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Graphic Abstract



Spirotriphenylamine Based Star-Shaped D-A Molecules Meeting AIE Chromophore for Both Efficient Solution-Processed Doped and Nondoped Blue Organic Light-Emitting Diodes

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Abstract

To explore the structure-property of donor-acceptor (D-A) type blue emitter, in this contribution, four star-shaped compounds of p-TPA, m-TPA, p-TPA-TPE and *m*-TPA-TPE using spirotriphenylamine as the donor unit and triazine as the acceptor core were designed and prepared. The tetraphenylethene (TPE) unit was introduced into the D-A molecules to enhance the emission efficiency in solid state. The photophysical properties of all compounds were comparatively studied through experimental and theoretical methods. All these D-A compounds displayed blue emission (443~487 nm) both in solution and neat film. Compared to p-TPA and *m*-TPA, *p*-TPA-TPE and *m*-TPA-TPE possessed clear aggregated-induced emission (AIE) property and higher emission efficiency in the solid state. Both the doped and non-doped organic light-emitting diodes (OLEDs) based on m-TPA and m-TPA-TPE were fabricated by solution-processable approach. The *m*-TPA-TPE based non-doped device showed a satisfying performance with a high current efficiency of 4.2 cd/A and an external quantum efficiency of 1.8 % in the bluish-green region. This research demonstrates that integrating AIE unit into D-A molecule is an effective strategy for design high efficient blue emitter in non-doped OLEDs.

Keywords

Spirotriphenylamine; Star-shaped molecule; Donor-acceptor framework; Aggregation-induced emission; Non-doped OLEDs

1. Introduction

 π -Conjugated chromophores consisting of electron donor (D) and electron acceptor (A) groups are always actively pursued by both the academia and industry as organic dyes for semiconductor devices due to their outstanding thermal stability, bipolar charge transporting property, enhanced polarizability and tuned energy band gap [1-6]. Especially, these D-A molecules have recently made great progress in organic light-emitting diodes (OLEDs), which covers the whole visable and near-infrared spectrum [7-11]. On the other side of the coin, the intrinsic intramolecular charge transfer (ICT) and largely separated HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) in D-A molecules usually leads to a severe bathochromic shift and low emission efficiency [12].

To this end, many groups put forth their efforts to achieve the efficient blue emitter based on D-A molecules [13-18]. One of the most effective strategies is to construct a twisting D-A compound *via* introducing additional conjugated linked bridge (π unit) to break the π -conjugation degree [19,20]. For instance, a series of phenanthroimidazole-based D- π -A/D- π -A- π -D molecules were prepared, which showed the deep blue electroluminescence with high external quantum efficiency (*EQE*) in doped device [21-26]. Futhermore, engineering the interconnection position between the donor/bridge/or acceptor moiety also effectively tuned the energy gap leading to the blue emission, substantiated by our recent research [27]. Another method to obtain the D-A type blue emitter is to employ the steric donor/or acceptor group. *Su* and his *co*-workers successfully grafted the bulky spiro[fluorene-9,9'-

thioxanthene-S,S-dioxide] unit into the blue emission material [28]. However, few of these D-A compounds were regarded as the non-doped blue emitters. Considering the potential phase separation and stability in the dopant–host system, therefore, it is necessary to develop the D-A compound as the blue emitter in the non-doped OLEDs [23,29,30].

Based on our previous work [27], the star-shaped D- π -A molecules containing triazine core have a good thermal bility and satisfied blue emission. Encouraged by our previous work and with an intention to further investigate the structure-property of the star-shaped blue emitter, in this contribution, we would like to focus on the triazine based D-A type blue emitter in non-doped OLEDs. Owing to the twist conformation [31], spiro-annulated triphenylamine was initially chosen as the donor unit, which is very scarce in the D-A blue emitter. To further enhance the efficiency of the non-doped devices, the aggregated-induced emission (AIE) concept, reported by Tang in 2001 [32], would be integrated into the D-A compound because they are non-emissive in dilution solutions but have very intense luminescence in the solid state [33,34]. As aforementioned, we designed two star-shaped D-A isomers with different interconnection position, p-TPA-TPE and m-TPA-TPE, in which TPA is the triazine core and spiro-annulated triphenylamine units and TPE is the tetraphenylethene moiety (Figure 1 and Scheme 1). For comparison, the parent compound without TPE unit, p-TPA and m-TPA, were also synthesized. Herein, the photophysical property were systematically explored by experimental and theoretical methods. As expected, all these D-A compounds showed the blue emission both in

