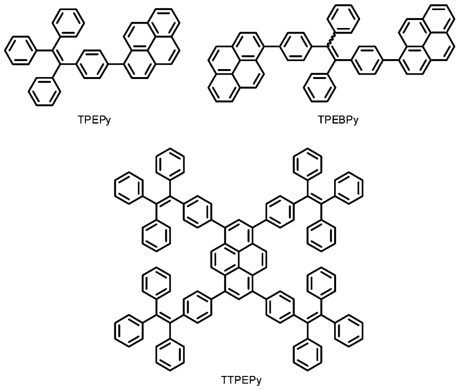

Chart 2 Chemical structures of TPE–pyrene adducts.

Adding one more pyrene ring to TPEPy generates TPEBPy (Chart 2).[20a] The Φ_F value (0.37%) of TPEBPy in solution is slightly higher than that of TPEPy (0.34%), presumably due to the presence of an additional emissive pyrene unit. Its Φ_F value in solution is still low (0.37%), indicating that the IMR process of the TPE unit works efficiently in the solution state. On the contrary, TPEBPy is highly emissive in the solid state with a unity Φ_F value. Its film emission (488 nm) is redder than that of TPEPy (468 nm), possibly due to stronger intermolecular interactions between the molecules. TPEBPy possesses higher thermal and morphological stabilities than TPEPy, exhibiting a high glass transition temperature (T_g) and thermal-decomposition temperature (T_d) of 142 and 494 °C, respectively. When four TPE units are attached to the pyrene core, the resulting molecule (TTPEPy) suffers no ACQ effect and shows AEE characteristics. The emission of TTPEPy in solution is not quenched completely by the TPE units and in THF, it is somewhat emissive at 462 nm. Although the Φ_F value is only 9.5%, it is still much higher than those of TPEPy and TPEBPy. This can be interpreted as its higher molecular conjugation and relatively stiffer molecular conformation. The PL spectrum of the amorphous TTPEPy film resembles that of a solution and peaks at 483 nm, suggesting that they originate from the same emitting species with similar intermolecular interactions. The Φ_F value is measured to be 70%,[21] more than 7-fold higher than the solution value. TTPEPy shows high T_g and T_d values of 240 and 460 °C, revealing that it enjoys high thermal and morphological stabilities.

The OLED [ITO/NPB (60 nm)/TPEPy (20 nm)/TPBi (10 nm)/Alq$_3$ (30 nm)/LiF (1 nm)/Al (100 nm)] fabricated using TPEPy as the emitter emits sky-blue light with a L_{max} of 13 400 cd m^{-2}. The EL efficiencies attained by the device are 7.3 cd A^{-1}, 5.6 lm W^{-1} and 3.0%. TPEBPy also exhibits good EL performance. The TPEBPy-based EL device [ITO/NPB (60 nm)/TPEBPy (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm)] shows green EL emission at 516 nm, which is red-shifted from the PL emission of the solid thin film due to the microcavity effect. The L_{max}, $\eta_{C,max}$ and $\eta_{ext,max}$ attained by the device are 25 500 cd m^{-2}, 6.0 cd A^{-1} and 2.1%., respectively. Thanks to the multiple TPE units, TTPEPy shows the best EL performance. Multilayer EL devices with configurations of ITO/NPB (60 nm)/TTPEPy (40 or 26 nm)/TPBi (20 nm)/LiF (1 nm)/Al (100 nm) (device A and B) are fabricated and give sky blue lights peaked at ~490 nm. The TTPEPy-based devices enjoy good spectral stability and no obvious change in the EL spectrum is observed when the voltage is raised up to 15 V. Fig. 4 shows the characteristic curves of the EL devices based on TTPEPy. Device A shows high EL efficiencies of 10.6 cd A^{-1}, 5.8 lm W^{-1} and 4.04%. Even better performance is observed in device B. It starts to emit at a lower voltage of 3.6 V, showing a L_{max} of 36 300 cd m^{-2}. The $\eta_{C,max}$ and $\eta_{ext,max}$ attained by the device are 12.3 cd A^{-1} and 4.95%,[21] respectively. The $\eta_{ext,max}$ approaches the limit of the possible and maintains a reasonably high value even at high current density. For example, the $\eta_{ext,max}$ at a high current density of 415 mA cm^{-2} is 3.5%. These results, although preliminary, are much better than those of pyrene-based materials reported previously.

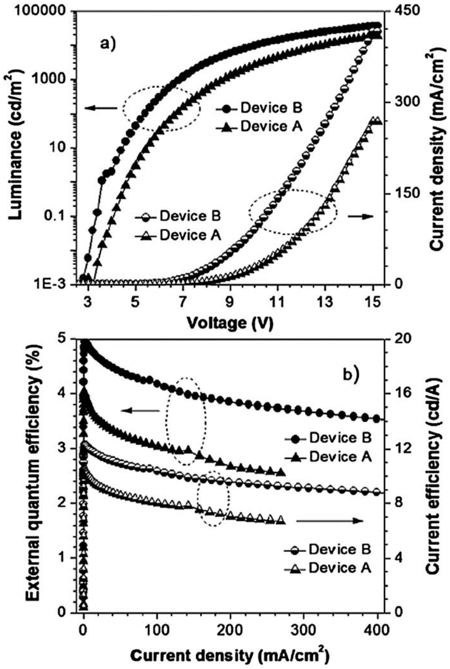

Fig. 4 a) Changes in luminance and current density with applied bias. b) Plots of external quantum efficiency and current efficiency *versus* current density in multilayer EL devices of TTPEPy. Reproduced with permission from ref. 21. Copyright (2010) The Royal Society of Chemistry.

The success in preparing efficient luminogens by melting TPE and pyrene at the molecular level suggests that this strategy is versatile to resolve the ACQ problem of conventional chromophores and meanwhile creates high-performance solid-state emitters for OLEDs. To verify the applicability of such a strategy, a series of luminogens composed of TPE and various aromatic hydrocarbons, such as naphthalene, anthracene and phenanthrene (Chart 3) are facilely synthesized by Suzuki coupling reaction.[20] Like TPEPy, all the luminogens are almost non-emissive in solutions but their solid thin films exhibit AIE characteristics with high Φ_F values up to 100%. They are promising light emitters for OLEDs. For example, the device utilizing TPE-2-Np as the emitter performs well with a L_{max} of 19 800 cd m^{-2}, a $\eta_{C,max}$ of 7.2 cd A^{-1}, a $\eta_{P,max}$ of 4.2 lm W^{-1} and a $\eta_{ext,max}$ of 2.7%.[20a]

Some research groups have worked on the synthesis of solid-state emitters for OLED application constructed from TPE and conventional luminophors. However, in most cases, the AIE or AEE attributes of the hybrid luminogens are not presented. Park

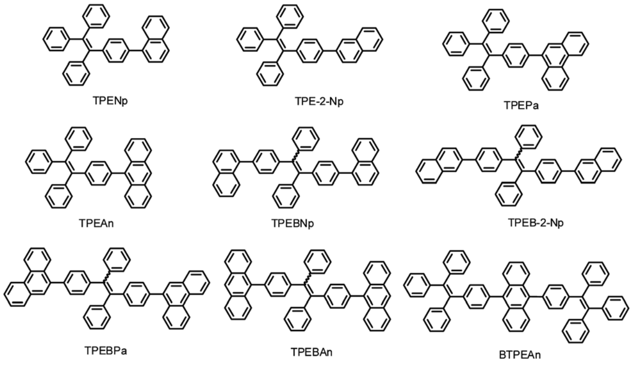

Chart 3 Examples of AIE luminogens constructed from TPE and conventional aromatic hydrocarbons.

