

# Aggregation-Induced Emission

# A New Approach to Prepare Efficient Blue AIE Emitters for Undoped OLEDs\*\*

Jing Huang,<sup>[a]</sup> Runli Tang,<sup>[a]</sup> Tian Zhang,<sup>[a]</sup> Qianqian Li,<sup>[a]</sup> Gui Yu,<sup>[b]</sup> Shuyi Xie,<sup>[a]</sup> Yunqi Liu,<sup>\*[b]</sup> Shanghui Ye,<sup>\*[c]</sup> Jingui Qin,<sup>[a]</sup> and Zhen Li<sup>\*[a]</sup>

**Abstract:** Two aggregation-induced emission active luminogens (TPE–*p*TPA and TPE–*m*TPA) were successfully synthesized. For comparison, another six similar compounds were prepared. Because of the introduced hole-dominated triphenylamine (TPA), fluorene groups with high luminous efficiency, and unconjugated linkages, the  $\pi$  conjugation length of

Introduction

Over the past few decades, following the achievements of the Kodak group, there has been great progress in the field of organic light-emitting diodes (OLEDs).<sup>[1]</sup> To realize full-color displays, it is essential to obtain red-, green-, and blue-emitters with high thermal stability, good electroluminescence (EL) efficiencies, and color purity. However, due to the intrinsic large band gap in blue luminogens, the performance of blue OLEDs is often inferior to that of their red and green counterparts.<sup>[2-3]</sup> Therefore, the development of blue-emitting materials with both high efficiencies and good color purity becomes particularly important.<sup>[4]</sup> In 2007, Cheng et al. reported efficient undoped deep-blue OLEDs with current efficiencies of up to 5.6 cd A<sup>-1</sup> by utilizing anthracene derivatives as emitters.<sup>[5]</sup>

[a]	J. Huang, R. Tang, T. Zhang, Prof. Q. Li, S. Xie, Prof. J. Qin, Prof. Z. Li Department of Chemistry, Hubei Key Laboratory on
	Organic and Polymeric Opto-Electronic Materials
	Wuhan University, Wuhan 430072 (P.R. China)
	Fax: (+ 86) 27-68756757
	E-mail: lizhen@whu.edu.cn
	lichemlab@163.com
[b]	Prof. G. Yu, Prof. Y. Liu
	Organic Solids Laboratories, Institute of Chemistry
	The Chinese Academy of Sciences
	Beijing 100080 (P.R. China)
	E-mail: liuyq@iccas.ac.cn
[c]	Dr. S. Ye
	Key Laboratory for Organic Electronics and
	Information Displays (KLOEID)
	Institute of Advanced Materials (IAM)
	Nanjing University of Posts and Telecommunications
	Nanjing 210046 (P.R. China)
	E-mail: yeshh@iccas.ac.cn
[**]	AIE = aggregation-induced emission, OLED = organic light-emitting diodes
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the obtained luminogens is effectively restricted to ensure their blue emission. The undoped organic light-emitting diodes based on TPE-*p*TPA and TPE-*m*TPA exhibited blue or deep-blue emissions, low turn-on voltages (3 V), and high electroluminescence efficiencies with  $L_{\text{max}}$ ,  $\eta_{\text{C,max}}$ , and  $\eta_{\text{P,max}}$ values of up to 26697 cd m<sup>-2</sup>, 3.37 cd A<sup>-1</sup>, and 2.40 Lm W<sup>-1</sup>.

formances, new design strategies should be explored in addition to the traditional approaches.

On the other hand, when fabricated as thin solid films in practical applications (including the aforementioned OLEDs), most emitters suffer badly from the notorious aggregationcaused quenching (ACQ) effect.<sup>[6]</sup> Considerable research has been performed to mitigate the ACQ effect,<sup>[7]</sup> for example, by using guest–host doped emitter systems, blending with transparent polymers or the attachment of bulky alicyclics. Nevertheless, there are still some side effects, including additional complexity and cost for device fabrication, jeopardizing the electronic conjugation in the emitters.

In 2001, the group of Benzhong Tang discovered an "abnormal" phenomenon: a series of propeller-like molecules turned from faint fluorophores in solution to strong emitters in the aggregated form.<sup>[8]</sup> It was exactly the opposite of the ACQ effect and is known as aggregation-induced emission (AIE).<sup>[9]</sup> The Tang group have also rationalized the restriction of intramolecular rotation (IMR) as the main cause for the AIE effect.<sup>[9]</sup> Consequently, AIE-active luminogens exhibit great potential in the field of OLEDs due to their unique luminescent characteristics.<sup>[10]</sup> Among the reported AIE fluorophores, tetraphenylethene (TPE) was a prototype molecule because of its facile synthesis and splendid AIE effect.<sup>[11]</sup> Recently, a lot of efficient solid-state emitters have been constructed by using TPE as the key building block (see the Supporting Information).<sup>[12]</sup> Nevertheless, blue AIE-active luminogens are still very scarce: if TPE is simply linked to other aromatic groups, the intrinsic extension of the  $\pi$  conjugation results in green–blue, green or even longer wavelength emission, although TPE itself is a blue emitter with poor performance. Similar cases have been reported for other AIE emitters.<sup>[12c-n]</sup> Thus, it is still a challenge to design AlE fluorophores with both blue emission and good electroluminescent performance.

Previously, we have reported several TPE-based blue-light emitters by tuning the conjugation between different con-

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struction blocks through different approaches.<sup>[13]</sup> For example, SFTPE and TPE–2Cz were constructed from the TPE moiety and twisted spirofluorene or carbazole by either sharing one phenyl ring or linking through a carbon–nitrogen bond. The undoped EL devices based on these two luminophors exhibited blue emissions at approximately 460 nm and enhanced efficiencies up to 3.33 cd A<sup>-1</sup>. In addition, we have obtained four deep-blue AIE luminogens, which were simply constructed from two TPE groups with different linking positions. The conjugation was effectively controlled, and all of the molecules exhibited deep-blue emission ranging from 435 to 459 nm and good electroluminescence efficiencies of up to 2.8 cd A<sup>-1</sup>.