solution and neat film. The compounds with TPE unit definitely have an enhanced emission efficiency in the solid state. To expolre the electroluminescent property of these D-A compounds, both doped and non-doped devices employing *m*-TPA and *m*-TPA-TPE as emitter were fabricated by solution-processable approach. The *m*-TPA-TPE based non-doped device achieved a high current efficiency of 4.2 cd/A and an *EQE* of 1.8 % in the bluish-green region.

2. Experimental Section

2.1 Materials and Measurement

2,7-dibromofluorenone 2-bromoiodobenzene, 2-bromofluorenone and are commercial from Energy Chemical Company Ltd. Other reagents were purchased from J&K Chemical and Aladdin companies. All reactions were carried out under N2 atmosphere. Compounds 1, 2, 5 and 6 were synthesized according to the reported procedure [27,31]. ¹H NMR and ¹³C NMR spectra were acquired using a Bruker Dex-400 NMR instrument using CDCl₃ as a solvent. Mass spectra (MS) were recorded on a Bruker Autoflex MALDI-TOF instrument using dithranol as a matrix. Elemental analysis was measured by Flash EA 1112. The UV-vis absorption and photoluminescence (PL) spectra were measured with a Varian Cray 50 and Perkin-Elmer LS50B luminescence spectrometer, respectively. Lifetimes and emission efficiency in solid state were measured with Edinburgh analytical instrument (FLS980 fluorescence spectrometer) in degassed toluene at room temperature. Thermogravimetric analysis (TGA) was carried out with a NETZSCH STA449 from

 50° C to 600° C at a 20° C/min heating rate under N₂ atmosphere. Electrochemical property was evaluated by cyclic voltammetry (CV) with three typical electrodes in degassed CH₃CN solution with a rate of 100 mV/s. The CV system employed Bu₄NPF₆ as electrolyte. Platinum disk was used as the working electrode, platinum wire was regarded as the counter electrode and silver wire was used as the reference electrode. Ferrocenium/ferrocen (Fc/Fc⁺) was used as the reference compound.

2.2 Devices fabrication and characterization

The devices employing m-TPA and m-TPA-TPE as the dopant were fabricated by solution-processed approach. In these OLEDs. poly(3,4-ethylenedioxythiophene:poly(styrenesulfonic acid) (PEDOT:PSS) was spin-coated onto ITO substrate, which is utilized as the hole injection layer. The 9-[3-(9H-carbazol-9-yl)phenyl]-9H-carbazole (mCP) is used as the host matrix. 1,3,5-tri(m-pyrid-3-yl-phenyl)benzene (TmPyPB) is the electron transporting layer with 40 nm thick. Liq and Al are used as the composite cathode. Electroluminescent spectra were recorded using an optical analyzer, Photo Research PR735. The features of current density and brightness versus applied voltage were simultaneously obtained by a source meter unit Keithley 2420 and PR735. EQE was calculated from the luminance, current density, and EL spectrum, assuming a Lambertian distribution. The device configurations are as follows:

Device I: ITO/PEDOT:PSS (30 nm)/mCP: m-TPA (90:10, 30 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al

Device II: ITO/PEDOT:PSS (30 nm)/mCP: m-TPA-TPE (90:10, 30 nm)/TmPyPB (40

nm)/Liq (1 nm)/Al

Device III: ITO/PEDOT:PSS (30 nm)/m-TPA (30 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al

Device IV: ITO/PEDOT:PSS (30 nm)/m-TPA-TPE (30 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al

2.3 Synthesis of compound 3

A mixture of 1-(4-bromophenyl)-1,2,2-triphenylethylene (4.0 g, 9.8 mmol), bis(pinacolato)diboron (3.7 g, 14.6 mmol), CH₃COOK (4.8 g, 48.8 mmol) and 1,1'-bis(diphenylphosphino)ferrocene palladium dichloride (214 mg, 0.3 mmol) in 1,4-dioxane (100 mL) was refluxed for 24 h under nitrogen. After cooling to room temperature, the mixture was poured into water and extracted with CH₂Cl₂ (3×20 mL). The organic phase was collected and washed with water (3×20 mL) and dried with anhydrous Na₂SO₄. The solvent was removed under vacuum, and then the residue was purified by column chromatography with petrolum ether (PE)/CH₂Cl₂ (4:1) as an eluent to give compound 3 (3.6 g, yield: 79%) as a green solid. ¹H NMR (400 MHz, CDCl₃), δ : 7.54 (d, *J*=8.0 Hz, 2H), 7.09-7.01 (m, 17H), 1.32 (s, 12H).