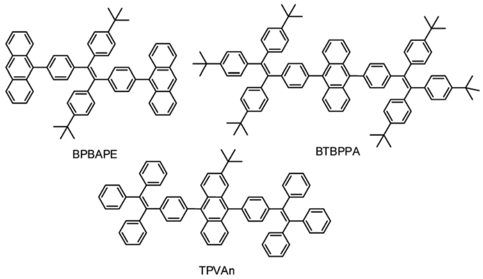

Chart 4 Examples of blue emitters prepared from TPE and anthracene building blocks.

and co-workers[22] reported a series of blue emitters from TPE and anthracene building blocks (Chart 4). Introduction of a *tert*-butyl group to the TPE unit partially hampers the bathochromic shift in the PL spectrum in the solid-state. The non-doped OLED based on BPBAPE shows blue EL at 475 nm with a high $\eta_{\mathrm{C,max}}$ of 10.33 cd A^{-1}. Shu and co-workers[23] prepared TPVAn by introduction of a *tert*-butyl group to the anthracene ring of BTPEAn and found that it shows AIE characteristics (Chart 4). The Φ_F value of its solid thin film is 89%, which is much higher than that in solution (6%). TPVAn is morphologically stable, showing a high T_g of 155 °C. The non-doped OLED utilizing TPVAn as emitter exhibits bright saturated-blue emission with Commission Internationale de L'Eclairage (CIE) coordinates of (0.14, 0.12) and a $\eta_{\mathrm{C,max}}$ of 5.3 cd A^{-1}. The $\eta_{\mathrm{ext,max}}$ achieved by the device is 5.3%, approaching to the limit of possible. With such efficient blue luminogen, as well as an orange fluorophor, a high-performance doped white OLED (WOLED) is fabricated, which displays a $\eta_{\mathrm{C,max}}$ of 13.1 cd A^{-1}, a $\eta_{\mathrm{ext,max}}$ of 4.9% and CIE coordinates of (0.33, 0.39).

Replacement of the phenyl ring(s) in TPE with pyrene ring(s) affords pyrene-substituted ethenes (TPPyE and DPDPyE; Chart 5), which show excimeric emission in the solution and aggregated states. The Φ_F values of TPPyE and DPDPyE in dilute THF solutions are low and equal to 2.8 and 9.8%, respectively. However, the Φ_F values of their amorphous films are much higher and reach 61 and 100%,[24] respectively. This demonstrates that both molecules emit more efficiently in the condensed phase than in a molecularly dispersed state, revealing that they are AEE-active. The π–π intermolecular interactions between the pyrene rings coupled with the multiple C–H···π hydrogen bonds have efficiently restricted the IMR process,[25] which blocks the nonradiative relaxation channel and hence makes the luminogens highly emissive in the solid state (Fig. 5). The involved *J*-aggregation may further help to improve the emission efficiency. The efficient excimeric emission from TPPyE and DPDPyE makes us think in a different way in the further design of materials.

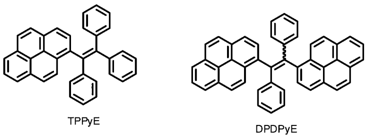

Chart 5 Chemical structures of pyrene-substituted ethenes.

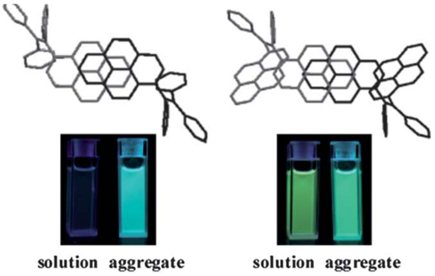

Fig. 5 The molecular packing of TPPyE and DPDPyE and their photos in solution and aggregated states taken under 365 nm UV illumination. Reproduced with permission from ref. 24. Copyright (2011) The Royal Society of Chemistry.

The EL devices of both pyrene-substituted ethenes perform outstandingly.[24] For instance, the EL device of DPDPyE [ITO/NPB (60 nm)/DPDPyE (20 nm)/TPBi (10 nm)/Alq_3 (30 nm)/LiF (1 nm)/Al (100 nm)] shows a green emission peak at 516 nm. The device is turned on at a quite low voltage of 3.2 V and radiates intensely with a L_{max} of 49 830 cd m^{-2} at 15 V. The $\eta_{\mathrm{C,max}}$ and $\eta_{\mathrm{ext,max}}$ of the device are 10.2 cd A^{-1} and 3.3%, respectively, which are much higher than those of the control device based on Alq_3, a well-known green EL emitter. The good EL performance of DPDPyE should be attributed to, not only its outstanding PL efficiency in the solid state, but also the enhanced carrier mobility due to π–π stacking interactions between the pyrene rings.

2.3 Luminogens with hole-transporting groups

Materials which possess multiple functional properties, such as light-emitting and hole- and/or electron-transporting capabilities are more useful for high-technological applications and are in great demand because they can simplify the device structure and reduce fabrication cost. Triphenylamine (TPA) is well-known for its high hole mobility and has been widely used as a building block in the construction of hole-transporting materials.[26] However, it suffers from the ACQ effect in the solid state, which undermines the device performance.[4] Delightfully, the ACQ problem is well solved by attachment of the TPE unit as a substituent to its molecular structure. A series of TPE–TPA adducts have been prepared that show not only high PL efficiency, but also good hole-transporting property. The molecular structures of some of these luminogens are illustrated in Chart 6 as examples.[27,28]

Thanks to the TPE unit, all the TPE–TPA adducts show AIE features and emit intense sky blue to green lights in solid films with high Φ_F values up to unity. Their PL emissions are not the summation of the fluorescence from individual TPE and TPE units but from the radiative decay of the excited state of the whole π-conjugated molecules. This accounts for their redder emissions than those of TPE and TPA. The orbital distributions of the HOMO and LUMO energy levels of these luminogens are close to those of NPB, a well-known hole-transporting material, revealing that they are in favor of hole-injection and transportation. For example, 2TPATPE possesses a high HOMO energy level of −5.15 eV determined by cyclic voltammetry. Its hole mobility measured by the time-of-flight technique is reasonably high and is equal to 5.2×10^{-4} cm^2 V^{-1} s^{-1}. A *p*-type

