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Engineering The Interconnection Position of Star-Shaped D-π-A Molecules Based on Triazine, Spirofluorene and Triphenylamine Moieties for Color Tuning from Deep blue to Green

Yafei Wang[†#§*], Wanhui Liu[†], Jiyong Deng[‡], Guohua Xie[△*], Yuanwei Liao[†], Zuoming Qu[†], Hua Tan[†], Yu Liu[†], Weiguo Zhu[#]

Abstract: π-Conjugated organic molecule featuring donor-bridge-acceptor (D-π-A) structure has been widely used in semiconducting materials due to their rigid structure, good thermal stability, excellent charge transfer and high emission efficiency. To investigate the effect of D-π-A molecular structure on the photophysical property, in this contribution, three star-shaped D-π-A isomers based on 2,4,6-tri(phenyl)-1,3,5-triazine, spirofluorene and triphenylamine moieties, *p*-TFT, *mp*-TFT and *m*-TFT, were synthesized *via* elaborately engineering the interconnection position among the building block units. The optophysical properties of these compounds were systematically explored by experiment and theory calculation. Definitely, the changed interconnection position in these molecules plays a significant role on the degree of π conjugation, which results in tunable emission colors from deep blue to green. Moreover, these isomers have been employed as the emissive dopants in organic light-emitting diodes. A highest external quantum efficiency and current efficiency of 2.3 % and 6.2 cd/A were respectively achieved by the *p*-TFT based device. This research demonstrates a feasible way to realize blue emitter *via* engineering D-π-A conjugation.

Introduction

Over the last two decades, π-conjugated organic molecules featuring donor-bridge-acceptor (D-π-A) structure, have garnered much interest as semiconductor materials in the field of organic light-emitting diodes (OLEDs),[1-3] organic photovoltaic devices (OPV)[4-6] and organic field effect transistors (OFET).[7,8] Since the D-π-A organic molecules possess the advantages of good charge transport, electron-rich feature and fascinating optical property, numerous these molecules have been developed as effective emitters or host materials in OLEDs.[9-11] However, few D-π-A molecules can be employed as a deep blue emitter because of the strong intramolecular charge transfer of D-π-A molecules usually leading to a red-shifted emission spectrum.[12-14] In addition, the conjugation length of D-π-A molecules also plays an important role in tuning the emission color. Therefore, these deficiencies are the major remaining obstacles for developing D-π-A blue emitters.

π-Conjugated star-shaped molecules possessing D-A framework have been widely used in the semiconductor materials due to their good solubility, film-forming properties and ease of the energy gap tuning.[15,16] 2,4,6-Tris(phenyl)-1,3,5-triazine is known to be dendritic framework, rigid skeleton and good electron conductor and therefore have been used as a promising acceptor core in star-shaped molecules.[17-20] For example, Wang and his coworkers synthesized the star-shaped compounds of 2,4,6-tris(di-2-pyridylamino)-1,3,5-triazine and 2,4,6-tris[p-(di-2-pyridylamino)phenyl]-1,3,5-triazine that exhibited blue emissions in OLEDs.[21] Matulaitis *et al.* prepared a series of bipolar star-shaped molecules based on 2,4,6-tri(phenyl)-1,3,5-triazine unit and carbazole derivatives. Although these star-shaped D-A compounds showed blue emission, relatively low current efficiency of 0.5 cd/A was achieved in the OLEDs.[13] Particularly, recent research has demonstrated that the triazine derivatives are the effective building block for the thermally-activated delayed fluorescence (TADF) molecule.[22,23] To this end, our recent efforts have focused on the push-pull effect of the 2,4,6-tri(phenyl)-1,3,5-triazine based starburst molecule on the photophysical property.

Compared to the acceptor units, the donor units have made much more progress in π-conjugated emission materials, such as triphenylamine,[24-27] carbazole,[28-30] phenothiazine[31] and so on. Considering blue emission, good charge-transporting and high emission efficiency,[32,33] the spirofluorene and triphenylamine units are chosen as the π-conjugated bridge and donor moiety, respectively. Herein, the motif in this work was to prepare a series of star-shaped D-π-A molecules with blue emission based on the triazine, spirofluorene and triphenylamine moieties. In this contribution, three star-shaped D-π-A isomers of *p*-TFT, *mp*-TFT and *m*-TFT (Chart 1) were designed and prepared, in which 2,4,6-tri(phenyl)-1,3,5-triazine (T) is employed as the acceptor core, spirofluorene as the π-conjugated bridge (F) and triphenylamine (T) as the donor unit. Through engineering the interconnection position (*p*, *mp* or *m*) between donor and bridge moieties (or bridge and acceptor), the structure-property relationship of these star-shaped D-π-A molecules have been systematically explored. Interestingly, the emission color is dramatically tuned over a wide wavelength range (from deep blue to green) by simple modification of the molecular structure, ascribed to the changed degree of conjugation.