2.4 Synthesis of compound 4

To a dry round bottom flask was added compound 2 (2.2 g, 3.8 mmol), compound 3 (1.6 g, 3.5 mmol), tetrakis(triphenylphosphine)palladium (120 mg, 0.1 mmol), potassium carbonate solution (2 M, 25 mL) and THF (80 mL). The mixture was refluxed for 24 h under nitrogen. After cooling to room temperature, the mixture was then poured into water and extracted with CH_2Cl_2 (3×20 mL). The organic phase was

washed with water (3×20 mL) and dried with anhydrous Na₂SO₄. After Removing the solvent under vacuum, the residue was purified by column chromatography with PE/CH₂Cl₂ (4:1) as an eluent to get the compound 4 as a green solid (1.2 g, yeild: 42%). ¹H NMR (400 MHz, CDCl₃), δ : 7.82 (d, *J*=8.4 Hz, 1H), 7.74 (t, *J*=7.6 Hz, 2H), 7.68-7.55 (m, 5H), 7.49 (d, *J*=8.0 Hz, 3H), 7.33 (d, *J*=8.4 Hz, 2H), 7.21-7.05 (m, 16H), 6.97 (t, *J*=8.4 Hz, 3H), 6.62 (t, *J*=7.6 Hz, 2H), 6.45 (d, *J*=7.6 Hz 2H), 6.39 (d, *J*=7.6 Hz, 2H).

2.5 Synthesis of *p*-TPA and *m*-TPA

A mixture of compound 1 or 2 (4 mol eq) , compound 5 or 6 (1 mol eq), tetrakis(triphenylphosphine)palladium (0.03 mol eq), potassium carbonate solution (2 M, 15 mL) and THF (45 mL) was refluxed for 24 h under nitrogen. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2 (3×20 mL). The organic phase was washed with water (3×20 mL) and dried with anhydrous Na₂SO₄. The solvent was removed under vacuum, and then the residue was purified by column chromatography using PE/CH₂Cl₂ (2:1) as an eluent to get the target compounds.

p-TPA: Light yellow solid. Yield: 45%. ¹H NMR (400 MHz, CDCl₃), δ: 8.83 (d, J=8.0 Hz, 6H), 7.95 (d, J=8.0 Hz, 6H), 7.87 (t, J=9.2 Hz, 6H), 7.77-7.62 (m, 12H), 7.58-7.50 (m, 12H), 7.44 (t, J=7.2 Hz, 3H), 7.33 (t, J=8 Hz, 3H), 6.96 (t, J=8.0 Hz, 6H), 6.64 (t, J=8.0 Hz, 6H), 6.54 (d, J=7.6 Hz, 6H), 6.43 (d, J=8.2 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃), δ: 171.29, 157.18, 156.79, 145.17, 141.43, 141.07, 140.48, 139.42, 138.61, 135.11, 131.19, 129.42, 128.59, 127.72, 127.36, 127.15, 125.86,

