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Systemic Studies of Tetraphenylethene–Triphenylamine Oligomers and a Polymer: Achieving Both Efficient Solid-State Emissions and Hole-Transporting Capability

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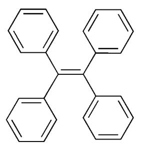
Abstract: By employing a new synthetic strategy, a series of oligomers and a polymer composed of different number of tetraphenylethene and triphenylamine units was designed and synthesised. The optical physics properties and electroluminescence behaviours were studied comparatively. All the molecules demonstrate an aggregation-induced emission (AIE) phenomenon and bear very high quantum yields in the solid state. The emission wavelengths and quantum efficiencies alternate with the change of the molecular configurations and achieve their maximum at the largest oligomer. The thermal stabilities also become higher along with the increase in the molecular weight. The molecules have suitable HOMO levels that match the work function of the indium tin oxide (ITO) anode. They can act as both light-emitting and hole-transporting materials in OLEDs. Thus the present strategy combines the intrinsic emissive nature of AIE materials and the good hole-transport capability of aromatic amines, thereby achieving a win–win for both optical and electrical properties.

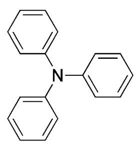
Keywords: aggregation · hole transport · luminescence · oligomerization · optical physics

Introduction

Organic materials with enhanced solid-state emissions have been thoroughly established in many optoelectronic applications for years.[1] For most of the organic conjugate chromophores, however, an intrinsic limitation still exists: they emit strongly in their dilute solutions but become weak fluorophores when fabricated into solid films or aggregated in their poor solvents on account of the strong intermolecular interactions.[2] This problem must be solved because luminogenic molecules are commonly used in the solid state in real applications.[3] Since the abnormal phenomenon of "aggregation-induced emission" (AIE) discovered by our group, many organic chromophores that have AIE properties have been explored by us and other groups.[4] This kind of dyes emits efficiently in the aggregate state and does not suffer from the common fluorescence "aggregation-caused quenching" effect. High-tech applications based on the AIE luminogens, such as fluorescence sensors (for explosivity, ions, pH, temperature, viscosity and pressure), biological probes and active layers in the fabrication of organic light-emitting diodes (OLEDs) have been realised.[5] Specifically, OLEDs that utilise AIE dyes exhibit outstanding performances.[4a,5f,g] Tetraphenylethene (TPE), a propeller-shaped molecule, is one of the most prominent representatives of AIE dyes. Because of the restriction of intramolecular rotations in aggregates and the severely twisted conformations, TPE derivatives have extreme solid-state fluorescence efficiencies. Furthermore, they have several other advantages such as facile synthesis, easy functionalization and chemical and thermal stability.[5b,c,e]



Tetraphenylethene (TPE)



Triphenylamine (TPA)

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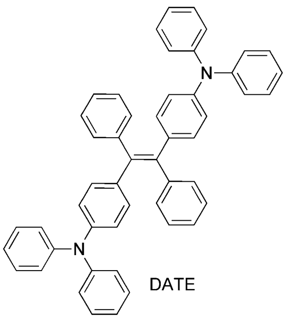
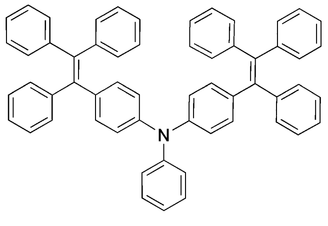
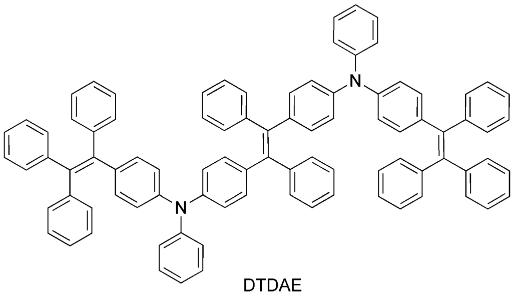
For optoelectronic applications, in addition to high optical efficiency, carrier (electron and hole) transportation is another crucial requirement. Normally a single compound cannot fulfil all the demands. In OLEDs, multilayer architectures are generally adopted to balance the charge injection and transportation.[6] In reality, it would be ideal to have emitters with both efficient solid-state emissions and good charge-transporting properties because it would simplify the device fabrication procedure and lower the construction costs. Triphenylamine (TPA) is well known for its ease in oxidation of the centre nitrogen and its ability to transport charge carriers through the radical cation species with high stability.[7] TPA-based organic semiconductors have been widely studied as hole-transporting materials for various optoelectronic applications such as xerography, OLEDs, photovoltaic cells and organic field-effect transistors (OFET).[8] In our previous work, by introducing TPA functionalities into TPE derivatives, luminogens with good hole-transporting ability were demonstrated.[5f,9]

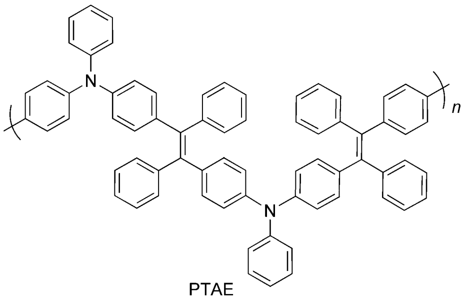
As shown in Scheme 1, four kinds of TPE–TPA derivatives have been studied in our previous work.[5f,9a] The TPE and TPA moieties were easily combined through classic Pd^0-catalysed Suzuki coupling reactions. As we know, TPA also suffers from the notorious effect of aggregation-caused emission quenching in the condensed phase.[9a] Combining TPA with TPE redeems its emissive ability and at the same time bestows the hybrid molecules with good hole-transporting properties. Compound **2** showed a hole mobility of $2.6\times10^{-3}\,cm^2V^{-1}s^{-1}$ in a thin film OFET.[9b] OLEDs that employ them as emitting and hole-transporting materials exhibited quite good performances.

Given that both TPE and TPA are really versatile materials, systemic studies of TPE–TPA oligomers and polymers are significant in the discovery of promising candidates for advanced optoelectronics applications and to understand their structure–property relationships. In this paper, we present the synthesis, characterisation and properties of a new series of TPE–TPA oligomers and polymer. By using a new synthetic strategy, TPE–TPA oligomers and a polymer with different numbers and configuration of units were prepared and their optical physics properties were studied comparatively.