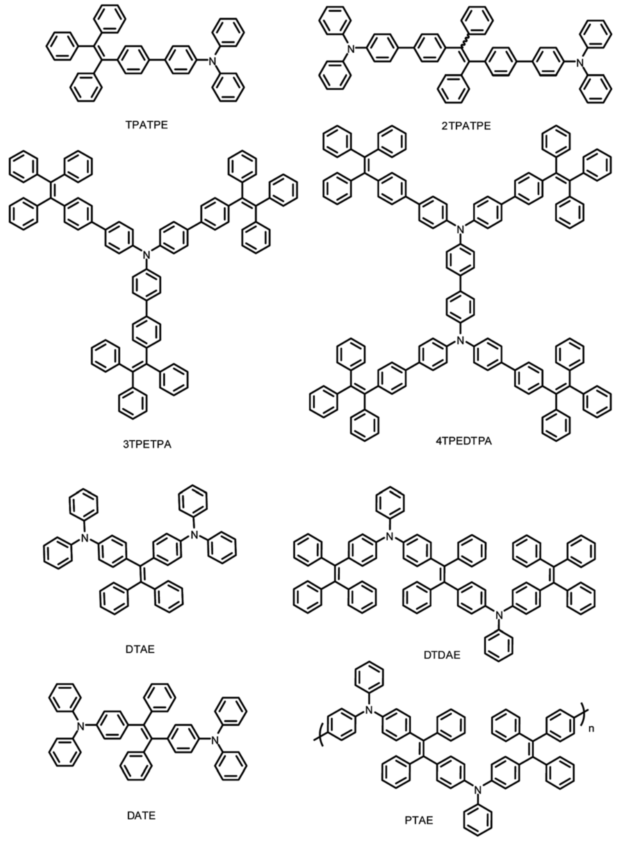

Chart 6 Chemical structures of TPE–TPA adducts.

field effect transistor based on the amorphous film of 2TPATPE is fabricated, which exhibits high field effect mobility up to 2.6 × 10^{-3} cm^2 V^{-1} s^{-1}.[29] The 2TPATPE-based OLED without a hole-transporting layer (HTL) [ITO/2TPATPE (60 nm)/TPBi (10 nm)/Alq$_3$ (30 nm)/LiF/Al (200 nm)] shows better performances than those with a HTL, thanks to the good hole-transporting property of the TPA units in the hybrid molecule. The device is turned on at a low voltage of 3.2 V and shows a $L_{\max}$ of 33 700 cd m^{-2}, a $\eta_{\mathrm{C,max}}$ of 13.0 cd A^{-1}, a $\eta_{\mathrm{P,max}}$ of 11.0 lm W^{-1} and a $\eta_{\mathrm{ext,max}}$ of 4.4%, which are better than those of OLED with NPB as the HTL.[27a] The use of NPB as an additional HTL may break the charge balance in the EL device and hence decrease the device performance. 4TPEDTPA also plays dual roles in the EL device. A device using 4TPEDTPA as both the light-emitting and hole-transporting layers shows high $L_{\max}$, $\eta_{\mathrm{C,max}}$, $\eta_{\mathrm{P,max}}$ and $\eta_{\mathrm{ext,max}}$ of 10 723 cd m^{-2}, 8.0 cd A^{-1}, 5.2 lm W^{-1} and 3.7%, respectively.[28] Oligomers and polymers built from TPE and TPA units are also promising OLED materials due to their high emission efficiency in the solid state and good hole-transporting capability. For example, the device of DTDAE emits intensely with a $L_{\max}$ of 40 940 cd m^{-2} and a $\eta_{\mathrm{C,max}}$ of 11.2 cd A^{-1}.[27b] These results demonstrate that the combination of the AIE property of TPE and the good hole-transporting property of TPA into one molecule allows the simplification of the device configuration without debilitating the EL performance. Coupled with their efficient PL and EL, these TPE–TPA adducts are anticipated to find an array of applications in organic electronics and optics.

Carbazole is another conventional ACQ chromophore with good electron-donating ability. It is widely used to construct materials with both good light-emitting[30] and hole-transporting properties.[31] In addition, its high resistance to thermolysis is favorable for the construction of luminogens with high thermal stability.[32] The TPE–carbazole adducts shown in Chart 7 show typical AIE characteristics and are highly emissive in the solid state with Φ_{F} values up to unity. The luminogens possess better thermal and morphological stabilities than those of their TPE–TPA counterparts. For example, the T_{g} and T_{d} of TTPECaP are 179 and 554 °C respectively, which are much higher than those of 3TPETPA ($T_{\mathrm{g}} = 143$ °C and $T_{\mathrm{d}} = 359$ °C).[33]

Owing to the good hole-transport property of the carbazole unit, the EL devices of the TPE–carbazole adducts work better in the absence of HTL than those in the presence of HTL. The OLED [ITO/TPECaP (80 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm)] using TPECaP as both light-emitting and hole-transporting layers gives a $L_{\max}$ of 12 930 cd m^{-2} and high $\eta_{\mathrm{C,max}}$ and $\eta_{\mathrm{ext,max}}$ of 5.5 cd A^{-1} and 2.2%, respectively. These values are much better than those of device with NPB layer (11 060 cd m^{-2}, 3.5 cd A^{-1} and 1.7%). *p*-BCaPTPE and TTPECaP also exhibit higher EL efficiencies in devices without HTL, affording reasonably high $\eta_{\mathrm{C,max}}$ of 6.3 and 6.6 cd A^{-1}, respectively.[34]

Generally, luminogens with three-dimensional (3D) structures can better hamper the close packing between molecules, preventing the formation of species that are detrimental to the light emission. Endowing molecules with 3D structures is a commonly used approach to achieve high emission efficiency and good thermal stability. This is also workable in the AIE system. The 3D luminogen BTPEBCF (Chart 8) is prepared by attachment of carbazole units to the 9,9-positons of a TPE-end-capped fluorene core and is AIE-active with a solid state Φ_{F} value of 100%.[35] Its T_{g} and T_{g} are 147 and 474 °C, respectively. Its HOMO energy level (−5.27 eV) is quite close to that of NPB, suggesting that it possesses good hole-transporting properties. OLED based on BTPEBCF [ITO/NPB (60 nm)/BTPEBCF (20 nm)/TPBi (10 nm)/Alq$_3$ (30 nm)/LiF (1 nm)/Al (100 nm)] affords high EL efficiencies up to 7.9 cd A^{-1} and 2.9%.

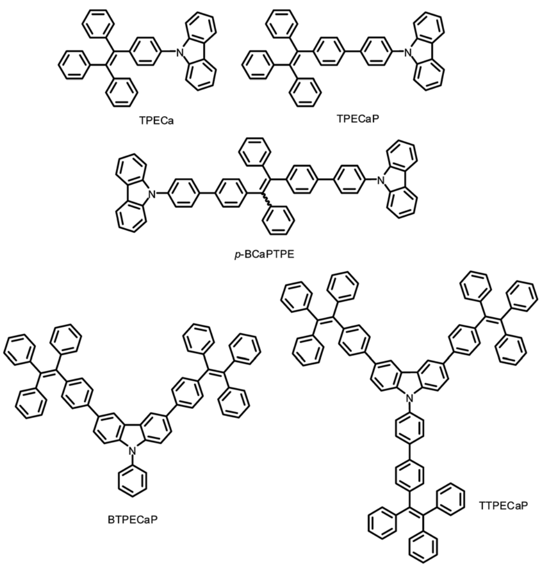

Chart 7 Chemical structures of TPE–carbazole adducts.