Thus, to further realize our design ideas and develop new blue AIE systems we incorporated triphenylamine (TPA) and fluorene into the TPE moiety through an unconjugated linking mode and obtained two blue emitters, TPE–*p*TPA and TPE–*m*TPA. It was expected that the introduction of fluorene, a known deep-blue-emitting building block, could contribute to the EL efficiencies of the emitters, while the hole-dominated triphenylamine group could enhance the hole mobility, and thus decrease the turn-on voltages of the devices. In addition, these two aromatic moieties would also make the two emitters more rigid and thermally stable. TPE and TPA were linked to



a fluorene core through the unconjugated 9,9'-positions, and the twisted conformations should effectively control the extension of the  $\pi$  conjugation to ensure the blue emission of the emitters and hamper the close packing of the adjacent molecules, preventing the formation of species detrimental to the emission. Furthermore, the conjugation of the whole molecules could be partially tuned by the meta- and para-linking mode of the TPE moiety and the phenyl ring at the 9-position of fluorene. The theoretical calculations confirmed the twisted conformation and special electron cloud distribution. For comparison, we have incorporated a toluene group instead of triphenylamine, lengthened the conjugation in the molecules, and obtained six other compounds, TPE-ptol, TPE-mtol, TPE-2ptol, TPE-2mtol, TPE-2pTPA, and TPE-2mTPA. The device performance has confirmed the validity of our design idea: when fabricated as emissive layers in undoped OLEDs, both TPEpTPA and TPE-mTPA exhibit deep-blue emission with current efficiencies of up to 3.37 cd  $A^{-1}$  and CIE (CIE = commission international de l'eclairage) coordinates of (0.16, 0.16) and (0.15, 0.15). More excitingly, owing to the lower energy barriers between emitters and adjacent layers, the luminescence of the devices has been greatly enhanced (up to 26697 cd m<sup>-2</sup>), accompanied with lower turn-on voltages of approximately 3 V. Although the device performance was inferior to those of the best deep-blue emitters, it is believed that better electroluminescence data could be obtained through rational molecular design and further device optimization. Herein, we would like to present the synthesis, characterization, photophysical properties, theoretical calculations, and OLED performances of these TPE-based luminogens in detail.

# **Results and Discussion**

#### Synthesis

The synthetic route to TPE-pTPA, TPE-mTPA, and six other derivatives is illustrated in Scheme 1. Compounds 1 and 2 were prepared from 9-fluorenone and 1,4- or 1,3-dibromobenzene in the presence of *n*-butyllithium according to literature procedures.<sup>[14,15]</sup> After dehydration with the aid of concentrated sulfuric acid or boron trifluoride diethyl etherate, the key intermediates 3-6 were obtained in good yields. The syntheses of the TPE boronic esters and diboronic esters were started from 4-bromobenzophenone and 4,4'-dibromobenzophenone and completed in three steps.<sup>[12e, 16]</sup> The final products were conveniently produced by the palladium-catalyzed Suzuki coupling reaction of the corresponding aromatic bromides and boronic esters with yields ranging from 60.4 to 85.9%. The compounds were all purified by column chromatography on silica gel by using petroleum ether-dichloromethane as the eluent and were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, mass spectrometry, and elemental analysis.

As reported in the literature, the spirofluorene group has often been utilized in conjugated molecules instead of the normal fluorene group to hamper the possible aggregation and intermolecular  $\pi$ - $\pi$  interactions due to the presence of the sp<sup>3</sup>-hybridized spiro carbon atom.<sup>[15]</sup> Inspired by this, in

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from the TPA group, and the possible improved emission efficiency from the fluorene moieties. Thus, the design idea for TPE–pTPA and TPE–mTPA should be considered to be a new approach for the further development of AIE-active blue and deep-blue emitters.

#### **Optical properties**

All eight molecules have good solubility in common organic solvents, such as dichloromethane, chloroform, and tetrahydrofuran (THF), but are insoluble in water. Figure S1 in the Supporting Information shows their absorption spectra in THF. The UV/Vis spectra of TPE-ptol and TPE-mtol are similar, with maxima at 324 and 323 nm, respectively. The spectra of TPEpTPA and TPE-mTPA, however, are considerably blueshifted (309 and 310 nm) and have higher absorptivity than those of TPEptol and TPE-mtol, suggesting that they possess lower conjugation. This is a reasonable supposition. The conformation of TPEpTPA and TPE-mTPA should be more twisted due to the nonplanar and bulky triphenylamine group, leading to their shorter effective conjugation lengths. Moreover, the similar maximum absorptions of TPE-pTPA and TPE-mTPA indicated that they