DATE

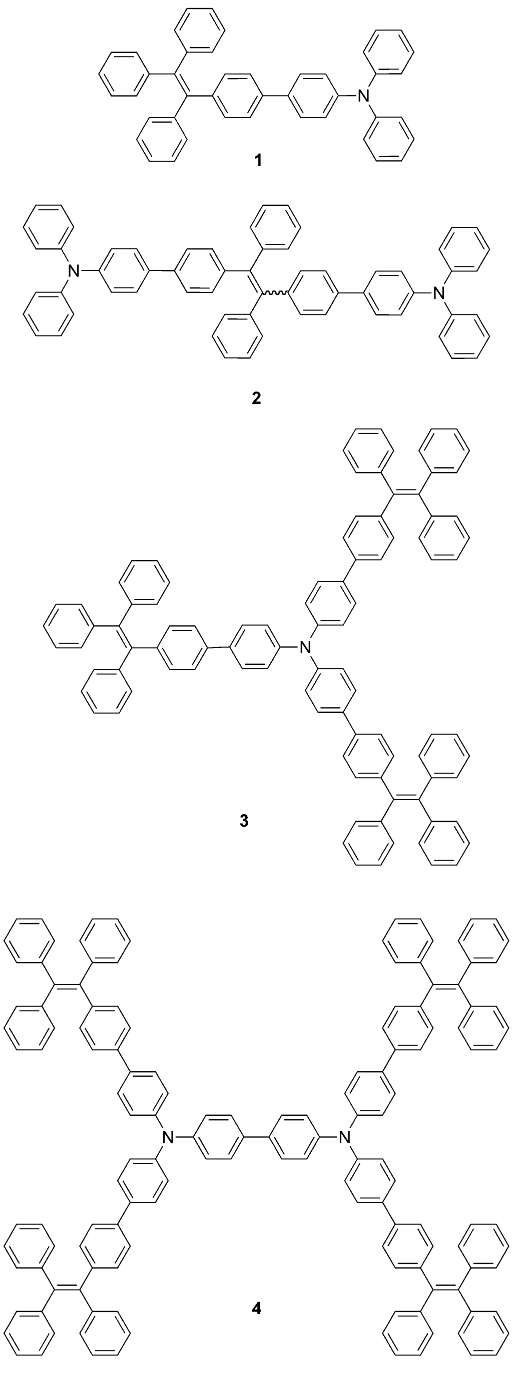

DTAE


DTDAE


PTAE

Results and Discussion

Synthesis: In our previous studies, TPE and TPA moieties were combined by Suzuki coupling. In this work, McMurry coupling[10] and the diphenylmethyllithium-mediated unsymmetrical synthetic method were adopted.[11] Schemes 2 and 3 depict the synthetic routes. First, TPA was converted to the key intermediates of [4-(diphenylamino)phenyl]-(phenyl)methanone (BOA) and 4,4′-(phenylazanediyl)-bis(1,4-phenylene)bis(phenylmethanone) (2BOA) facilely by $AlCl_3$-catalysed Friedel–Crafts acylation.[12] Then the McMurry coupling of BOA catalysed by $Zn/TiCl_4$ gave DATE in a high yield. Similarly, McMurry coupling of the bis-ketone intermediate 2BOA produced the TPE–TPA polymer PTAE. The polymer was purified by precipitation from methanol/chloroform (30:7) mixtures. PTAE dissolves well in THF. The molecular weight measured by gas-phase chromatography (GPC) is 5010 (polydispersity index (PDI) = 1.67). Perhaps because of the rigid structure, polymer molecules with long chains will precipitate from the reaction solutions and stop growing due to the limited solubility, and therefore the molecular weight was relatively low. The reaction of the bis-ketone 2BOA with an excess amount of diphenylmethyllithium (1:3 molar ratio) afforded the bis-alcohol intermediate. Then the bis-alcohol intermediate was dehydrated to obtain the product DTAE with two TPE moieties under a catalytic amount of *p*-toluenesulfonic acid in boiled toluene. In a like manner, the reaction of



Scheme 1. Chemical structures of explored triphenylamine-containing tetraphenylethenes in our laboratory.

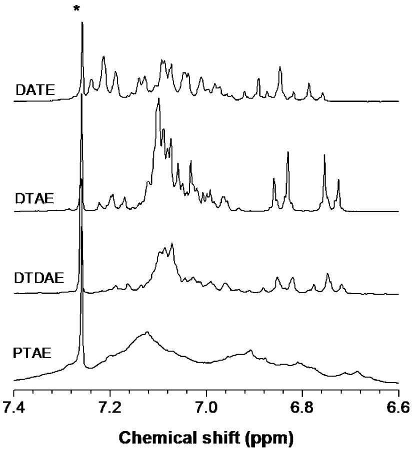


Figure 1. ^{1}H NMR spectra of TPE–TPA oligomers and polymer in [D]chloroform. The solvent peak is marked with an asterisk.