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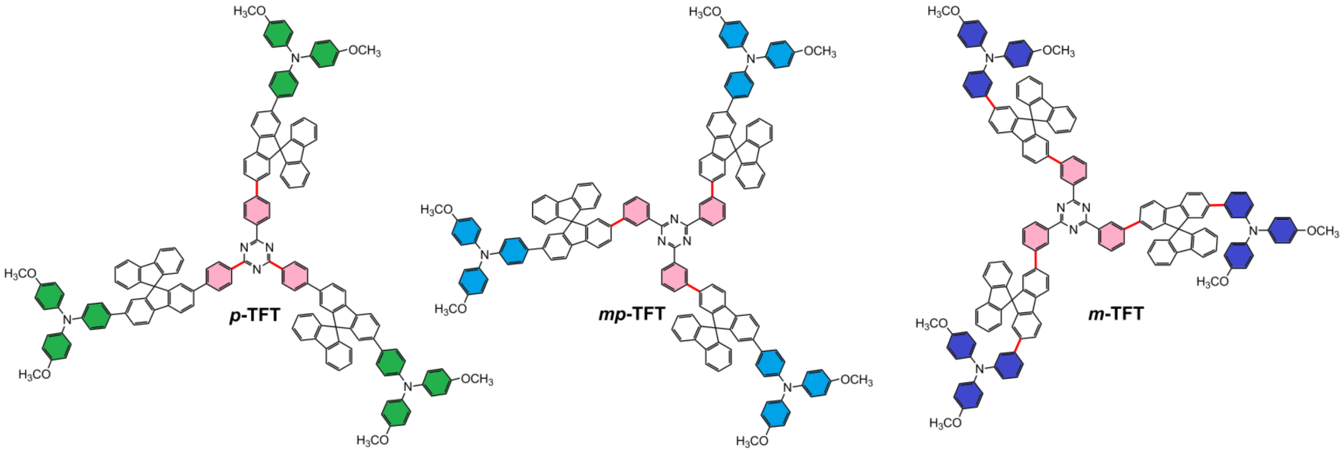
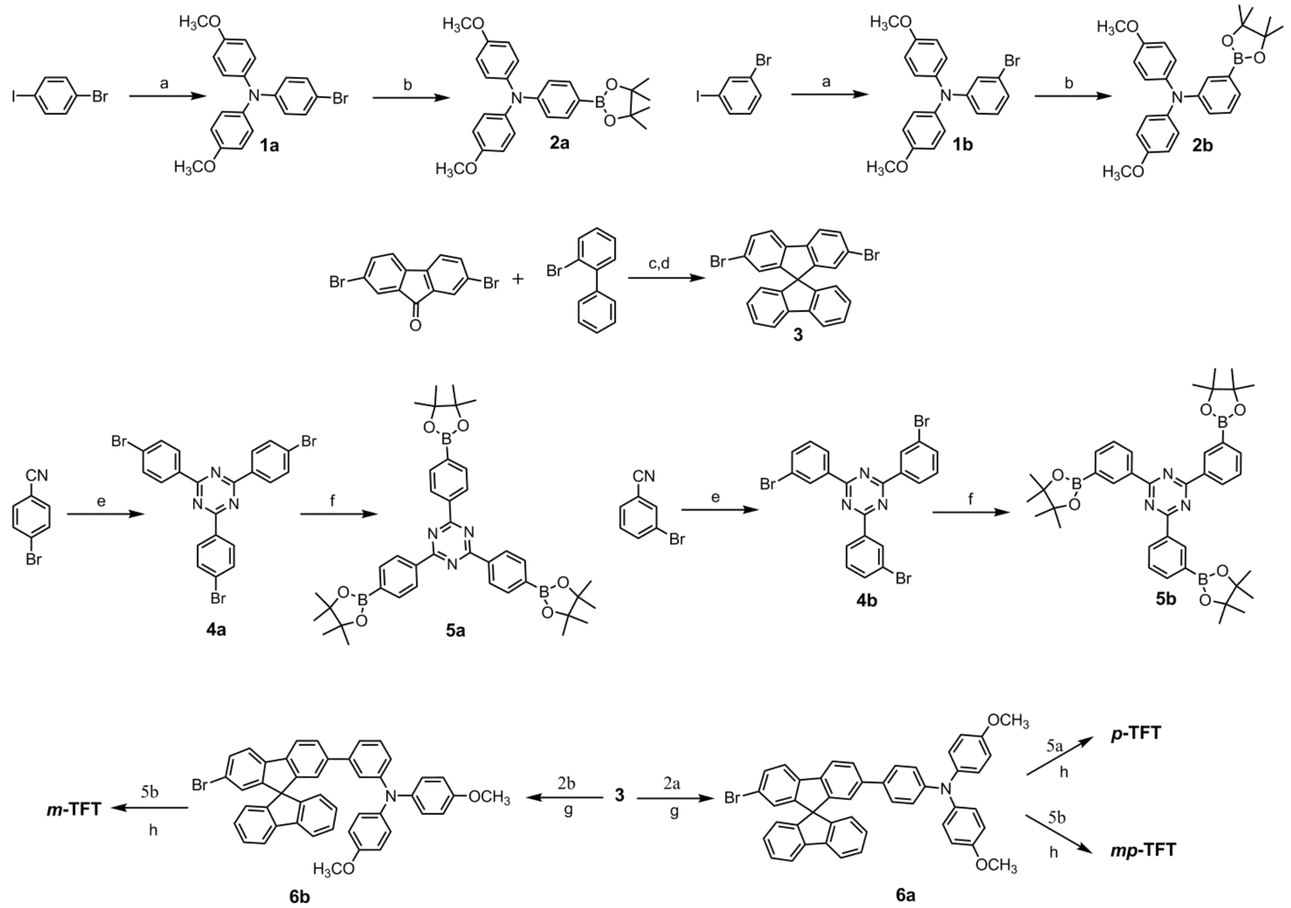