124.78, 124.57, 120.70, 120.38, 120.17, 114.76, 77.36, 77.05, 76.73, 57.10 ppm; TOF-MS (EI): m/z: calcd for $C_{114}H_{72}N_6$: 1524.582 [M⁺]; found: 1525.000. CHN: calcd for $C_{114}H_{72}N_6$, C, 89.74; H, 4.76; N, 5.51%; found: C 89.40, H 4.81, N 5.70%. *m*-**TPA**: Light yellow solid. Yield: 39%. ¹H NMR (400 MHz, CDCl₃), δ : 9.01 (s, 3H), 8.61 (d, *J*=8.0 Hz, 3H), 7.97 (d, *J*=8 Hz, 3H), 7.91 (d, *J*=8.8Hz, 6H), 7.80 (dd, *J*=8.0 Hz, 13.2 Hz, 6H), 7.49-7.35 (m, 21H), 7.35 (t, *J*=8.4 Hz, 4H), 6.98 (t, *J*=8.8 Hz, 6H), 6.64 (t, *J*=8.0 Hz, 6H), 6.57 (d, *J*=8 Hz, 6H), 6.42 (d, *J*=7.8 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃), δ : 171.72, 157.28, 156.18, 141.39, 140.67, 139.97, 138.90, 138.00, 137.52, 136.60, 131.30, 131.07, 129.05, 128.48, 127.90, 127.46, 126.89, 125.53, 124.56, 123.64, 120.58, 120.16, 114.72, 77.23, 76.75, 76.01, 57.15 ppm. TOF-MS (EI): m/z: calcd for $C_{114}H_{72}N_6$: 1524.582 [M⁺]; found: 1525.027. CHN: calcd for $C_{114}H_{72}N_6$, C, 89.74; H, 4.76; N, 5.51%; found: C 89.92, H 4.63, N 5.44%.

2.6 Synthesis of *p*-TPA-TPE and *m*-TPA-TPE

A mixture of compound 4 (4 mol eq), compound 5 or 6 (1 mol eq), *tetrakis*(triphenylphosphine)palladium (0.03 mol eq), potassium carbonate solution (2 M, 15 mL) and THF (45 mL) was refluxed for 24 h under nitrogen. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2 (3×10 mL). The organic phase was washed with water for three times and dried with anhydrous Na₂SO₄. The solvent was removed under vacuum, and then the residue was purified by column chromatography with PE/CH₂Cl₂ (2:1) as an eluent to get the target compounds.

p-**TPA-TPE**: Light green solid. Yield: 41%. ¹H NMR (400 MHz, CDCl₃), δ: 8.83 (d, *J*=8.4 Hz, 6H), 7.92 (dd, *J*=7.6 Hz, 14.8 Hz, 6H), 7.84-7.62 (m, 24H), 7.54 (d, *J*=7.6 Hz, 6H), 7.37 (d, J=8.4 Hz, 6H), 7.14-7.07 (m, 60H), 6.65 (t, J=7.6 Hz, 6H), 6.58 (d, J=8.0 Hz, 6H), 6.43 (d, J=7.6 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃), δ : 171.31, 157.50, 157.18, 143.79, 141.28, 131.83, 131.37, 130.08, 129.44, 128.02, 127.61, 126.46, 120.76, 120.60, 114.79, 77.23, 77.03, 76.71, 57.20 ppm. TOF-MS (EI): m/z: calcd for C₁₉₂H₁₂₆N₆: 2515.004 [M⁺]; found: 2515.823. CHN: calcd for C₁₉₂H₁₂₆N₆, C, 91.62; H, 5.05; N, 3.34%; found: C 91.39, H 5.14, N 3.17%.

m-**TPA-TPE**: Light green solid. Yield: 31%. ¹H NMR (400 MHz, CDCl₃), δ : 9.00 (s, 3H), 8.61 (d, *J*=8.4 Hz, 6H), 7.86 (m, 21H), 7.69 (d, *J*=7.6 Hz, 6H), 7.41 (m, 24H), 7.11 (m, 42H), 6.98 (t, *J*=8.8 Hz, 6H), 6.63 (dd, *J*=8.0 Hz, 8.0 Hz, 12H), 6.42 (d, *J*=8.0 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃), δ : 171.71, 157.58, 156.54, 143.80, 142.85, 141.62, 141.10, 140.84, 140.51, 138.72, 137.93, 136.59, 131.83, 131.42, 131.05, 128.36, 127.19, 126.54 , 126.16, 125.06, 124.34, 120.77, 120.36, 114.74, 77.35, 77.04, 76.72, 57.21 ppm. TOF-MS (EI): m/z: calcd for C₁₉₂H₁₂₆N₆: 2515.004 [M⁺]; found: 2514.673. CHN: calcd for C₁₉₂H₁₂₆N₆, C, 91.62; H, 5.05; N, 3.34%; found: C 91.45, H 5.40, N 3.05%.