TPE-pTPA and TPE-mTPA, the TPE and TPA moieties were combined into one molecule through the sp<sup>3</sup>-hybridized carbon atom of a fluorene block. The twisted structure would avoid the possible intermolecular  $\pi$ - $\pi$  interactions to a large degree. Furthermore, due to the presence of the sp<sup>3</sup>-hybridized carbon atom, there were very weak conjugation effects among the three main construction blocks in TPE-pTPA and TPE-mTPA, that is, the TPA, fluorene, and TPE groups. Actually, these three units could emit deep-blue light or even shorter wavelengths. Thus, the special linking mode would not lead to the conjugation effects throughout the molecule, but retain the properties of the three moieties. To subtly adjust the structure further, the linking position of the TPE group was either the meta- or paraposition, with the aim of controlling the weak conjugation effects and extent of twisting in the structure. In comparison with the TPE molecule, there were some advantages of TPEpTPA and TPE-mTPA, such as the good hole mobility derived

possess similar conjugation lengths. It was originally expected that the different linking mode might lead to a different intermolecular conjugation pattern, as mentioned in the introduction, due to their different degree of twisting of the aromatic rings. However, the almost identical absorption behavior does not agree with this theory. The reason for this might be that these two luminogens possess a highly twisted structure, and thus, the difference caused by the different linking mode could be nearly canceled out by the twisted structure. Interestingly, different phenomena were observed for the other four fluorophores, TPE-2*p*TPA, TPE-2*m*TPA, TPE-2*p*tol, and TPE-2*m*tol with similar peak maxima in the range 304-307 nm. Perhaps, the aryl groups attached to the TPE core make the phenyl rings of TPE more twisted, thus affecting the conjugation in the molecules.

To investigate the AIE properties of these new luminogens, their fluorescent behavior was recorded. THF and water were



Scheme 1. Synthetic routes to the TPE-Ar luminogens.

chosen as the solvent pair due to their miscibility. They are all nearly nonemissive when molecularly dissolved in pure THF, but become strongly emissive in the aggregated state. Figures 1 and 2 clearly show the PL change, guantum yield, and fluorescent images of the fluorophores in THF and THF/water mixtures. Taking TPE-pTPA and TPE-mTPA as examples, the PL curves are virtually flat lines parallel to the abscissa, demonstrating that they are faint emitters in the solution state. When a large amount of water is added, the aggregates form step by step. For TPE-pTPA, when the water fraction of the solvent is over 60%, the fluorescence intensity increases rapidly, indicating the formation of aggregates. At a water fraction  $(f_w)$  of 99%, the PL intensity is over 420 times that in pure THF. The quantitative enhancement of emission was evaluated by the PL quantum yields ( $\Phi_{\rm F}$ ) by using 9,10-diphenylanthracene as the standard. From a solution in pure THF to the aggregated state in a 99% aqueous mixture, the  $\Phi_{\rm F}$  values of TPE-pTPA increased from nearly 0 to 32.8%. Similar PL behaviors were also observed for the other six fluorophores. However, for TPEmTPA, when the water fraction was increased from 70 to 80%, the PL peak redshifts from 440 to 485 nm, which is probably caused by the morphological change from the aggregated, amorphous form to the crystalline state. As TPE-mTPA is more twisted than TPE-pTPA, the aggregates should be crystallized more easily, confirming the subtle adjustment of their emitting properties by accurate modification of the structure through the different linking position.

Closer inspection of the PL spectra of the luminogens in the solid state was carried out because they should be fabricated as thin solid films in the OLEDs. As shown in Figure 3, all of the films exhibit sky-blue emission ranging from 470 to 481 nm. The PL peaks of the films are almost the same as the values obtained from the corresponding PL spectra of the aggregates in the 99% water fraction, suggesting the aggregates in  $f_w$ = 99% are in the amorphous state. It should be pointed out that

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for AIE luminogens, the emitting behavior is, generally, different from that in the thin solid film, possibly due to the different approaches for the preparation of the thin films. In our previous research, the EL spectra of blue AIE luminogens are considerably blueshifted in comparison to their corresponding PL spectra, as a result of the crystalline state of the luminophors in the emitting devices.[11] The phenomenon is known as "crystallization-induced blueshifted emission."[9a, 11] Furthermore, the key reason for this phenomenon is the highly twisted structure. Here, with a twisted conformation, TPE-pTPA and TPE-mTPA should exhibit considerably blue-



**Figure 1.** Plots of the fluorescence quantum yields determined in THF/H<sub>2</sub>O solutions by using 9,10-diphenylanthracene ( $\Phi = 90\%$  in cyclohexane) as the internal standard versus the fraction of water in the solvent. Insets: photographs of the TPE-Ar luminogens in the THF/water mixture ( $f_w = 99\%$ ) taken under the illumination of a 365 nm UV lamp. Excitation wavelengths [nm]: 320 for TPE-*p*tol and TPE-*m*tol, and 310 for the other six fluorophores.





**Figure 2.** PL spectra of a) TPE–*p*TPA and b) TPE–*m*TPA in THF/H<sub>2</sub>O mixtures with different water fractions. Concentration [ $\mu$ M]: 10; excitation wavelength [nm]: 310.

shifted EL emission, rather than the sky-blue emission shown in the PL spectra of spin-coated thin films. In fact, the PL spectrum of TPE–mTPA (Figure 2), when the water fraction is 70%, partially disclosed this possibility. Thus, unlike the sky-blue emission of the thin films (Figure 3), blue, even deep-blue, emissions could still be achieved in the LED devices.

#### **Thermal properties**

Good thermal stability of an emitter is closely related to the process of vacuum deposition and the operating stability of the LED devices. The thermal properties of all of the new compounds were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. As depicted in Figure S2 in the Supporting Information and Table 1, because of the bulky and rigid structures of the TPE, triphenylamine, and fluorene groups, all of the fluorophores are thermally stable with  $T_d$  values (5% weight loss) in the range 391-549°C. Clearly, compounds 13-16 possess higher thermal stability than compounds 9-12, possibly due to the longer molecular structures and larger molecular weights. Moreover, as a result of their more rigid structures, all of the triphenylamine-substituted compounds have higher T<sub>d</sub> values than the toluene-substituted ones. In addition, molecules with the meta-linking mode of TPE and the phenyl ring at the 9-position of fluorene are less stable than the analogues with the



**Figure 3.** The PL spectra of the films of the TPE–Ar luminogens. The thin films were spin-coated onto ITO glass from dilute THF solutions with concentrations of 1 mg mL<sup>-1</sup>. Excitation wavelengths [nm]: 320 for TPE–2*p*TPA and TPE–2*m*TPA, 350 for TPE–2*p*tol and 340 for the rest of the fluorophores.