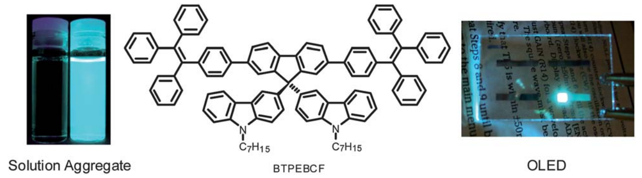

Chart 8 Chemical structure and photos of THF solution, aqueous suspension and OLED of BTPEBCF. Reproduced with permission from ref. 35*a*. Copyright (2011) The Royal Society of Chemistry.

Melding TPE with TPA or carbazole can generate efficient emitters with good hole-transporting properties as discussed above. In these luminogens, the TPE units undergo free rotations in the solution state, which consume the energy of the excitons, thus rendering the luminogens weakly fluorescent. In our previous studies, we found that the RIR process can be activated by many external factors, such as solvent viscosity, temperature, pressure, *etc.*[7] Rigidification of the conformation of TPE can also effectively hinder the IMR process and change its emission behavior accordingly. Two TPE derivatives [(*Z*)-*o*-BCaPTPE and (*Z*)-*o*-BTPATPE; Chart 9] were synthesized stereoselectively by the McMurry coupling reaction of 2-substituted benzophenones. Owing to the intramolecular π–π interactions, the luminogens adopt a rigid chiasmatic configuration with high T_g and T_d up to 222 and 427 °C, respectively. Both (*Z*)-*o*-BCaPTPE and (*Z*)-*o*-BTPATPE emit strongly with Φ_F values of 43 and 38%, respectively, in dilute THF solutions, which are much higher than those of their linear counterparts (2TPATPE and *p*-BCaPTPE). The rigid chiasmatic conformation of the luminogens has partially hampered the IMR process and hence makes them somewhat emissive in solutions. In the solid state, the IMR process is further restricted, which increases the Φ_F values of (*Z*)-*o*-BCaPTPE and (*Z*)-*o*-BTPATPE to 100 and 85%, respectively.

The chiasmatic conformation coupled with intramolecular π–π stacking has endowed (Z)-*o*-BCaPTPE and (Z)-*o*-BTPATPE with fascinating properties. Whereas their counterparts with linear structures exhibit hole-transporting property only, (*Z*)-*o*-BCaPTPE and (*Z*)-*o*-BTPATPE show bipolar charge mobility as revealed by TOF measurement, although they are constructed from electron-donating groups. High hole and electron mobilities up to 4.9 × 10^{-4} and 4.3 × 10^{-4} $cm^2\ V^{-1}\ s^{-1}$, respectively, are achieved in (*Z*)-*o*-BCaPTPE.[34] Both chiasmatic luminogens can serve well as multifunctional materials in OLEDs. The OLED of (*Z*)-*o*-BCaPTPE [ITO/NPB (60 nm)/(*Z*)-*o*-BCaPTPE (60 nm)/LiF (1 nm)/Al (100 nm)], in which (*Z*)-*o*-BCaPTPE serves as both light-emitting and electron-transporting layers and exhibits high EL efficiencies up to 7.9 cd A^{-1} and 3.1%. Further optimization of the device structure would lead to better results. These merits make chiasmatic luminogens a new class of promising materials for optoelectronic devices.

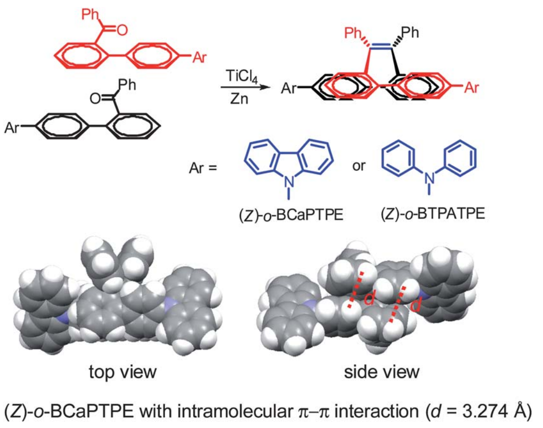

Chart 9 Synthesis and structures of the chiasmatic luminogens. Reproduced with permission from ref. 34. Copyright (2011) Wiley-VCH.

2.4 TPE-substituted silanes

Aryl-substituted silanes are usually used as light emitters as well as hole-blocking layers in blue OLEDs.[36] Recently, they have been considered as attractive host materials for blue electrophoresence devices.[37] Current studies focus on the improvement of their morphological stability as well as their triplet energy. Attachment of rigid and bulky carbazole into non-conjugated silanes turns out to be an effective approach.[38] However, the ACQ problem of the resulting hybrid materials remains unsolved.

Merging TPE with silane affords AIE-active blue materials (Chart 10) with high Φ_F values (55–64%) in the solid state. OLEDs fabricated using these luminogens as emitters show blue EL with good performances. For example, the device based on $TPESiPh_3$ shows a deep blue light of 452 nm with a $\eta_{C,max}$ of 2.1 cd A^{-1} and a $\eta_{ext,max}$ of 1.6%.[39] Thanks to the flexible sp^3 hybridized silicon atom, these TPE-substituted silanes possess high HOMO and LUMO energy levels of −5.2 and −1.8 eV, respectively, and large band gaps of ~3.4 eV. These suggest that they are good candidates as host materials.[40] Further introduction of chromophores with high triplet energy, such as carbazole and TPA, helps further increase their performances, where the ACQ effect is alleviated as well.

Siloles, such as methylpentaphenylsilole (MPPS), are AIE luminogens with high PL efficiency in the solid state. Their unique σ*–π* conjugation endows them with low-lying LUMOs and hence high electron affinity and fast electron mobility.[41] The OLEDs fabricated from silole derivatives afford remarkably impressive performances with EL efficiencies up to theoretical limit.[42] Connecting TPE and MPPS at the molecular level in

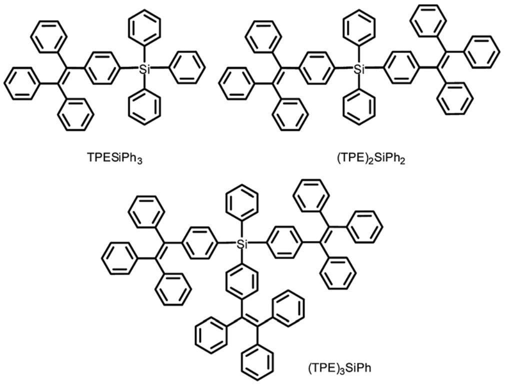

Chart 10 Chemical structures of TPE-substituted silanes.