3. Results and Discussion

3.1 Synthesis

The synthetic route of *p*-TPA, *m*-TPA, *p*-TPA-TPE and *m*-TPA-TPE are depicted in Scheme 1. According to the previous report [27,31], The Ullmann reaction between 2-bromoiodobenzene and diphenylamine yielded N-(2-bromophenyl)-Nphenylbenzenamine, which was followed by cyclization reaction with the commerical 2,7-dibromo-9H-fluoren-9-one (or 2-dibromo-9H-fluoren-9-one) to afford the key

precursors 1 and 2. 1-Bromo-4-(1,2,2-triphenylvinyl)benzene reacted with bis(pinacolato)diboron to yield compound 3 in the present of CH₃COOK and PdCl₂(dppf) [dppf=1,1'-bis(diphenylphosphino)ferrocene]. Compound 4 and the target compounds were achieved through the typcial Suzuki coupling reaction in good yields. Definitely, *p*-TPA, *m*-TPA, *p*-TPA-TPE and *m*-TPA-TPE were characterized by ¹H NMR, ¹³C NMR, TOF-MS and elemental analysis. Evidenced by thermogravimetric analysis (TGA), all compounds displayed good thermal stability with the decomposition temperature (at 5 % weight loss) above $320^{\circ}C$ (ESI[†], Table 1).

3.2 Optical Properties

The UV-vis absorption property was investigated in toluene solution (10^{-5} M) at room temperature (Figure 1), and the relevant photophysical data are summarized in Table 1. Compounds *p*-TPA and *m*-TPA have the clear dual-absorption bands between 250 nm and 400 nm. The absorption bands at short wavelength (ca. 285±5 nm) are attributed to the the π - π electron transition of aromatic rings [27,35]. Another absorption band at 357 nm (*p*-TPA) and 325 (*m*-TPA), respectively, are assigned to the intramolecular charge transfer (ICT) transition, as also evidenced by therotical calculation (*vide infra*). On the other hand, compounds *p*-TPA-TPE and *m*-TPA-TPE mainly present the ICT absorption band. Compared to the *para*- substituent isomers, the *mata*- counterparts display narrow optical energy gap due to the changed π -conjugation degree. Owing to the the intermolecular interaction, all compounds show a distinctly red-shifted absorption spectra in the neat film compared to that in solution (Figure 1 and ESI[†]).

The photoluminescent (PL) property of all compounds measured in toluene (10^{-5} M) at room tempearture are shown in Figure 2a. All compounds exhibit the structureless emission profiles in the range of 440-486 nm, implying a nonnegligible ICT feature. It is noted that compounds p-TPA and m-TPA have the nearly identical emission in the solution, while p-TPA-TPE displays an apparent hypochromatic shift compared to *m*-TPA-TPE. It is assumed that the distorted donor moity has a responsibility for this result. In addition, the PL emissions in different solvents, such as CH₂Cl₂, THF and toluene, present strong solvatochromism effect (ESI⁺), further proving the ICT in these D-A molecules. In toluene solution, the emission lifetime (τ) of compounds p-TPA and m-TPA were evaluated to be 11.5 ns and 12.1 ns, respectively, indicating the emission originates from singlet-excited state. Unfortunately, the lifetime of compounds with TPE unit could not be detected owing to the poor emission in the solution. Compared to the emission in solution, all compounds showed a slight red shift in the neat film (Figure 2b), suggesting the reduced intermolecular interaction caused by the steric structure (Table 1). Definitely, p-TPA-TPE and m-TPA-TPE possess very strong emission in the solid state due to the TPE-based AIEgens.

Therefore, the PL spectra of both *p*-TPA-TPE and *m*-TPA-TPE were further studied in the THF/water mixture with different water fractions (f_w) to verify the AIE property (Figure 3 and ESI[†]). Taking *m*-TPA-TPE for example, the negligible emission are observed in the pure THF solution even when the f_w increases to 30 %, implying that the compound still have a good solubility in this mixture [36]. Then, the PL intensity has a sharply increase at $f_w > 50\%$, suggesting the aggregation suspension is formed. When f_w was increased to 90 %, the emission intensity reaches its maximum in the blue region (482 nm). Additioanly, the emission has a minor shift in the THF/water mixture with different f_w . As shown in Figure 3b, the emission intensity of *m*-TPA-TPE at f_w of 90% is 71 times higher than that in pure THF, which clearly elucidates the AIE character. Similar AIE behaviors with a hypochromatic shift were also observed for *p*-TPA-TPE, whose emission intensity increased by 41-fold (ESI[†]). To further validate the AIE activity of both compounds, their emission quantum efficiencies in solid state were determined to be 60% and 24% for *p*-TPA-TPE and *m*-TPA-TPE, respectively, which is much higher than that in solution.