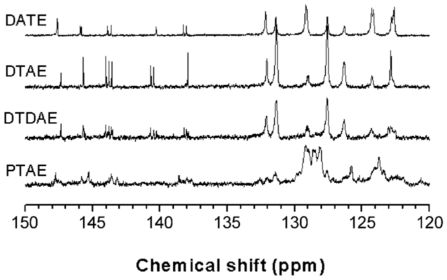
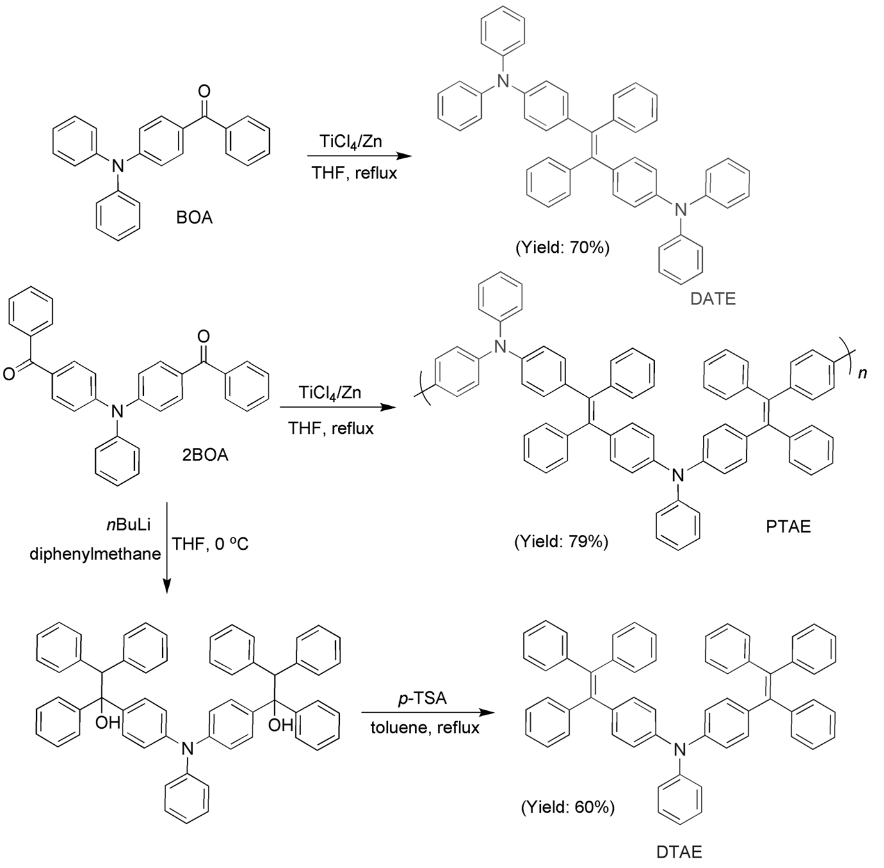
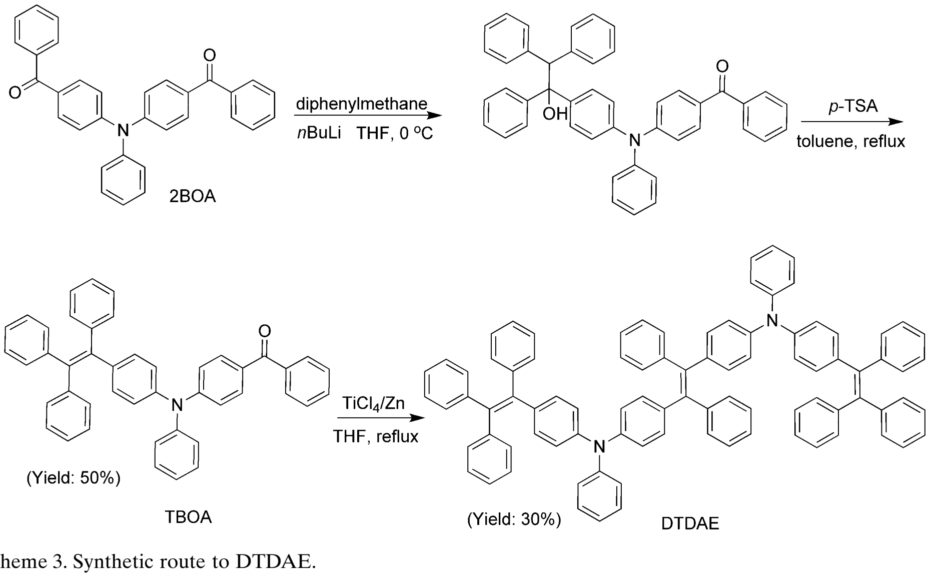


Figure 2. ^{13}C NMR spectra of TPE–TPA oligomers and polymer in [D]chloroform.

2BOA with diphenylmethyllithium in a molar ratio of 1:1.2 afforded the intermediate with one alcohol and a ketone. Upon dehydration, the alcohol yielded the intermediate threo-β-benzyloxyaspartic acid (TBOA). McMurry coupling of TBOA by using its ketone group produced the oligomer DTDAE, which has three TPE and two TPA moieties. All the dye molecules were characterised by NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra (Figures 1 and 2) all gave satisfactory signal integrations. As shown in Figure 1, because the molecules have similar chemical structures, their ^{1}H NMR spectra showed similar profiles. Each of the spectra was composed of peaks at $\delta \approx 6.8$ ppm (mainly from the contributions of TPA moieties) and more peaks at low fields (mainly from the contributions of TPE moieties and the N *meta* positions of TPA). The NMR spectroscopic signals of the oligomers DATE, DTAE and DTDAE are quite sharp; for the polymer PTAE, the peaks broadened. The presence of a large number of repeat units in the polymer backbone and the chemical environment distributions of the units generally led to broad NMR spectroscopic signals. The rigid backbone of PTAE might further lower the mobility of the polymer in solution, which will also result in broad peaks. The ^{13}C NMR spectra offer clearer profiles. As shown in Figure 2, the three oligomers showed quite similar carbon resonance positions. Following the same trend as in the ^{1}H NMR spectra, the signal peaks broadened when it came to the polymer PTAE. In all of the spectra, no other unexpected signals were observed, thus verifying the identity and high purity of their molecular structures. The identities of the three oligomers were further proven by the M^{+} peaks in their high-resolution mass spectra (Figures S1, S2 and S3 in the Supporting Information), thereby confirming the occurrence of the reactions and the formation of the expected products. The purity of the molecules was also confirmed by



Scheme 2. Synthetic routes to oligomers DATE and DTAE and the polymer PTAE.



Scheme 3. Synthetic route to DTDAE.

elemental analysis with satisfactory results. Because of the McMurry coupling reactions involved in the synthetic routes of DATE, DTDAE and PTAE, there are *E* and *Z* isomers in the products. (For DTAE, there is no McMurry reaction in its synthetic route, thus no isomers should be present.) According to the ^{1}H NMR spectra, the *E*/*Z* ratio is ambiguous. The different isomers have quite close polarities and are hard to isolate by chromatography or recrystallization methods. Later studies are based on the mixtures of the isomers. Both the theoretical and experimental studies revealed that the isomers should have very similar properties and the presence of the different isomers does not significantly affect the overall properties.

Aggregation-induced emission: All four kinds of dyes dissolved readily in common organic solvents such as chloroform and THF but were insoluble in water. The three oligomers are practically non-emissive when molecularly dissolved in the solutions, but emit intensely in the aggregate state.[9] As shown in Figure 3, the PL (photoluminescence) spectra of DATE, DTAE and DTDAE in THF are basically flat lines parallel to the abscissa, thereby revealing that they are genuinely weak emitters in the solution state. When a large amount of water was added to their solutions in THF, intense PL signals were recorded under identical measurement conditions at 521, 501 and 519 nm, respectively. The higher the water fraction, the stronger the emission intensity. As shown in Figure 4, from the molecular solutions in THF to the aggregate suspension in 90 % aqueous mixtures, their PL intensities increase several hundreds of times. The inset photographs of Figure 3 and Figure 4 further demonstrate the non-luminescent and emissive natures of the molecular isolated species and nano-aggregates. The PL behaviour of the polymer PTAE is a little different than that of the three oligomers. In THF, the fluorescence of the polymer is not totally quenched. A moderate emission at the short wavelength of approximately 410 nm can be de-