Table 1. The thermal, electrochemical, and photophysical data of the TPE-Ar luminogens.									
	τ <sub>d</sub> <sup>[a]</sup> [°C]	<i>T</i> g <sup>[b]</sup> [°C]	<i>E</i> g <sup>[c]</sup> [eV[	E <sub>HOMO</sub> <sup>[d]</sup> [eV]	E <sub>LUMO</sub> <sup>[e]</sup> [eV]	PL λ <sub>ma</sub> aggr <sup>[f]</sup> [nm]	film [nm]	$arPsi_{\sf F}$ aggr $^{{ m (f)}}$ [%]	λ <sub>max,abs</sub> soln <sup>[g]</sup> [nm]
TPE-ptol	409	82	3.28	-5.49	-2.21	486	479	17.9	324
TPE- <i>m</i> tol	391	80	3.29	-5.53	-2.24	479	474	21.6	323
TPE-pTPA	451	106	3.37	-5.22	-1.85	480	476	32.8	309
TPE- <i>m</i> TPA	450	-	3.38	-5.22	-1.84	478	477	30.1	310
TPE-2ptol	517	-	3.20	-5.46	-2.26	492	481	26.5	307
TPE-2 <i>m</i> tol	492	110	3.21	-5.49	-2.28	483	476	29.6	307
TPE-2pTPA	549	174	3.33	-5.21	-1.88	490	480	20.7	305
TPE-2 <i>m</i> TPA	506	-	3.36	-5.14	-1.78	480	470	24.8	304
[a] 5% weight-loss temperature measured by TGA under N <sub>2</sub> . [b] Glass- transition temperature measured by DSC under N <sub>2</sub> . [c] Band gap estimat- ed from the optical absorption band edge of the solution. [d] Calculated from the onset oxidation potentials of the compounds. [e] Estimated by using the empirical equation $E_{LUMO} = E_{HOMO} + E_g$ . [f] Determined in THF/ H <sub>2</sub> O = 1:99. [g] Observed from absorption spectra in dilute THF (10 µM).									

*para*-linking mode as a result of their more twisted conformations. Among these compounds, TPE–2pTPA possesses the highest thermal stability and exhibits a glass-transition temperature ( $T_q$ ) of 174 °C. With the thermal and morphological stabil-



ity of these compounds, homogeneous and stable amorphous thin films should be possible to be obtained by vacuum deposition, which is desirable for OLEDs with high stability and efficiency.

#### **Theoretical calculations**

To better understand the correlation between the structure and photophysical properties, as well as the OLED performance, density functional theory (DFT) calculations (B3LYP/ 6-31g\*) were conducted to obtain the orbital distributions of the HOMO and LUMO energy levels. As shown in Figure 4, for



Figure 4. Calculated molecular orbital amplitude plots of HOMO and LUMO levels of the TPE-Ar luminogens.

toluene-substituted compounds TPE-2ptol, TPE-2mtol, TPEptol, and TPE-mtol, the electron clouds of the HOMOs and LUMOs are all located on the TPE moieties, showing their weak intramolecular charge transfer and corresponding to their lower absorbance shown in the UV/Vis spectra (see the Supporting Information, Figure S1). However, the electron distributions of the HOMO and LUMO orbitals are centralized on TPE and triphenylamine separately for the TPA-substituted compounds, that is, TPE-2pTPA, TPE-2mTPA, TPE-pTPA, and TPEmTPA, suggesting the electron-donating properties of triphenylamine, and thus their better hole-transporting ability. Further inspection of their optimized molecular structures was carried out. From Figure S4 in the Supporting Information, we can see that the dihedral angles between the toluene group or the triphenylamine and fluorene plane are all over 75°, suggesting weak conjugation. This is consistent with our synthetic idea of combining the classically fluorescent moieties together without bringing about the side effect of lengthened conjugation. Moreover, the bulky nonplanar triphenylamine makes the molecules more twisted. This is beneficial for decreasing the intermolecular  $\pi$ - $\pi$  stacking compared to the toluene-substituted compounds, leading to crystallization-induced blueshifted emission for TPE-pTPA and TPE-mTPA.

#### **Electrochemical properties**

Cyclic voltammetry (CV) was carried out to investigate the electrochemical behavior of these materials. The HOMO energy levels were estimated from the onset oxidation potentials according to the equation HOMO =  $-(4.8 + E_{ox})$  eV, whereas the LUMO energy levels were obtained from the optical band gap energies (estimated from the onset wavelengths of the UV absorptions) and the HOMO values. The HOMO values for TPEpTPA and TPE-mTPA (-5.22 eV for both) are higher than those of TPE-ptol and TPE-mtol (-5.49 and -5.53 eV), suggesting that they possess better hole-transporting properties due to the introduction of the triphenylamine unit. Furthermore, the higher band gap energies of TPE-pTPA and TPE-mTPA (3.37 and 3.38 eV) have clearly demonstrated their shorter effective conjugation lengths, which is closely related to their twisted conformations. Therefore, it could be rationalized that the turn-on voltages of TPE-pTPA and TPE-mTPA will be decreased in comparison with those of TPE-ptol and TPE-mtol. As seen in Table 1, the other four luminogens, TPE-pTPA, TPE-mTPA, TPE-ptol, and TPE-mtol, are in the same situation. They all possess longer conjugation lengths than the aforementioned ones, which will result in redshifted EL emissions.