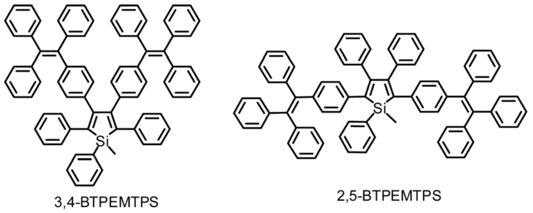

Chart 11 Chemical structures of TPE–MPPS adducts.

different patterns generates new AIE luminogens (Chart 11),[43] which serve as models to understand the AIE mechanism and structure–property relationship. Compared with 3,4-BTPEMTPS, 2,5-BTPEMTPS shows higher morphological and thermal stabilities. In the solution and aggregate states, it also shows redder and more efficient emission than 3,4-BTPEMTPS, presumably due to its higher conjugation. Similarly, 2,5-BTPEMTPS-based OLED [ITO/NPB (60 nm)/2,5-BTPEMTPS (40 nm)/TPBi (20 nm)/LiF (1 nm)/Al (100 nm)] exhibits yellow EL peaked at 552 nm, which is 32 nm bathochromically shifted from that of its 3,4-regioisomer. The OLED of 2,5-BTPEMTPS enjoys outstanding spectral stability, with no spectral change being observed when the applied voltage is increased from 8 to 15 V. The device shows a L_{max} of 12 560 cd A^{-1} and a $\eta_{C,max}$ of 6.4 cd A^{-1}, which are much higher than those attained by the EL device based on 3,4-BTPEMTPS (3980 cd m^{-2} and 4.96 cd A^{-1}).

Doping of small amounts of fluorescent dyes into host materials is a widely used technique to overcome the concentration quenching or ACQ effect. The emission from dopant is usually considered to occur *via* the Förster energy transfer and/or charge transfer from host to dopant. Therefore, chromophores with efficient solid-state emission and wide energy band gaps are good candidates as host materials.[44] A wide variety of host materials have been developed and utilized in doped OLEDs. The possibility of using AIE-active luminogens as host materials has, however, been rarely explored. As discussed above, the amorphous film of BTPE emits efficiently at 499 nm. The OLED using BTPE as the emitter affords EL emission at 488 nm with high efficiencies of 7.26 cd A^{-1} and 3.17%. Since the solid-state PL and EL spectra of BTPE partially overlap with the absorption spectrum of 2,5-BTPEMTPS, this may allow the former and the latter to act as host and guest materials, respectively. The OLED with a configuration of [ITO/NPB (60 nm)/2,5-BTPEMTPS:BTPE (20 nm)/TPBi (10 nm)/Alq_3 (30 nm)/LiF (1 nm)/Al (100 nm)] shows no EL peak from the BTPE host, indicative of an efficient energy transfer from the BTPE host to the 2,5-BTPEMTPS guest. The luminogenic blend with 20% 2,5-BTPEMTPS exhibits a yellow EL located at 544 nm, which is blue-shifted from that of pure 2,5-BTPEMTPS (552 nm) due to the segregation of its molecules and hence intermolecular interactions by BTPE. The L_{max} (10 480 cd A^{-1}) and $\eta_{C,max}$ (7.02 cd A^{-1}) are higher than those achieved by a non-doped device, revealing that BTPE can serve not only as the emitter but also as the host material for doped OLEDs.

2.5 TPE-substituted boranes

Luminogens containing boron species have recently drawn much attention due to their distinctive electronic properties and promising applications as functional materials for optoelectronic devices, chemosensors and cell imaging, *etc.*[45] The unique properties of such a kind of luminogen arise from the p_π–π^* conjugation between the vacant p orbital of the boron atom and the π^* orbital of the π-conjugated framework. The empty p_π orbital has endowed these luminogens with a strong electron-accepting capability, enabling them to serve as both light-emitting and electron-transporting materials. The success in the creation of efficient solid-state emitters with good hole-transporting properties encourages us to develop AIE luminogens with high electron affinity by melding TPE and borane at the molecular level. It is anticipated that luminogens with emission colors covering from blue to red will be prepared when different organoborons are used.

Chart 12 shows examples of TPE-decorated boranes. These luminogens are thermally stable and are highly emissive in the solid state. Their PL and EL emission colors cover from sky-blue (BTPEPBN), green (BTPEPPBN), yellow (BTPPzBN) to red (BTPEBodipy and TTPEBodipy). TPEDMesB is an example of such a luminogen, which possesses a simple chemical structure but shows impressive PL and EL properties. It is AIE-active and luminesces intensely at 478 nm in the solid state with a Φ_F value of unity.[46] Thanks to the boron atom and the TPE unit, it exhibits bifunctionality as a light emitter and electron-transporting material. The device using TPEDMesB as the light-emitting layer [ITO/NPB (60 nm)/TPEDMesB (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm)] shows EL emission at 496 nm with a $\eta_{C,max}$ of 5.78 cd A^{-1} and a $\eta_{ext,max}$ of 2.3%. Even better device performance is achieved when TPEDMesB is used as both the light-emitting and electron-transporting layers. The EL device [ITO/NPB (60 nm)/TPEDMesB (60 nm)/LiF (1 nm)/Al (100 nm)] exhibits high EL efficiencies up to 7.13 cd A^{-1} and 2.7%. Evidently, TPEDMesB possesses a good electron-transporting property. Luminogens with four-coordinate organoborons also show good EL properties. For instance, the device of BTPEPBN exhibits a $\eta_{C,max}$ of 4.43 cd A^{-1}, a $\eta_{P,max}$ of 1.64 lm W^{-1} and a $\eta_{ext,max}$ of 1.52%, which are much better than

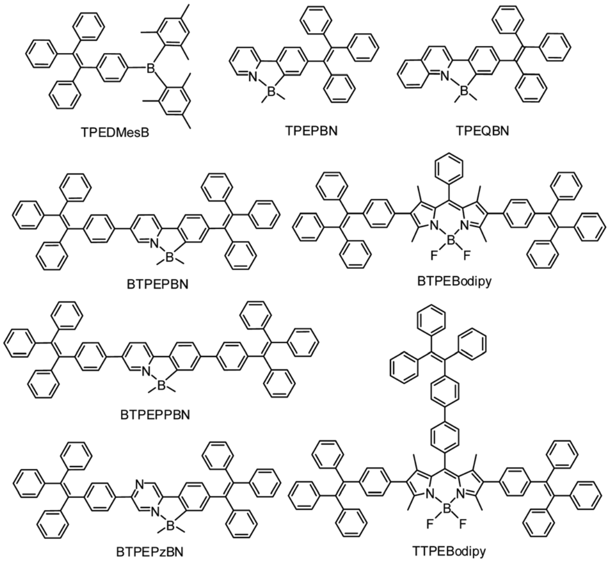

Chart 12 Chemical structures of TPE-substituted boranes.