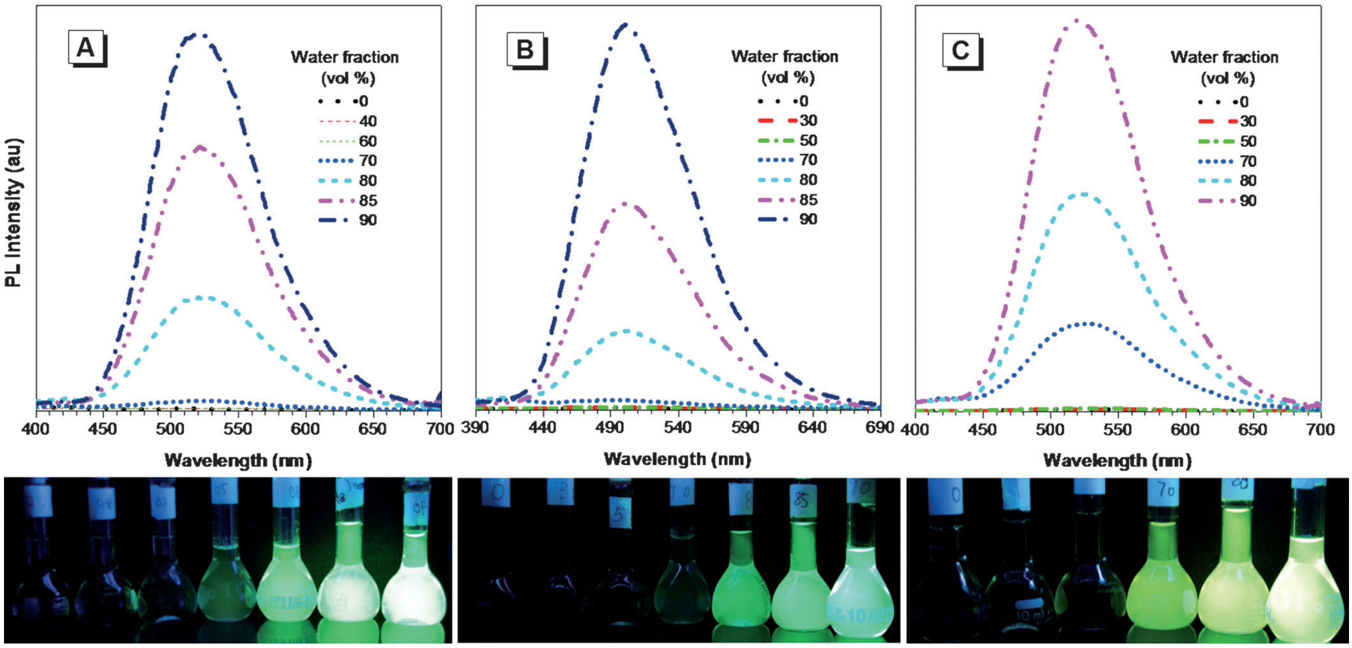


Figure 3. PL spectra of A) DATE, B) DTAE and C) DTDAE in THF/water mixtures with different water fractions. Concentration: 10 μM. Bottom: fluorescent images of each dye in corresponding fractions of THF/water mixtures.

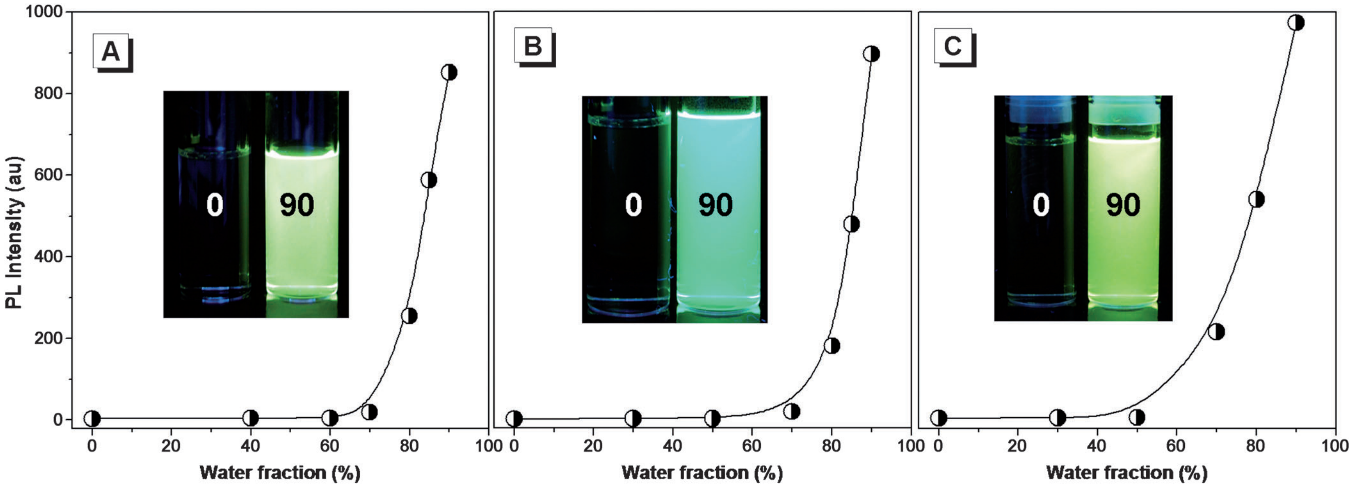


Figure 4. Plots of PL intensities versus compositions of the THF/water mixtures of A) DATE, B) DTAE and C) DTDAE. Inset: fluorescent images of each dye in THF and THF/water mixtures with 90% of water.

tected in the spectrum, and the solution appears violet blue under UV irradiation. Upon adding water, the emission band at shorter wavelength decreases its intensity and disappears after the water fractions are larger than 50%. Meanwhile, an emission at longer wavelength of 510 nm appears and increases along with the increase in the water fractions. The growing trend of this longer-wavelength emission band is the same as that of the oligomers. The spectra and photographs in Figure 5 depict the changes. After aggregation, the polymer only showed the bluish-green emission with the wavelength of around 510 nm. We posit that in solutions the shorter emission band at approximately 410 nm comes from the TPA moieties of the molecularly dissolved polymer. Because of the long and rigid backbone of the polymer, the intramolecular rotations of the phenyl blades around the TPE stator cannot completely deactivate the excited states of the entire molecule through the rotational energy relaxation channels. Thus a portion of fluorescence from TPA chromophores is released. While in the aggregate state, the emission at longer wavelength recovers due to the restriction of intramolecular rotations, and the shorter wavelength emission will quench through Förster resonance energy transfer to the longer-wavelength emission. The decrease in the shorter-wavelength emission and the increase in the longer one are both evidence of the process of aggregation formation. Since water is a non-solvent for all four of the dyes, their