#### Electroluminescence

The efficient solid-state emission and good thermal and morphological stability of these luminogens prompted us to investigate their electroluminescence properties. Undoped multilayer OLEDs with configurations of indium tin oxide/polyethylenedioxythiophene-polystyrene sulfonic acid (ITO/PEDOT:PSS, 30 nm)/NPB (1,4-bis(1-naphthylphenylamino)biphenyl, 30 nm)/ EML (emissive layer, 10–30 nm)/TPBI (1,3,5-tris(*N*-phenylbenzimidizol-2-yl)benzene, 10 nm)/Alq3 (tris(8-oxoquinoline) aluminum(III), 30 nm)/Ca:Ag(100 nm) were fabricated in which NPB and TPBI work as the hole-transporting and hole-blocking layers, respectively, PEDOT:PSS was used to smooth the ITO surface and decrease the hole injection barrier, and the AIE luminogens served as emitters.

As summarized in Table 2, the devices based on the four triphenylamine-containing emitters (TPE-pTPA, TPE-mTPA, TPE-2pTPA, and TPE-2mTPA) possess lower turn-on voltages (3.0-3.6 V) and higher current densities than those of the toluenesubstituted compounds (3.9-4.5 V), reflecting their smaller injection barriers from transporting layers. This confirmed that the TPA moieties were beneficial for increasing the hole-transporting capability compared to toluene moieties, which is consistent with our design idea. As shown in the current-densityvoltage–luminance (J–V–L) curves (Figure 5 a), the current densities increase rapidly as the voltage increases. All of the devices containing TPA-based emitters show better EL efficiencies than the toluene-based compounds. In detail, devices based on TPE-ptol and TPE-mtol exhibit maximum luminances  $(L_{max})$ of 8540 and 10494 cd m<sup>-2</sup>, maximum current efficiencies  $(\eta_{C,max})$  of 1.64 and 2.18 cd A<sup>-1</sup>, and maximum power efficiencies ( $\eta_{P,max}$ ) of 0.70 and 0.96 lm W<sup>-1</sup>, respectively. As expected, much better EL performances were observed for TPE-pTPA

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Table 2. EL performance of the TPE-Ar luminogens. <sup>[a]</sup>								
	λ <sub>εL</sub> [nm]	V <sub>on</sub> [V]	L <sub>max</sub> [cd m <sup>-2</sup> ]	$\eta_{ m C,max}$ [cd A <sup>-1</sup> ]	$\eta_{ extsf{P,max}}$ [lm/W]	CIE [ <i>x,y</i> ]		
TPE-pTPA	448	3.0	26697	3.37	2.40	0.16, 0.16		
TPE- <i>m</i> TPA	451	3.3	14854	2.76	1.80	0.15, 0.15		
TPE– <i>p</i> tol	448	4.5	8540	1.64	0.70	0.16, 0.19		
TPE- <i>m</i> tol	450	3.9	10494	2.18	0.96	0.16, 0.14		
TPE–2 <i>p</i> tol	511	3.9	9578	1.68	0.39	0.17, 0.24		
TPE-2 <i>m</i> tol	484	3.9	7 382	1.37	0.57	0.16, 0.27		
TPE-2 <i>p</i> TPA	488	3.3	14173	5.65	3.68	0.19, 0.31		
TPE-2 <i>m</i> TPA	489	3.6	10275	4.24	2.10	0.14, 0.28		
[a] Abbreviations $V_{i}$ turn on voltage at 1 adm <sup>-2</sup> $V_{i}$ mavinum lumi								

[a] Abbreviations:  $V_{on} =$  turn-on voltage at 1 cd m<sup>-2</sup>,  $L_{max} =$  maximum luminance,  $\eta_{Cmax}$  and  $\eta_{Pmax} =$  maximum current and power efficiencies, respectively. CIE = commission international de l'eclairage coordinates.



**Figure 5.** a) Current-density–voltage–luminance characteristics of multilayer EL devices of TPE–*p*TPA, TPE–*m*TPA, TPE–*p*tol, and TPE–*m*tol. b) Change in current efficiency with current density in multilayer EL devices. c) EL spectra of the devices. Device configurations: ITO/PEDOT:PSS (30 nm)/NPB (30 nm)/ EML (15 nm)/TPBI (10 nm)/Alq<sub>3</sub> (30 nm)/LiF (1 nm)/Ca:Ag (100 nm).

and TPE–mTPA with  $L_{\rm max}$ ,  $\eta_{\rm C,max}$ , and  $\eta_{\rm P,max}$  values of 26697 and 14854 cd m $^{-2}$ , 3.37 and 2.76 cd A $^{-1}$ , and 2.40 and 1.80 Lm W $^{-1}$ , respectively, showing more efficient carrier transport and exciton combination in the emissive layer. Interestingly, although the chemical structures of TPE-pTPA and TPE-mTPA are similar, their device performance is quite different. This is reasonable; the conformation of TPE-pTPA is more planar than that of TPE-mTPA, which is good for carrier transport when serving as an emitter. Furthermore, as TPE and TPA or toluene groups are linked to the fluorene core through the 9,9'-positions, the molecules are quite twisted, and the  $\pi$ -conjugation lengths are effectively controlled. Thus, all four emitters exhibit deep-blue emission with EL peaks at 448-451 nm. From the CIE coordinates, devices made from TPE-mtol (0.16, 0.14) and TPE-mTPA (0.15, 0.15) are bluer than those made from TPE-ptol and TPEpTPA because the meta-linkage of TPE and the fluorene core contributes less to the elongation of the conjugation than the para-linkage, as evidenced by our previous study.[13c] Compared to TPE alone, the incorporation of TPA and fluorene not only could increase the thermal stability, but also could greatly enhance the OLED performance without sacrificing the deep-blue emission because of the special linking mode through the sp<sup>3</sup>hybridized carbon atom, as discussed above.