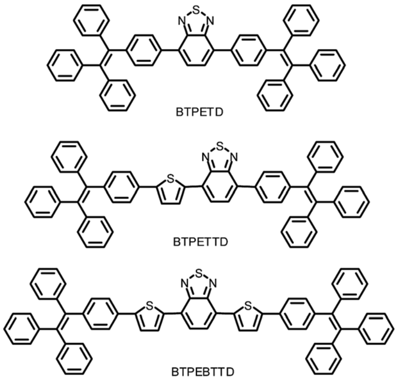

Chart 13 Examples of TPE-endcapped benzo-2,1,3-thiadiazoles.

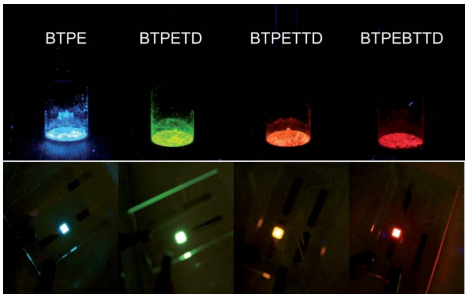

Fig. 6 Photos of powders of BTPE, BTPETD, BTPETTD and BTPEBTTD taken under illumination of a UV lamp (top) and their EL devices (bottom). Reproduced with permission from ref. 50. Copyright (2011) The Royal Society of Chemistry.

those attained by the device based on its parent luminogen without B–N coordination (0.46 cd A^{-1}, 0.14 lm W^{-1}, and 0.21%). Similar enhancement in EL efficiencies is also observed in the devices of BTPEPzBN and BTPEPPBN, suggesting that introduction of B–N coordination benefits the EL properties of the luminogens.

2.6 Emission color tunability

For full color display and white lighting applications, robust blue, green and red materials with good thermal stabilities, reasonably high Φ_F values and excellent color fidelity are desired. Most red chromophores, such as polycyclicaromatic hydrocarbons, pyran-containing dyes, Nile red, difluoro-boradiazaindacene (BODIPY) derivatives as well as transition metal-containing complexes are highly susceptible to concentration quenching due to the severe intermolecular π–π interactions and/or active dipole–dipole interactions.[47] Material chemists attempted to solve their ACQ problem by disrupting chromophore aggregation using various methods such as the introduction of branched and non-planar molecular architectures.[48] Most of the approaches, however, have met with limited success and red solid-state emitters that function efficiently in non-doped devices are still extremely rare.

Based on the experience of the creation of efficient solid-state blue, green and yellow emitters as presented above, efficient red materials are achieved by the covalent incorporation of TPE to heterocyclic benzo-2,1,3-thiadiazole core, a well-known strong electron-withdrawing unit and building block for red light-emitting materials.[49] The presence of heteroatoms in the luminogens can induce electronic perturbation such as polarization caused by intramolecular charge transfer. This will alter the photophysical properties and tune the emission colors of the luminogens. The insertion of a thiophene unit can further provoke push–pull interactions as well as molecular conjugation. Thus, BTPETD is green emissive, while BTPETTD and BTPEBTTD emit orange-red and red PL upon photoexcitation (Chart 13). All the luminogens exhibit reasonably high Φ_F values in the solid state and possess high thermal and morphological stabilities. For example, the BTPETTD film emits at 600 nm with a Φ_F value of 55%, which is slightly higher than the solution value (37%). Its T_g and T_d are measured to be 139 and 495 °C, respectively.[50]

The OLEDs of BTPETD, BTPETTD and BTPEBTTD [ITO/NPB (60 nm)/emitter (20 nm)/TPBi (10 nm)/Alq_3 (30 nm)/LiF (1 nm)/Al (100 nm)] show EL emission peaks at 540, 592 and 668 nm, respectively, which are close to the PL of their films. A device based on BTPETD shows a L_{max} of 13 540 cd m^{-2}, a $\eta_{C,max}$ of 5.2 cd A^{-1} and a $\eta_{ext,max}$ of 1.5%. Even better performances are observed in BTPETTD. The device of BTPETTD radiates orange-red light brilliantly with a L_{max} of 8330 cd m^{-2}, a $\eta_{C,max}$ of 6.4 cd A^{-1} and a $\eta_{ext,max}$ of 3.1%, which are much higher than the values attained by most non-doped red OLEDs. Combined with BTPE, the EL emission colors of these luminogens cover most of the visible spectral range (Fig. 6).

BTPEBTTD exhibits red EL but its L_{max} and $\eta_{ext,max}$ are merely 1640 cd m^{-2} and 1.0%. When one more TPE unit is further attached to BTPEBTTD, a new luminogen TTPEBTTD is generated (Chart 14).[51a] This luminogen exhibits stronger solid-state emission and higher T_g (174 °C) and T_d (465 °C) than BTPEBTTD. Compared with BTPEBTTD, TTPEBTTD possesses a more distorted molecular conformation, as revealed by its shorter emission wavelength. Non-doped OLED with improved EL performance is achieved using TTPEBTTD as the

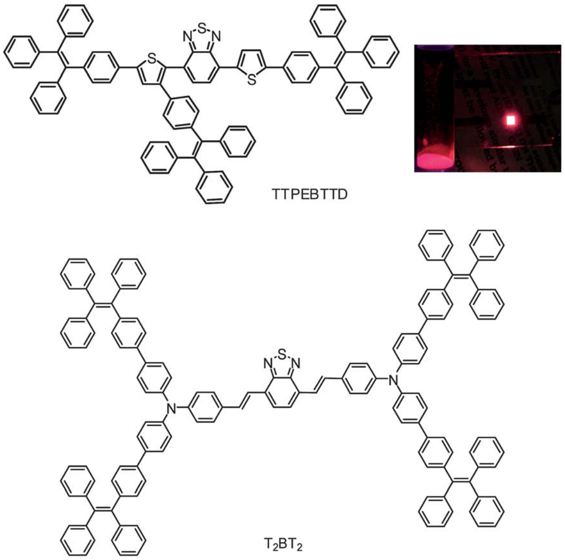

Chart 14 Chemical structures of TTPEBTTD and T_2BT_2 and photos of TTPEBTTD powder taken under illumination of a UV lamp and its EL device.

emitter. The device exhibits red light (CIE = 0.67, 0.32) with efficiencies ($\eta_{ext,max} = 3.7\%$ and $\eta_{C,max} = 2.4$ cd A^{-1}) higher than those of the BTPEBTTD-based device. This is probably due to the further intramolecular energy transfer from the additional TPE unit as well as a weakening in the intermolecular interaction between the benzo-2,1,3-thiadiazole core and the thiophene rings. This suggests that the device performance increases with the number of TPE units, thanks to its high PL efficiency in the solid state.