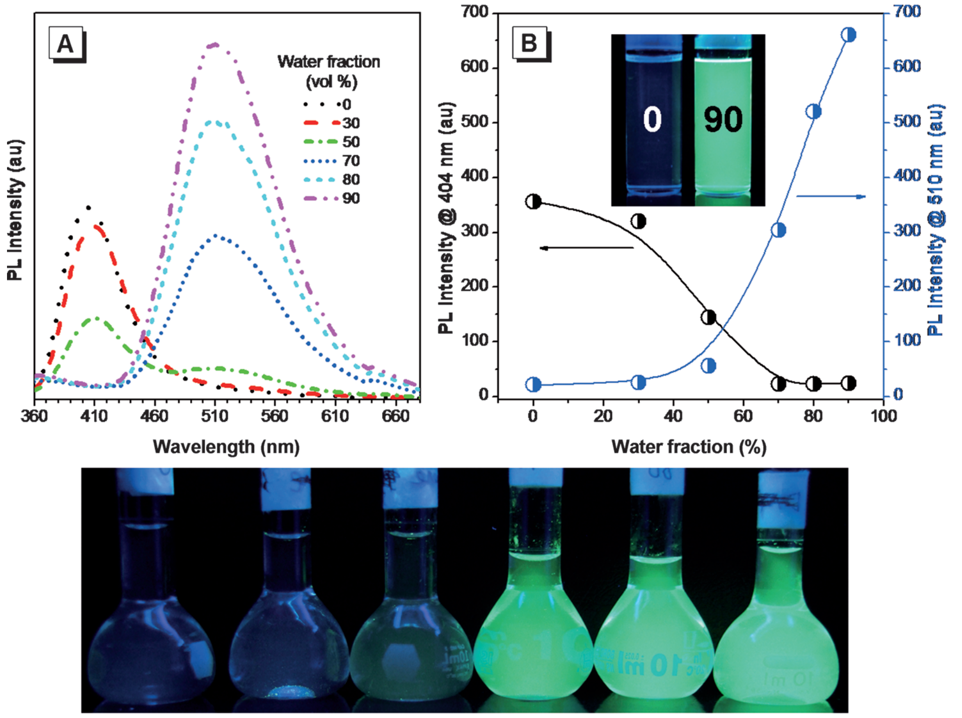


Figure 5. A) PL spectra of PTAE in THF/water mixtures with different water fractions. Concentration: 10 μM. B) Plots of PL intensity versus compositions of the THF/water mixtures. Inset: fluorescent images of PTAE in THF/water mixtures with different water fractions.

molecules must be aggregated in the solvent mixtures with high water fractions. The aqueous mixtures are, however, macroscopically homogenous with no precipitates, thereby suggesting that the aggregates are nano-dimensional.[13] This is proven by the TEM images. As shown in Figure 6, in the 90% aqueous mixtures, DATE aggregates into nanoparticles with dimensions of dozens of nanometers, and the electron-diffraction pattern displays many clear diffraction spots, which suggests that they are crystalline, whereas the aggregates of the polymer PTAE look like nanoscale vesicles, and the electron-diffraction pattern only depicts an obscure diffuse halo, thereby suggesting their amorphousness in nature. This should be attributable to the poor crystallisability of PTAE because of the long polymer chain.

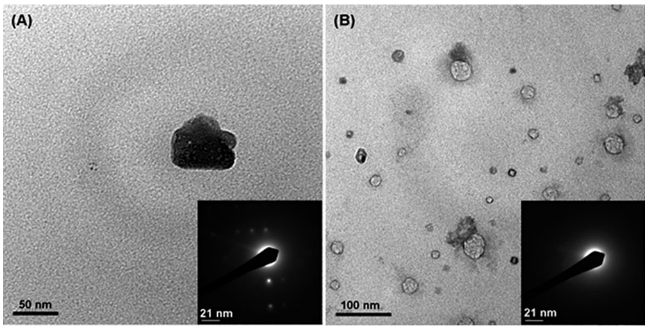


Figure 6. TEM images of nano-aggregates of A) DATE (scale bar: 50 nm) and B) PTAE (scale bar: 100 nm) formed in THF/water mixtures with 90% water fractions. Insets: electron diffraction patterns of the nano-aggregates (scale bar: 21 nm).

These dyes are very emissive in the aggregate state. Figure 7 shows the PL spectra of DTAE, DATE, DTDAE and PTAE in the solid state and the corresponding fluorescent images. In the solid state (cast films), DTAE shows the most blue emission wavelength of 470 nm among the four molecules. For DATE, although it has similar molecular weight to that of DTAE, its two side donor groups (TPA) make it a D–π–D structure with intense intramolecular charge transfer, thus its emission at 500 nm is longer than that of the former. For the oligomer DTDAE, which has three TPE and two TPA units, the emission comes to 519 nm. At 525 nm, the polymer PTAE has the longest emission wavelength of the four. Their absolute quantum yields were measured by using a calibrated integrating sphere. Among the three oligomers, the largest one is DTDAE, which has the most efficient emission with a quantum yield of 99%; the D–π–D-structured DATE stands in second place with a yield of 93%; the bluest one, DTAE, has a relatively low efficiency of 77%.

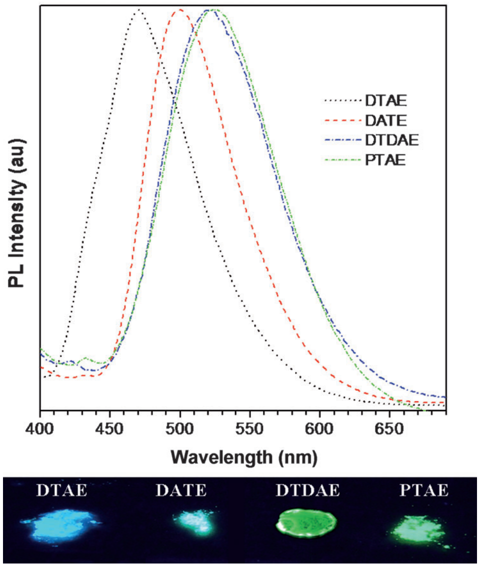


Figure 7. PL spectra of DTAE, DATE, DTDAE and PTAE in the solid state and the corresponding fluorescent images.