Moreover, as the conjugation lengths are effectively lengthened, the OLED performance of TPE-2pTPA and TPE-2mTPA is greatly enhanced with  $L_{max}$ ,  $\eta_{C,max}$ , and  $\eta_{P,max}$  values of 14173 and  $10\,275 \text{ cd m}^{-2}$ , 5.65 and 4.64 cd A<sup>-1</sup>, and 3.68 and 2.10 Lm W<sup>-1</sup>, respectively (Figure 6). However, their EL emissions are no longer in the deep-blue region, with EL peaks at 488 and 489 nm, and CIE coordinates of (0.19, 0.31) and (0.14, 0.28), demonstrating the difficulty of generating AIE emitters with both deep-blue emission and high OLED efficiencies. TPE-2ptol and TPE-2mtol possess worse device performance, probably due to the imbalance between charge injection and transportation in OLEDs. In comparison with the PL spectra of these four disubstituted TPE derivatives, the EL spectra exhibit some redshifting. This phenomenon is totally different from in the monosubstituted TPE compounds, including TPE-pTPA, TPE-mTPA, TPE-mtol, and TPE-ptol, which could not be explained only by the transformation from the crystalline state to the amorphous one. Analyzing their structures carefully, the results could be understood. In the four disubstituted TPE derivatives (TPE-2pTPA, TPE-2mTPA, TPE-2ptol, and TPE-2mtol), the  $\pi$  systems are much longer than those of in the monosubstituted compounds. Thus, in the compacted films of LED devices their coplanarity might be better than that in the loosely aggregated nanoparticles in a 90% water/THF solution or in spincoated films, which would lead to the redshifted emission as a result of the enhanced conjugation throughout the molecule. On the other hand, as shown in Table 1, the PL emission wavelengths of these four disubstituted TPE derivatives in thin films are blueshifted in comparison with those in the aggregated state due to the transformation from the amorphous state to the crystalline one. Thus, in the compacted films of LED devices, there are two conflicting parameters, coplanarity and states (amorphous vs. crystalline). From these results, coplanarity is the main parameter causing the redshifted emission. As



**Figure 6.** a) Current-density-voltage-luminance characteristics of multilayer EL devices of TPE-2*p*TPA, TPE-2*m*TPA, TPE-2*p*tol, and TPE-2*m*tol. b) Change in current efficiency with current density in multilayer EL devices. c) EL spectra of the devices. Device configurations: ITO/PEDOT:PSS (30 nm)/NPB (30 nm)/EML (15 nm)/TPBI (10 nm)/Alq3 (30 nm)/LiF (1 nm)/Ca:Ag (100 nm).

to the cases of the four monosubstituted TPE derivatives, the coplanarity and different state compete; fortunately, the transformation from the amorphous to the crystalline state contributes considerably to the blueshifted EL emissions for these relatively shorter  $\pi$  systems and lower molecular weights. These phenomena have never been observed for AIE luminogens with blue or deep-blue emission, possibly due to their shorter  $\pi$  systems. However, the results obtained here remind us of another point in the design of AIE luminogens with blue and deep-blue emissions: the possibly improved coplanarity of the AIE luminogens in the compacted thin films of LED devices derived from long  $\pi$  systems.

As is known, it is difficult to obtain blue and deep-blue emitters with good EL performance. Definitely, a lot of excellent AIE emitters could be obtained by attaching the TPE moiety to classical molecules, such as pyrene,<sup>[12d,k]</sup> anthracene,<sup>[12a-b,k]</sup> and fluorene<sup>[12h]</sup>, because the nonplanar TPE molecule could suppress the intermolecular  $\pi$ - $\pi$  stacking of the molecules, although TPE itself is a weak emitter. However, it will certainly result in the intrinsic extension of the conjugation length through common linkage modes. The good device performance and deep-blue emission of TPE-*p*TPA and TPE-*m*TPA have fulfilled our synthetic idea of utilizing less- or unconjugated linking modes, and shed some light on our further rational molecular design.

## Conclusion

In this work, we have successfully synthesized two deep-blue fluorophores, TPE-pTPA and TPE-mTPA, and also another six molecules with toluene groups or different conjugation lengths for comparison. All of the luminogens show splendid AIE effects and exhibit good thermal and morphological stability due to the bulky aromatic groups. By incorporating holedominated triphenylamine, fluorine groups with high luminous efficiency, and the TPE moiety together through unconjugated linkages, we partially overcame the intrinsic inconsistency between high efficiencies and deep-blue emission for constructing AIE-active blue luminogens. When fabricated as emissive layers in OLEDs, TPE-pTPA and TPE-mTPA exhibit the best EL performance with  $L_{max}$ ,  $\eta_{C,max}$ , and  $\eta_{P,max}$  values of up to 26697 cd m<sup>-2</sup>, 3.37 cd A<sup>-1</sup>, and 2.40 Lm W<sup>-1</sup>, and CIE coordinates of (0.16, 0.16) and (0.15, 0.15), respectively, suggesting the more efficient carrier transport and exciton combination in these devices and less effective conjugation lengths compared to other emitters. Evidently, the electroluminescence properties of TPE could be greatly enhanced without sacrificing the deepblue emission through rational molecular design. By utilizing this design idea, we believe that more efficient blue or deepblue TPE-based emitters will be developed and find applications in OLEDs.