3.3 Electronic Properties

To further elucidate the relationship of structure and electronic distribution, density functional theory (DFT) calculation was carried out using Gaussian 09 program with B3LYP/6-31G(d) basis sets. From the optimized geometry (Figure 4), the spiro-triphenylamine has an orthogonal structure, which to some extent suppresses the intermolecular interaction. Furthermore, the torsion angles between the spiro-triphenylamine moiety and the triazine core/or TPE unit are both $\sim 36^{\circ}$. Therefore, these molecules could be an effective emitter in solid state. In all D-A compounds, the HOMO are localized on the spiro-triphenylamine moiety. In contrast, the LUMO has a different spatial distributions for these molecules. For the *p*-TPA and p-TPA-TPE, the LUMO is delocalized on both triazine and fluorene unit, while the LUMO of *m*-TPA and *m*-TPA-TPE are mainly localized on the triazine moiety. Actually, the TPE unit has little contribution for the electron distribution. The

observed separated orbitals demonstrate the intrinsic ICT property in these molecular systems.

3.4 Eletrochemical Properties

Cyclic voltammetry (CV) was carried out to evaluate the electrochemical property of all compounds calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as an reference, and the data are listed in Table 1. All compounds show several irreversible oxidation potential in the region of 0.5-1.8 V (ESI†), while their reduction potential did not be detected between 2.0 and –2.0 V. Compared to *para* substituents, the *mata* counterparts have a large oxidation potential caused by the effect of π -conjugated degree. After introducing the TPE unit into the D-A molecules, an increased oxidation potential were observed. Apparently, the connection position between donor and acceptor and additional TPE unit have a clear effect on the electrochemical property. According to the empirical fomular of $E_{HOMO} = -(4.8 + E_{ox} - E_{FC/FC+})$ eV, the HOMO energy levels of all compounds are calculated to be –5.37 \sim –5.45 eV (Table 1). Based on the HOMO values and the optical energy gap, the LUMO energy levels were estimated in the region of –2.0 \sim –2.4 eV.

3.5 Eletroluminescent Properties

Owing to the poor solubility of *p*-TPA and *p*-TPA-TPE in chlorobenzene, the devices prior employing compounds *m*-TPA (**device I**) and *m*-TPA-TPE (**device II**) as the emitter were fabricated with the configuration of ITO/PEDOT:PSS (30 nm)/mCP:compound (90:10, 30 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al (100 nm). In this device, mCP (9-[3-(9H-carbazol-9-yl)phenyl]-9H-carbazole) is used as the host

matrix due to its high triplet energy, which doped with the *m*-TPA/or *m*-TPA-TPE serves as the emitter. TmPyPB (1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene) is the electron-transporting and hole-blocking layer. Liq and Al are served as the composite cathode

At 12 V, the devices I and II present the maximum electroluminescence (EL) at 420 nm and 472 nm, respectively (insert Figure 5). Their corresponding commission international de L'Eclairage (CIE) coordinates are (0.19, 0.16) and (0.19, 0.26) (Figure 5b), implying blue emission. The current density-voltage-luminance (*J-V-L*) curves and external quantum efficiency (*EQE*) curves are illustrated in Figure 5 and Figure 6. Obviously, *m*-TPA based device (device I) possesses an inferior performance with a maximum luminance of 430 cd/m², a current efficiency of 0.12 cd/A and EQE of 0.15 %. Conversely, the device based on *m*-TPA-TPE (device II) exhibits a maximum luminance of 4431 cd/m², a current efficiency of 2.0 cd/A and EQE of 1.1 %. It is noted that the performances of device II is roughly 10- to 20-fold higher than that of the device I. It is apparent that introducing the TPE unit into this D-A molecule plays a key role on enhancing the device performance. Unfortunately, the turn-on voltages of both devices I and II are not dissatisfied (Table 2).