We suggest that the reason why these dyes show opposite luminescence abilities in solution and in aggregates is as follows: in a dilute solution, the peripheral phenyl rotors in the TPE moieties can undergo dynamic intramolecular rotations against their double-bond stator at the excited states, which will non-radiatively annihilate their energy and render the molecules non-luminescent, whereas in the aggregates the intramolecular rotations of the aryl rotors are greatly restricted on account of the spatial constraints. This restriction of intramolecular rotations blocks the non-radiative pathway and opens up the radiative channel. As a result, the molecules become emissive in the aggregate state.[4] Furthermore, the propeller-like TPE and TPA unit would efficiently hamper the close packing between the chromophores, thereby preventing the formation of detrimental species such as excimers and exciplexes that cause emission quenching and redshift.[14] Therefore all the factors convert these molecules from weak fluorophores in solution into strong emitters in aggregates. Additionally, there is another noticeable phenomenon: from aggregates in THF/water mixtures to the cast films, the emission of DTAE blueshifts by 31 nm; DATE blueshifts by 21 nm; there is no change in DTDAE; the polymer PTAE redshifts by 15 nm. That is to say, as the molecules grow larger, the emission blueshifts from aqueous suspensions to cast films become smaller and ultimately the redshift appears in the polymer PTAE. (For details, see Table 1.) We propose that this evolution is caused by the increasing intermolecular interactions when the molecules become bigger.[15] In our previous work, we have proven that the AIE-active dyes normally possess special crystallisation-induced blueshift characteristics. The emission wavelength relies heavily on the crystallinity of the materials. For the smaller molecules, their crystallinities in the cast films are higher than those in the aqueous suspensions, therefore they showed blueshifts in the cast films. For the molecules with longer chains, they have more tendency to form amorphous aggregates; and the intermolecular interactions in the films are stronger than those in the nano-aggregates.

Table 1. Optical and thermal properties of DATE, DTAE, DTDAE and PTAE.[a]

	λ_{em} [nm]			Thermal properties	
AIE luminogen	Solution	Aggregate	Film (Φ_F)	T_d [°C]	T_g [°C]
DATE	513	521	500 (93)	344	80
DTAE	496	501	470 (78)	374	108
DTDAE	519	519	519 (99)	422	137
PTAE	404	510	525 (57)	364	172

[a] Abbreviations: λ_{em} = emission maximum in THF (solution; 10 μM), THF/water mixtures (aggregate; 10 μM; 10:90 by volume), and solid thin films with quantum yields (Φ_F [%]) given in the parenthesis, T_d = onset degradation temperature and T_g = glass transition temperature. The Φ_F values of the solid films were measured by using a calibrated integrating sphere.

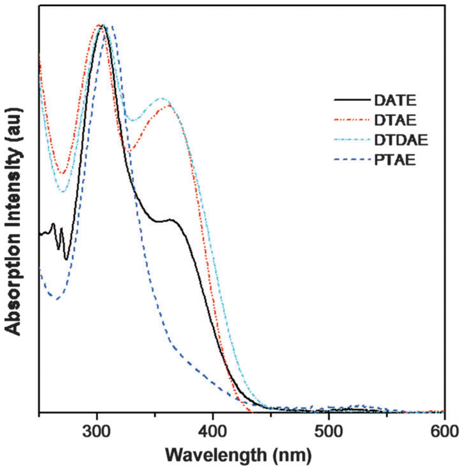


Figure 8. UV/Vis absorption spectra of the four TPE–TPA derivatives in THF.

The molecular band gaps of the dyes in solution were investigated through the UV/Vis absorption spectra (Figure 8). In THF, the three oligomers display two absorption peaks at around 305 and around 360 nm. Although the longer absorption band is quite inconspicuous for the polymer PTAE, it has a tail extending to a similar cut-off wavelength. This demonstrates that the molecules have similar band gaps.

Thermal properties: The thermal stabilities of these dyes were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analyses. As shown in Figure 9, for the three oligomers, as the molecular weight increases, the degradation temperature (T_d) increases from 344 (DATE) to 374 °C (DTAE), and then to 422 °C (DTDAE). The T_d of the polymer PTAE is 364 °C, which is slightly below that of DTAE. However, the residue percent-

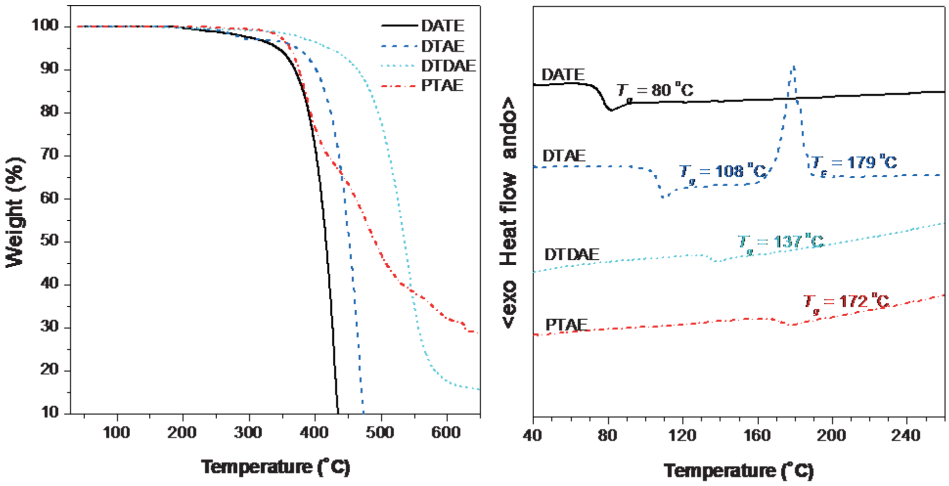


Figure 9. TGA and DSC (second heating cycle) thermograms of DATE, DTAE, DTDAE and PTAE recorded under N_2 at a heating rate of (TGA) 20 and (DSC) 10 °C min^{-1}.

age of the polymer is much higher than that of the oligomers. Following a regular trend, the glass transition temperature (T_g) of the molecules increases gradually as the molecular weight increases. From the 80 °C of DATE, it increases to 108 °C (DTAE), then to 137 °C (DTDAE) and finally to 173 °C of the polymer PTAE. Except for DATE, all the T_g values of the molecules are relatively high for optoelectronic applications. The good morphological stabilities, coupled with their efficient solid-state emissions, the dyes are thus promising electroluminescent (EL) materials.[16]

Electroluminescence: Similar to the TPE–TPA derivatives in our previous works, these oligomers possess high HOMO levels of around 5.2 eV derived from the electrochemical measurements (Figure S5 in the Supporting Information), which are close to that of the most widely used hole-transporting material, *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbenzidine (NPB).[9a] Thus to prove the hole-transporting ability of the dyes, multilayer OLEDs with and without a dedicated hole-transporting layer (HTL) were designed and constructed. That is, ITO/X/1,3,5-tris(*N*-phenylbenzimiazole-2-yl)benzene (TPBi; 30 nm)/LiF/Al (100 nm), in which X stands for NPB (40 nm)/LEL (20 nm) in the "with HTL" devices and stands for LEL (60 nm) in the "without HTL" devices (LEL = DATE or DTAE or DTAAE; TPBi serves as the electron-transporting material). Because we used the evaporation method to fabricate the devices, the polymer PTAE was not included.