## **Experimental Section**

#### Preparation of the compounds

All other chemicals and reagents were obtained from commercial sources and used as received. Solvents for chemical synthesis were purified according to standard procedures. Compounds **3–6** were synthesized according to literature procedures.<sup>[1]</sup>

#### Synthesis of compound 7

A solution of *n*-butyllithium in hexane (2.3 M, 15.0 mmol, 6.5 mL) was added to a solution of 4-bromotetraphenylethene (2, 4.12 g, 10.0 mmol) in anhydrous tetrahydrofuran (60 mL) at -78 °C under an atmosphere of argon. After stirring for 4 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.1 mL) was added. After 2 h, the mixture was slowly warmed to room temperature. After stirring overnight, the reaction was terminated by the addition of brine. The mixture was extracted with dichloromethane and the organic

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layers were combined and dried over anhydrous sodium sulfate. After filtration and evaporation of the solvent, the crude product was purified by silica gel column chromatography using petroleum ether (60–90 °C)/dichloromethane (5:1 v/v) as the eluent. A white powder (**7**) was obtained in a yield of 60% (2.30 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =7.55–7.52 (m, 2H), 7.08–7.01 (m, 17 H), 1.31 ppm (s, 12 H).

#### Synthesis of compound 8

A mixture of 4,4'-dibromotetraphenylethene (**3**, 4.90 g, 10 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (6.35 g, 25 mmol), potassium acetate (6.87 g, 70 mmol), and [Pd(dppf)Cl<sub>2</sub>] (0.15 g, 0.2 mmol) in anhydrous 1,4-dioxane (80 mL) was heated at reflux under N<sub>2</sub> for 12 h, and then water (20 mL) was added. The crude product was extracted into ethyl acetate, washed with water, and dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified by column chromatography using petroleum ether (60–90 °C)/ethyl acetate (10:1 v/v) as the eluent. A white powder (**8**) was obtained in a yield of 68.9% (4.2 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.53–7.47 (m, 4H), 7.11–7.09 (m, 4H), 7.07–7.05 (m, 6H), 7.00–6.98 (m, 4H), 1.27 ppm (s, 24H).

# General procedure for the synthesis of TPE-*p*tol, TPE-*m*tol, TPE-*p*TPA, TPE-*m*TPA, TPE-2*p*tol, TPE-2*m*tol, TPE-2*p*TPA, and TPE-2*m*TPA

#### TPE-ptol

A mixture of **3** (412 mg, 1 mmol), **7** (463 mg, 1.01 mmol), [Pd(PPh<sub>3</sub>)<sub>4</sub>] (60 mg), and potassium hydroxide (280 mg, 5 mmol) in THF (15 mL) and distilled water (5 mL) was heated at reflux for two days under N<sub>2</sub> in a Schlenk tube (50 mL). The mixture was extracted with dichloromethane. The combined organic extracts were dried over anhydrous  $\mathsf{Na}_2\mathsf{SO}_4$  and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using dichloromethane/petroleum ether (1:50 v/v) as the eluent. A white powder was obtained in a yield of 69.4% (460 mg). M.p.: 108–110 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.77–7.75 (m, 2H), 7.38-7.32 (m, 6H), 7.23-7.20 (m, 4H), 7.09-7.04 (m, 23H), 2.29 ppm (s, 3 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 151.4$ , 145.3, 143.9, 143.8, 143.0, 142.8, 141.2, 140.7, 140.3, 138.9, 138.5, 136.5, 131.9, 131.6, 131.5, 129.2, 128.7, 128.2, 127.9, 127.8, 127.6, 126.8, 126.6, 126.3, 126.2, 120.4, 21.2 ppm; IR (thin film): v = 2959, 2886, 1722, 1443, 1188, 1064, 962, 845 cm<sup>-1</sup>; MS (El): m/z calcd for  $C_{52}H_{38}$ : 662.86; found: 662.17 [*M*<sup>+</sup>]; elemental analysis calcd (%) for C<sub>52</sub>H<sub>38</sub>: C 94.22, H 5.78; found: C 94.45, H 5.72.

#### TPE-mtol

White powder (yield: 69.4%). M.p.: not observed; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.78–7.75 (m, 2H), 7.38–7.33 (m, 6H), 7.23–7.20 (m, 4H), 7.09–7.05 (m, 23 H), 2.29 ppm (s, 3 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 151.4, 146.7, 143.9, 143.8, 143.1, 142.9, 141.1, 140.6, 140.5, 140.3, 138.9, 136.4, 131.9, 131.5, 129.1, 128.1, 127.9, 127.8, 127.6, 127.2, 126.6, 126.4, 126.3, 125.4, 120.3, 21.2 ppm; IR (thin film):  $\tilde{\nu}$  = 2959, 2890, 1722, 1442, 1190, 1064, 966, 851 cm<sup>-1</sup>; MS (EI): *m/z* calcd for C<sub>52</sub>H<sub>38</sub>: 662.86; found: 662.16 [*M*<sup>+</sup>]; elemental analysis calcd (%) for C<sub>52</sub>H<sub>38</sub>: C 94.22, H 5.78; found: C 94.37, H 5.36.

#### TPE-pTPA

White powder (yield: 84.6%). M.p.: 155–158 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =7.78–7.76 (m, 1H), 7.44–7.34 (m, 6H), 7.30–7.19 (m, 14H), 7.07–7.05 (m, 21H), 6.98–6.96 (m, 1H), 6.92–6.89 ppm (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =151.7, 147.8, 146.7, 145.1, 143.8, 142.7, 141.1, 140.6, 140.5, 139.5, 138.9, 138.6, 131.9, 131.7, 129.5, 128.9, 128.4, 127.6, 126.8, 126.2, 124.6, 123.4, 122.7, 120.5 ppm; IR (thin film):  $\tilde{\nu}$ =2958, 2886, 1726, 1492, 1188, 1068, 956, 851, 700 cm<sup>-1</sup>; MS (EI): *m/z* calcd for C<sub>63</sub>H<sub>45</sub>N: 816.04; found: 816.13 [*M*<sup>+</sup>]; elemental analysis calcd (%) for C<sub>63</sub>H<sub>45</sub>N: C 92.73, H 5.56, N 1.72; found: C 92.45, H 5.18, N 1.71.