To further optimize the device performance, two non-doped devices (devices III and IV) with the structure of ITO/PEDOT:PSS (30 nm)/compound (30 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al (100 nm) were fabricated. In this device, the pure compound *m*-TPA/or *m*-TPA-TPE serves as the emitter. As shown in insert Figure 7, both devices show the bluish-green emission with the maximum peak at about 486 nm and 500 nm

for *m*-TPA and *m*-TPA-TPE, respectively. The EL spectra of these devices are similar with their corresponding PL profiles, indicating the EL emission originated from the intrinsic emission of the molecules. Correspondingly, the CIE coordinates of devices III and device IV are located in (0.21, 0.32) and (0.22, 0.38). Interestingly, devices III and IV have the relatively low turn-on voltage (*ca.* 4V) compared to devices I and II, implying a better bipolar carriers transport in the non-doped devices.

As shown in Figure 7 and 8, the non-doped devices (III and IV) possess an apparently enhanced performance compared to the corresponding dopant-host system, probably due to the twisted D-A molecular structure. *m*-TPA based non-doped device (device III) display a maximum luminance of 985 cd/m², a current efficiency of 0.5 cd/A and EQE of 0.3 %. The device IV (*m*-TPA-TPE based device) exhibits a satisfying EL efficiency with the maximum luminance of 3629 cd/m², current efficiency of 4.2 cd/A and *EQE* of 1.8 %. The performance of non-doped devices increases by \sim 1 time than their counterpart doped devices.

4. Conclusions

In summary, four novel star-shaped blue emitter bearing D-A framework were synthesized and characterized. In these molecules, the different interconnection position between donor and acceptor unit has a distinct effect on the solubility and photophysical property. After grafted the TPE moiety into D-A compound, p-TPA-TPE and m-TPA-TPE showed strong AIE emission and improved emission efficiency in the solid state. The devices based on m-TPA-TPE showed 6~10 folds

higher performance than that of *m*-TPA based devices. Furthermore, the non-doped devices had a better performance than the doped counterpart. This result implys that the additional TPE moiety plays a position role on improving the emission efficiency, which provides an effective strategy for design D-A blue emitter with high efficient emission in non-doped OLEDs

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Supporting Information

The Supporting Information is available free of charge on the Publications website. Detailed information on TGA, lifetime, PL spectrum and CV curves..

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Tables Captions

 Table 1. Thermal properties of platinum complexes



Table 1. Photophysical data of all compounds

Compound	^a UV-Vis	Emission/nm		${}^{b}\tau$	${}^{c}T_{d}$	${}^{d} {oldsymbol {\varPhi}}$	^e E _{ox}	^f E _{HOMO}	^g E _{LUMO}	${}^{h}E_{\rm g}^{\rm opt}$
	/nm	^a Solution	Film	/ns	/ºC	/%	/ V	/eV	/eV	/eV
p-TPA	280, 357	454	479	11.5	491	7	0.57	-5.37	-2.32	3.05
<i>p</i> -TPA-TPE	276,	443	485	<5	533	60	0.60	-5.4	-2.46	2.94
	301, 370									
<i>m</i> -TPA	295, 325	458	466	12.1	320	0.8	0.60	-5.4	-2.0	3.40

m-TPA-TPE	270,	485	487	<5	335	24	0.65	-5.45	-2.41	3.04
	292, 353									

Measure conditions: *a,b*) in toluene solution (10⁻⁵ M) at room temperature; *c*) 5% weight loss in N₂; *d*) in solid state at room temperature; *e*) mesured in CH₃CN solution at room temperature, and the data collected from the turn-on potential verse Fc/Fc⁺, $E_{ox}^{Fc/Fc^+} = 0.076 \text{ V}$; *f*) $E_{HOMO} = -(E_{ox} + 4.8) \text{ eV}$; *g*) evaluated from the UV-vis absorption spectra, $E_{LUMO} = (E^{opt}_{g} - E_{HOMO}) \text{ eV}$; *h*) $E^{opt}_{g} = 1240/\lambda_{absorption}$.