Figure 10 depicts the PL and EL spectra of the solid thin films of each oligomer. Compared with the PL spectra, the EL of DATE and DTAE redshift a little (16–32 nm), whereas that of DTDAE has no change. In the OLEDs a dedicated HTL does not affect their emission wavelengths, which suggests the recombination region remains unvarying. Figure 11 shows the current density–luminance characteristics of the devices based on each dye. We can see that the devices with simple structures (i.e., no dedicated HTL) show comparable brightness at the same current density. Table 2 provides all details of the devices. Without an NPB layer, OLEDs based on DATE exhibit superior performances in terms of both lu-

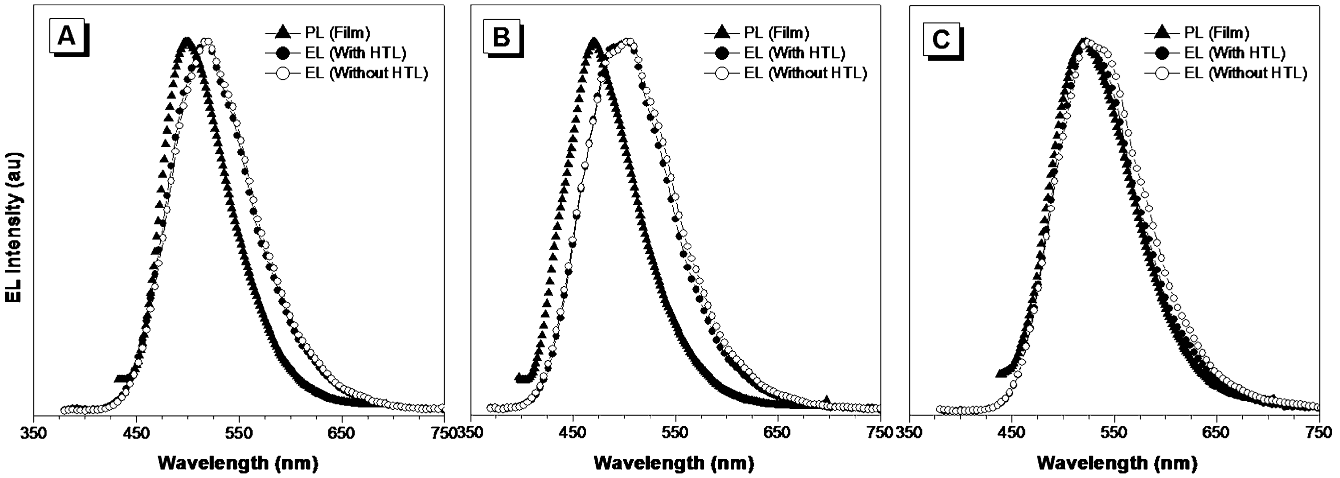


Figure 10. PL and EL spectra of solid thin films of A) DATE, B) DTAE and C) DTDAE.

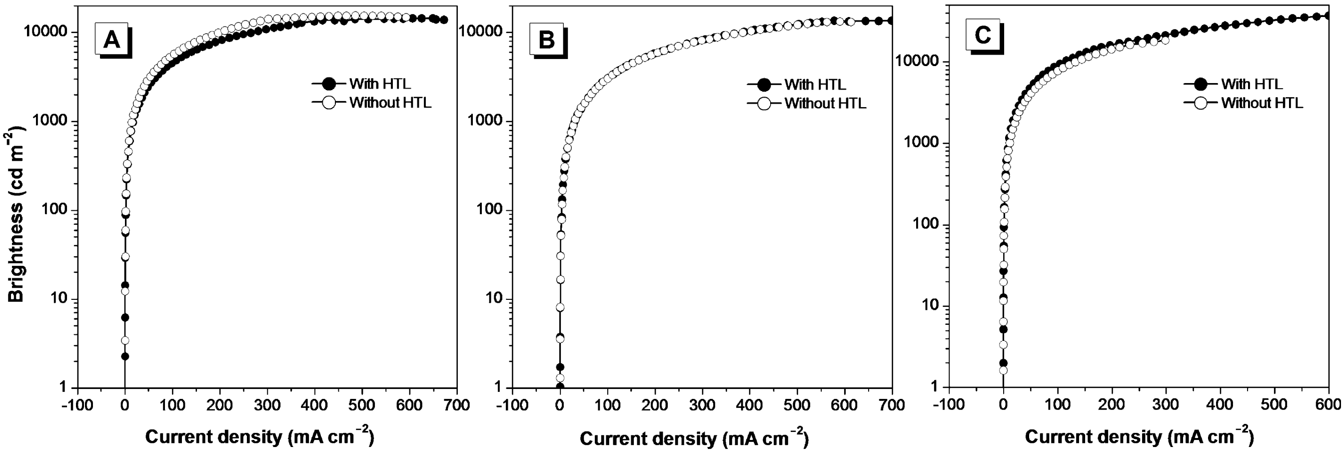


Figure 11. Current density–luminance characteristics of EL devices based on A) DATE, B) DTAE and C) DTDAE.