Similar findings have been observed by other groups. For example, Xu and co-workers[51b] reported a star-shaped red luminogen (T_2BT_2) containing a benzo-2,1,3-thiadiazole core, TPA bridges and TPE peripheries. Due to the presence of multiple TPE units, the luminogen is AEE-active and shows high T_g and T_d values of 199 and 529 °C, respectively. The non-doped OLED using T_2BT_2 as the light-emitting layer exhibits red light with a L_{max} of 13 535 cd m^{-2} and a $\eta_{C,max}$ of 6.81 cd A^{-1}. Wang and co-workers[51c] prepared a series of luminogens composed by the electron-deficient core of [1,2,5]thiadiazolo[3,4-g]quinoxaline or benzo[1,2-c; 4,5-c′]bis[1,2,5]thiadiazole and TPE end-cappers. The resulting luminogens show the AEE effect and their films emit near-infrared (NIR) PL and EL emissions peaked in the range of 704–883 nm. Efficient non-doped NIR OLEDs are achieved using these materials as emitting layers, which afford a maximum radiance and a $\eta_{ext,max}$ up to 2917 mW Sr^{-1} m^{-2} and of 0.89%, respectively. These results reveal that TPE is an efficient building block to construct red and NIR materials for non-doped OLEDs.

3. Applications in white OLEDs

3.1 White OLEDs with doped emitters

Development of high-performance WOLEDs is a hot research topic in recent years due to their practical applications in flat panel displays and solid-state lighting. To realize white light emission, two or three emitters that emit complementary colors or three primary colors are needed. No matter whether they are fluorescent or phosphorescent, the emitters, in general, have to be doped into wide band-gap hosts to reduce the ACQ effect. As discussed above, BTPE is an AIE luminogen with a high solid-state Φ_F. In addition, it possesses a large band gap of 3.1 eV as determined by cyclic voltammetry measurement. Preliminary results demonstrate that it is not only an excellent blue emitter for non-doped OLEDs, but also a good host material for doped OLEDs. Such a luminogen is anticipated to find wide applications in OLEDs.

Due to the commercial availability of red and green fluorescent dyes C545T and DCJTB, the application of BTPE as a host material for the construction of red, green and white OLEDs is further investigated.[52] BTPE shows sky-blue EL at 488 nm in non-doped OLED, which completely vanishes and is replaced by a green (520 nm) or red emission peak (588 nm) when a tiny amount of C545T or DCJTB (1% wt) is doped (Fig. 7). This clearly demonstrates an efficient energy transfer from the BTPE host to the dopant owing to the good spectral overlap between the emission spectrum of BTPE with the absorption spectrum of the dopant. Efficient energy transfer and the exciton formation due to the narrow band gaps of the dopants results in current efficiency up to 5 and 18 cd A^{-1} for the red and green OLEDs (ROLED and GOLED), respectively.

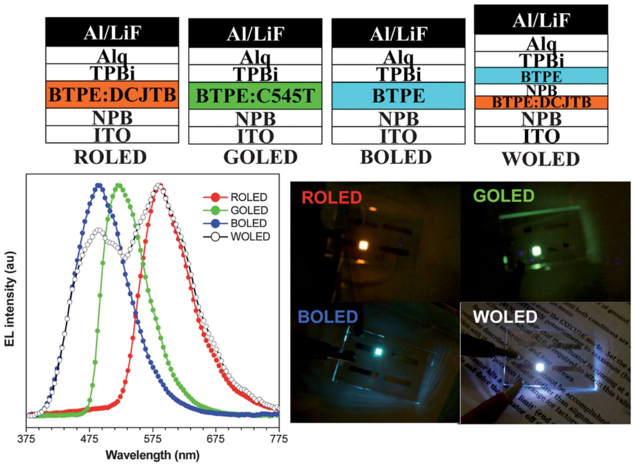

Fig. 7 Configurations, EL spectra and photos of the R, G, B and WOLEDs.

By employing BTPE as both the blue emitter and host for DCJTB, a WOLED is fabricated. The EL spectrum consists of two peaks at 488 and 588 nm originated from the emissions of the BTPE and BTPE:DCJTB layers, respectively (Fig. 7). The WOLED exhibits a moderate color stability as the CIE coordinates change from (0.36, 0.38) at 8 V to (0.38, 0.40) at 16 V. A high color rendering index of 84 and L_{max} and $\eta_{C,max}$ of 10 319 cd m^{-2} and 7 cd A^{-1}, however, are attained by the WOLED. Compared to conventional WOLEDs, which generally require three dopants (R, G and B) and at least two hosts to generate the white light, the WOLED presented here only adopts two kinds of materials (BTPE and BTPE:DCJTB) as the emitting layers and thus can significantly reduce the construction costs and simplify the fabrication procedures. These preliminary results demonstrate that BTPE is a good candidate for constructing full color and WOLEDs for display and lighting applications.

3.2 Non-doped white OLEDs based on AIE luminogens

As described above, doping is an effective method to address the ACQ problem but it may not be applicable for the fabrication of WOLEDs because such a low (~1%) and precise control on the doping concentration is required. Insufficient energy transfer from the host to the guest and/or phase separation often occurs, which leads to the decrease in the PL efficiency upon the passage of current and low stability in color chromaticity. Many non-doped WOLEDs have been reported that suffer no such problems.[53] However, these devices are usually fabricated using an ultrathin layer (~1 Å) of fluorescent dye such as C545T, DCJTB and rubrene. Accurate deposition of such an ultrathin emitting layer is thus rather difficult, making the construction of such a kind of non-doped WOLED a daunting task. Thus, exploration of new luminogenic materials that suffer no ACQ problem with high solid-state Φ_F values is important and in urgent demand for non-doped WOLEDs. In this regard, AIE luminogens are ideal candidates for such application.

Non-doped fluorescent WOLEDs based on AIE emitters have been explored for the first time using TTPEPy as the blue emitter

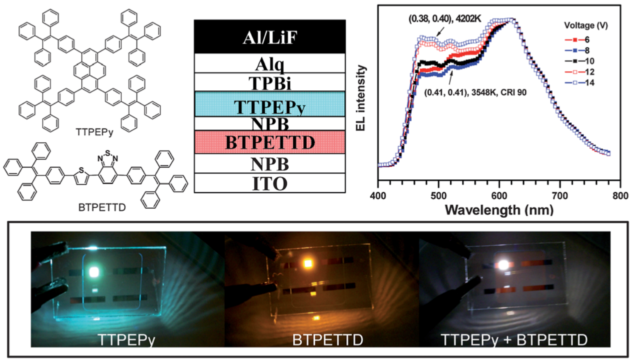

Fig. 8 Configuration and EL spectra at different bias voltages of WOLED constructed from TTPEPy and BTPETTD and photos of the B, R, and WOLEDs. Reproduced with permission from ref. 54. Copyright (2010) IOP Publishing Ltd.

and BTPETTD as the red emitter, whose device configuration is displayed in Fig. 8.[54] Due to the AIE characteristics of the emitters, the device exhibits reduced efficiency roll off. The efficiency, white color purity, CRI and color stability can be tuned by varying the thickness of the NPB layer. The WOLED exhibits a $L_{\max}$ of 18 000 cd m^{-2}, a $\eta_{\mathrm{C,max}}$ of 7.4 cd A^{-1}, a $\eta_{\mathrm{P,max}}$ of 4 lm W^{-1} and a high CRI of 90. It shows impressive color stability, suffering little change in CIE coordinates in a wide range of driving voltage.