#### TPE-mTPA

White powder (yield: 70.5%). M.p.: not observed; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =7.77-7.75 (m, 1H), 7.45-7.34 (m, 3H), 7.26-7.19 (m, 24H), 7.10-6.98 (m, 16H), 6.91-6.88 ppm (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =151.4, 147.8, 146.7, 146.4, 143.9, 142.9, 141.2, 140.6, 140.4, 140.2, 139.7, 138.9, 131.9, 131.5, 129.3, 129.1, 128.0, 127.9, 127.8, 127.7, 126.6, 126.4, 125.4, 124.5, 123.3, 122.9, 120.4 ppm; IR (thin film):  $\tilde{\nu}$ =2958, 2883, 1721, 1491, 1188, 1066, 963, 852, 745, 698 cm<sup>-1</sup>; MS (EI): *m/z* calcd for C<sub>63</sub>H<sub>45</sub>N: 816.04; found: 816.09 [*M*<sup>+</sup>]; elemental analysis calcd (%) for C<sub>63</sub>H<sub>45</sub>N: C 92.73, H 5.56, N 1.72; found: C 92.37, H 5.51, N 1.81.

#### TPE-2ptol

White powder (yield: 60.4%). M.p.: 204–207 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.87–7.85 (m, 4H), 7.48–7.45 (m, 12H), 7.38–7.27 (m, 30H), 7.17–7.04 (m, 4H), 2.38 ppm (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 151.4, 145.2, 143.9, 143.0, 142.8, 141.3, 140.2, 138.9, 138.5, 136.4, 132.0, 131.5, 129.1, 128.6, 128.2, 127.9, 127.6, 126.7, 126.6, 126.4, 126.2, 126.1, 120.3, 21.2 ppm; IR (thin film):  $\tilde{\nu}$  = 2960, 2891, 1716, 1640, 1442, 1368, 1346, 1322, 1190, 1065, 963, 927, 849 cm<sup>-1</sup>; MALDI-TOF: *m/z* calcd for C<sub>78</sub>H<sub>56</sub>: 992.4382; found: 992.4396 [*M*<sup>+</sup>]; elemental analysis calcd (%) for C<sub>78</sub>H<sub>56</sub>: C 94.32, H 5.68; found: C 94.01, H 5.81.

#### TPE-2mtol

White powder (yield: 84.5%). M.p.: 206–209°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =7.77–7.75 (m, 4H), 7.42–7.33 (m, 13H), 7.28–7.18 (m, 10H), 7.08–7.03 (m, 11H), 7.02–7.00 (m, 12H), 2.29 ppm (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =151.5, 146.7, 144.0, 143.1, 140.4, 139.1, 136.5, 132.0, 131.6, 129.2, 128.3, 128.0, 127.7, 127.3, 126.8, 126.5, 126.4, 125.5, 120.4, 21.2 ppm; IR (thin film):  $\tilde{\nu}$ =2960, 2890, 1722, 1643, 1442, 1368, 1344, 1190, 1066, 963, 926, 850 cm<sup>-1</sup>; MALDI-TOF: *m/z* calcd for C<sub>78</sub>H<sub>56</sub>: 992.4382; found: 992.4370 [*M*<sup>+</sup>]; elemental analysis calcd (%) for C<sub>78</sub>H<sub>56</sub>: C 94.32, H 5.68; found: C 93.88, H 5.31.

#### TPE-2pTPA

Light-yellow powder (yield: 85.9%). M.p.: 217–220°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.77–7.75 (m, 4H), 7.45–7.33 (m, 11H), 7.29–7.26 (m, 11H), 7.22–7.17 (m, 15), 7.09–7.04 (m, 25H), 6.98–6.88 ppm (m, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 151.5, 147.9, 146.4, 145.3, 142.9, 140.3, 139.7, 138.6, 132.0, 131.6, 129.4, 129.1, 128.7, 127.9, 127.7, 126.8, 126.4, 126.2, 124.6, 123.4, 123.0, 120.4 ppm; IR (thin film):  $\tilde{\nu}$  = 2959, 2886, 1715, 1443, 1346, 1188, 1060, 960, 854 cm<sup>-1</sup>; MALDI-TOF: *m/z* calcd for C<sub>100</sub>H<sub>70</sub>N<sub>2</sub>: 1298.5539; found: 1298.5559 [*M*<sup>+</sup>]; elemental analysis calcd (%) for C<sub>100</sub>H<sub>70</sub>N<sub>2</sub>: C 92.40, H 5.48, N 1.88.

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#### TPE-2mTPA

Light-yellow powder (yield: 80.5%). M.p.: 190–192°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =7.61–7.57 (m, 4H), 7.25–7.13 (m, 9H), 7.11–7.08 (m, 19H), 7.05–7.00 (m, 8H), 6.88–6.80 (m, 27H), 6.81–6.70 ppm (m, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =151.5, 147.9, 144.0, 140.4, 132.0, 131.6, 129.4, 129.2, 128.8, 128.0, 127.7, 126.8, 126.5, 125.5, 124.6, 123.3, 123.0, 120.4 ppm; IR (thin film):  $\tilde{\nu}$ =2959, 2888, 1715, 1590, 1489, 1446, 1189, 1061, 959, 747 cm<sup>-1</sup>; MALDI-TOF: *m/z* calcd for C<sub>100</sub>H<sub>70</sub>N<sub>2</sub>: 1298.5539: found: 1298.5586 [*M*<sup>+</sup>]; elemental analysis calcd (%) for C<sub>100</sub>H<sub>70</sub>N<sub>2</sub>: C 92.42, H 5.43, N 2.16; found: C 92.18, H 5.72, N 2.19.

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