Table 2. Electroluminescence performances of DATE, DTAE and DTDAE.[a]

Emitter	HTL	λ_{EL} [nm]	V_{on} [V]	L_{max} [cd m^{-12}]	CE_{max} [cd A^{-1}]
DATE	√	516	4.3	14383	6.72
	×	520	4.4	15487	7.04
DTAE	√	502	3.2	13694	3.28
	×	506	3.7	13227	3.24
DTDAE	√	524	3.6	40940	11.2
	×	524	6.0	18400	8.7

[a] With device configurations of ITO/(HTL)/emitter/TPBi/LiF/Al. Abbreviations: HTL = hole-transporting layer, λ_{EL} = EL maximum, V_{on} = turn-on voltage at 1 cd m^{-12}, L_{max} = maximum luminance, CE_{max} = maximum current efficiency, PE_{max} = maximum power efficiency and EQE_{max} = maximum external quantum efficiency.

minance (15487 versus 14383 cd m^{-12}) and efficiencies (7.04 versus 6.72 cd A^{-1}); for DTAE the difference is negligible (13227 versus 13694 cd m^{-12} and 3.24 versus 3.28 cd A^{-1}); for DTDAE the performance shows some decrease in the devices without HTL (18400 versus 40940 cd m^{-12} and 8.7 versus 11.2 cd A^{-1}). Figure 12 depicts the current and power efficiencies versus voltage characteristics of the devices. We can see that OLEDs without a dedicated HTL exhibited better stabilities, especially at high voltage. For DATE and DTAE, the simple devices maintain higher efficiencies at almost all voltages. Even for DTDAE, the simple device possesses lower maximum efficiency than that of the device with HTL; whereas at high voltage, the efficiency becomes greater than that of the latter thanks to a more gentle decrease in efficiency along with the increase in bias. The voltage-dependent stability is very helpful for practical use and should be attributed to the balanced energy level.[17] Matching the suitable HOMO level to the work function of the anode enables them to exhibit better electronic characteristics in the EL devices.

Photopatterning: To explore the applications of the polymer, its photo-patterns were developed. When a thin film of PTAE spin-coated on a silicon wafer was irradiated with UV light for 15 min through a copper mask, a two-dimensional photoresist pattern was fabricated. Upon excitation, the unexposed square parts of the pattern emitted bright green light, whereas the exposed patterned lines suffer from photo-oxidative bleaching and are thus not emissive. The sharp line edges of the patterns are clearly observed under the fluorescence microscope (Figure 13). The generation of fluorescent patterns is of great importance for the constructions of photonic and electronic devices and biological probing systems.

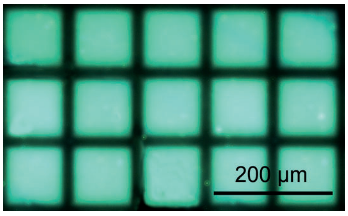


Figure 13. Two-dimensional fluorescent photopattern of PTAE. The photograph was taken under a fluorescence optical microscope.

Conclusion

In this work, we have designed and synthesised a series of TPE–TPA derivatives with different numbers of TPE and TPA units. Their optical physics, thermal stabilities and electroluminescence properties were studied comparatively. All the molecules demonstrate an AIE phenomenon and have very high quantum yields in the solid state. Thanks to their intrinsic hole-transport capability, they can act as both light-emitting and hole-transporting materials in OLEDs. The present strategy offers a win–win situation for both optical and electrical properties. More advanced optoelectronic potentials (e.g., electrical pumping organic laser diodes) were imagined.[18] By tuning the electrical properties of AIE molecules, we hope the candidates offer the opportunity for a breakthrough in these fields.

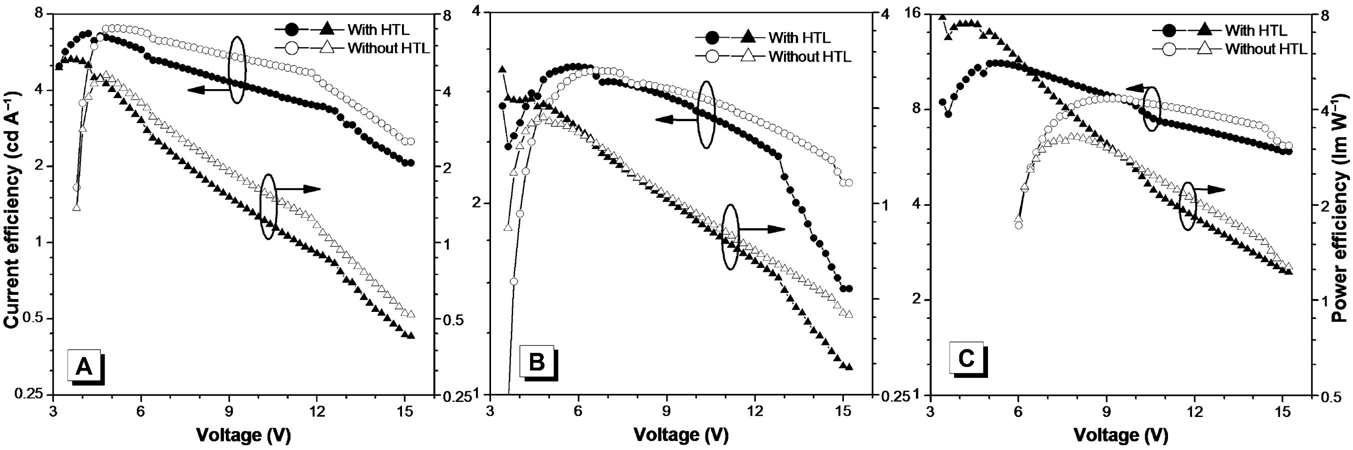


Figure 12. Power and current efficiencies of EL devices based on A) DATE, B) DTAE and C) DTDAE.

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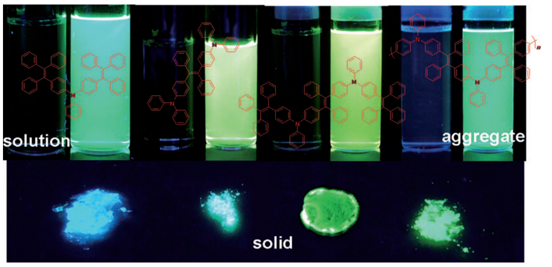

Glowing recommendation: A series of oligomers and a polymer composed of different numbers and configuration of tetraphenylethene and triphenylamine units have been synthesised. Their optical and electroluminescence behaviours were studied systematically. All the molecules demonstrate aggregation-induced emission (see figure) and have very high quantum yields in the solid state.

Solid-State Emitters

Y. Liu, X. Chen, Y. Lv, S. Chen,
J. W. Y. Lam, F. Mahtab, H. S. Kwok,
X. Tao, B. Z. Tang* .... ▮▮▮▮–▮▮▮▮

Systemic Studies of Tetraphenylethene–Triphenylamine Oligomers and a Polymer: Achieving Both Efficient Solid-State Emissions and Hole-Transporting Capability