To further reduce the material and fabrication costs, bilayer non-doped WOLED with two emitters of complementary emission colors is constructed (Fig. 9). BTPETTD is used as the red emitting component and 4,4′-bis(1-phenylphenanthro[9,10-d]imidazol-2-yl)biphenyl (DPPi) is utilized as the blue emitter. Meanwhile, BTPETTD and DPPi also function as the hole and electron-transporting layers, respectively. In the WOLED with such a configuration, most of the excitons recombine in the DPPi layer, which gives blue emission. Some excitons are captured by BTPETTD, whose radiative decay gives red EL. Additionally, part of the blue emission is converted to red light by either a color down-conversion process and/or interface Förster energy transfer. The combination of blue and red emissions yields an efficient and extremely stable white color, regardless of the driving voltage. If the positions of ITO and LiF/Al or BTPETTD and DPPi are reversed, red, instead of blue, EL will be generated, which cannot serve as the excitation source to generate blue emission and hence white light. The bilayer WOLED performs well, displaying a current efficiency of 4.2 cd A^{-1} at 1000 cd m^{-2}, CIE coordinates of (0.31, 0.31) and a high CRI of 92 in a wide range of driving voltage. Such a simple, non-doped WOLED helps simplify the device fabrication procedures and reduces the material cost.[55]

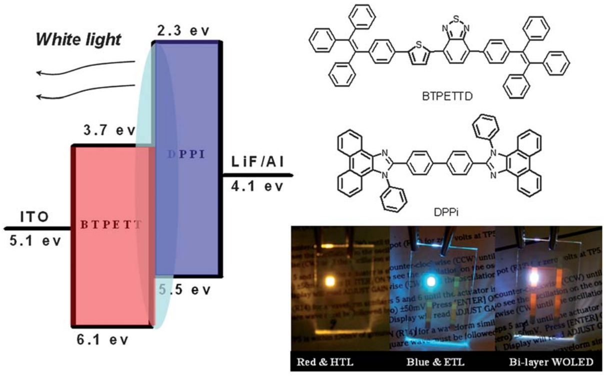

Fig. 9 Energy level diagram of the bilayer WOLED and photos of ROLED, BOLED and bilayer WOLED. Reproduced with permission from ref. 55. Copyright (2011) IOP Publishing Ltd.

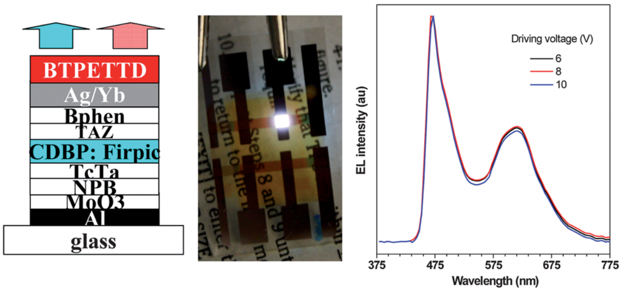

Fig. 10 Configuration, photo and EL spectra of the top-emitting WOLED. Reproduced with permission from ref. 57. Copyright (2011) Elsevier.

Development of top-emitting WOLEDs by combining blue OLEDs with color down conversion layer (CCL) is another efficient approach to simplify the fabrication process and achieve high color stability.[56] Since BTPETTD is an orange-red emissive AIE luminogen, it may serve as a promising CCL for a top-emitting blue OLED. By thermal evaporation of the BTPETTD layer on the top of a top-emitting blue OLED, 74.5% of the blue photon energy is absorbed and converted to red light with a conversion efficiency of 40%.[57] Combining with the residual blue emission, the resulting top-emitting WOLED exhibits a broad spectrum with CIE coordinates of (0.34, 0.35), a high color stability and efficiencies of 6.6%, 17.7 cd A^{-1} and 8.7 lm W^{-1} (Fig. 10). Such remarkable device performance is partly attributed to the high PL efficiency of the BTPETTD film, which is beneficial to the conversion efficiency.

4. Conclusions and outlook

Since the observation of the AIE phenomenon in 2001, luminogenic materials with AIE characteristics have attracted particular research interest due to their potential applications in optics, electronics and environmental and biological sciences. AIE luminogens refer to molecules or polymers, whose emissions are induced by aggregate formation. So far, remarkable progress on the investigation and development of AIE systems has been achieved, which enables us to gain deeper insight into the AIE mechanism and guides us to design and synthesise efficient luminogenic materials with specific properties. The works done in this area by other groups, including typical examples of different categories of AIE luminogens, the structure–property relationships as well as technological applications, have been recently reviewed in our critical review.[7d]

Among many AIE luminogens, TPE is an archetypal molecule with an outstanding AIE effect. Its facile synthesis and ready functionalization have made it a versatile building block for functional materials to cater the needs of a wide range of high-technological applications. On the other hand, conventional chromophores are usually flat disc-like aromatic molecules because it is a general consensus that fluorophores with high planarity and rigidity show efficient light emission. These molecules, however, experience strong molecular interactions and thus suffer from the severe ACQ effect. Previous techniques to tackle the ACQ problem have focused on preventing aggregation but have inevitable side effects and thus have resulted in limited success. In this feature article, we present a new synthetic strategy to create efficient solid-state luminescent materials by melding TPE with conventional chromophores at the molecular level. Detailed investigations on the PL and EL of these hybrid molecules show that such a strategy can solve the ACQ problem without causing adverse effects. The resulting adducts show AIE or AEE characteristics and exhibit high fluorescence quantum yields in the solid state. Meanwhile, the intrinsic functional properties such as hole- or electron-transporting capabilities of the segments are preserved as well. In addition, the introduction of heteroatoms can further control the electronic structures and tune the emission wavelengths of the luminogens. Thereby, efficient luminogenic materials with multi-functionalities and various emission colors are achieved, revealing the versatility and applicability of the strategy. The application of the TPE-based materials in OLEDs is exclusively described in this feature article. All the AIE luminogens ranging from pure hydrocarbons to heteroatom-containing molecules exhibit remarkably good EL performances. Efficient fluorescent R, G, B and WOLEDs have been fabricated, demonstrating that the luminogens generated through such strategy are of practical utility.

As a final remark, the AIE phenomenon opens a new door for studying the solid-state luminescence processes. Because it is of academic value and practical implication, many research groups have worked on the AIE research and generated a large amount of excellent work with tremendous prosperous results. Here, we wish to point out that AIE luminogens constructed from TPE also show great potentials in other research fields, particularly in fluorescent chemosensors and bioprobes. Due to the space limitation, we are not going to discuss these works here and interested readers are encouraged to read the papers published by our and other groups. Some recently published representative papers are given in the reference section of this article.[58,59] With great imagination, many new possibilities are waiting to be explored. For example, although several molecules with aggregation-induced phosphorescent emissions have been reported,[60] their utility in electrophosphorescence devices remain unexplored. There are also a few reports on utilizing AIE hosts to construct electrophosphorescence devices. We are enthusiastically looking forward to new advancements in this exciting area of research and more and more efficient light emitters with practical applications will be generated to meet the requirement of optoelectronic devices.

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