Table 2. The EL performance of devices I-IV

Device	V _{turn-on}	L	CE	РЕ	EQE
	(V)	(cd/m^2)	(cd/A)	(lm/W)	(%)
Device I	8	430	0.12	0.03	0.15
Device II	8	4431	2.0	0.5	1.1
Device III	4	985	0.5	0.3	0.3
Device IV	4	3629	4.2	1.66	1.8

Figures Captions

Chart 1 Structural evolutions of p-TPA, m-TPA, p-TPA-TPE and m-TPA-TPE

Scheme 1 Synthetic route of *p*-TPA, *m*-TPA, *p*-TPA-TPE and *m*-TPA-TPE

Figure 1 Normalized UV-vis spectra of compounds in toluene at room temperature

Figure 2 PL spectra of compounds both in toluene (a) and neat film (b) at room temperature

Figure 3 PL spectra (a) of *m*-TPA-TPE in THF/water mixture with different water fractions (f_w) at

room temperature; Plot of $(I/I_0, \mathbf{b})$ values versus the compositions of the aqueous mixtures. I_0 = emission intensity in pure THF solution. The inset graph is fluorescence images of *m*-TPA-TPE in THF/water mixtures with different f_w (0 % and 90%) taken under UV illumination.

Figure 4 Optimized geometries and spatial distributions of HOMO (green color) and LUMO (red/blue color) in S_0 state calculated using the B3LYP/6-31G(d) basis set

Figure 5 The EQE-current density curves, EL spectra and CIE coordinate for device I and II

Figure 6 The current density-voltage-luminance (J-V-L) curves for device I and II

Figure 7 The *EQE*-current density curves, EL spectra at 12 V and CIE coordinate for device III and IV

Figure 8 The current density-voltage-luminance (J-V-L) curves for device III and IV

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Chart 1 Structural evolutions of *p*-TPA, *m*-TPA, *p*-TPA-TPE and *m*-TPA-TPE



Reaction conditions: a) n-BuLi, THF, -78°C, 4 h; b) HCl, CH3COOH, reflux, 1 h; yield: 1: 63%, 2: 62%; c) bis(pinacolato)diboron, CH₃COOK, PdCl₂(dppf), 1,4-dioxane, 80°C, 24 h; yield: 79%; d) 2 M K₂CO₃, Pd(PPh₃)₄, THF, 85°C, 24 h; yield: 42%; e) 2 M K₂CO₃, Pd(PPh₃)₄, THF, 85°C, 24 h; yield: 42%; e) 2 M K₂CO₃, Pd(PPh₃)₄, THF, 85°C, 24 h; yield: *p*-TPA: 45%, *m*-TPA: 39%, *p*-TPA-TPE: 41%, *m*-TPA-TPE: 31%.

Scheme 1 synthetic route of *p*-TPA, *m*-TPA, *p*-TPA-TPE and *m*-TPA-TPE



Figure 1 Normalized UV-vis spectra of compounds in toluene at room temperature



Figure 2 PL spectra of compounds both in toluene (a) and neat film (b) at room temperature



Figure 3 PL spectra (**a**) of *m*-TPA-TPE in THF/water mixture with different water fractions (f_w) at room temperature; Plot of (I/I_0 , **b**) values versus the compositions of the aqueous mixtures. I_0 = emission intensity in pure THF solution. The inset graph is fluorescence images of *m*-TPA-TPE in THF/water mixtures with different f_w (0 % and 90%) taken under UV illumination.



m-TPAm-TPA-TPEFigure 4 Optimized geometries and spatial distributions of HOMO (green color) and LUMO(red/blue color) in S₀ state calculated using the B3LYP/6-31G(d) basis set



Figure 5 The EQE-current density curves, EL spectra and CIE coordinate for device I and II



Figure 6 The current density-voltage-luminance (J-V-L) curves for device I and II



Figure 7 The *EQE*-current density curves, EL spectra at 12 V and CIE coordinate for device III and IV



Figure 8 The current density-voltage-luminance (J-V-L) curves for device III and IV

Research Highlights

- Spirotriphenylamine based star-shaped D-A molecules were prepared and characterized.
- > All these D-A molecules display intense blue emission in solution and neat film.
- ▶ Both *p*-TPA-TPE and *m*-TPA-TPE show aggregation-induced emission property.
- \succ *m*-TPA-TPE exhibits satisfied performance in both doped and non-doped OLEDs.