Chart 1. Molecular structures of *p*-TFT, *mp*-TFT and *m*-TFT.



Reaction conditions: (a) 1,10-Phenanthroline hydrate, CuI, KOH, toluene, 135°C, 12 h, yield, 1a: 76%, 1b: 64%; (b) bis(pinacolato)diboron, CH_3COOK, $PdCl_2(dppf)$, 1,4-dioxane, 80°C, 24 h, yield, 2a: 82%, 2b: 76%; (c) *n*-BuLi, THF, -78°C, 4 h. (d) HCl, CH_3COOH, reflux, 1 h, yield, 60%; (e) TfOH, CH_2Cl_2, room temperature, overnight, yield, 4a: 64%, 4b: 59%; (f) bis(pinacolato)diboron, CH_3COOK, $PdCl_2(dppf)$, 1,4-dioxane, 80°C, 24 h, yield, 5a: 76%, 5b: 72%; (g) 2 M K_2CO_3, $Pd(PPh_3)_4$, THF, 85°C, 18 h, yield, 6a: 52%, 6b: 48%; (h) 2 M K_2CO_3, $Pd(PPh_3)_4$, THF, 85°C, 24 h, yield: *p*-TFT: 48%, mp-TFT: 46%, m-TFT: 42%.

Scheme 1. Synthetic routes of *p*-TFT, *mp*-TFT and *m*-TFT.

Results and Discussion

Synthesis and Characterization

The synthetic routes of *p*-TFT, *mp*-TFT and *m*-TFT are shown in Scheme 1, and the detailed synthetic procedures are described in the experimental section. Compounds 2 (2a and 2b) were prepared via Ullmann coupling using CuI and 1,10-phenanthroline as the catalysts, and then followed by borylation reaction. Spirofluorene derivative (3) was synthesized according to the previous report.[34] The condensation reaction of 4-bromobenzonitrile afforded 1,3,5-triazine core (4a and 4b) in the presence of trifluoromethanesulfonic acid. Then, compounds 4 reacted with bis(pinacolato)diboron to yield the precursors 5 (5a and 5b) using PdCl$_2$(dppf) as the catalyst. Finally, the target compounds were achieved through continuous two-step Suzuki coupling reaction. All the target compounds were characterized by ^{1}H NMR, ^{13}C NMR and TOF-MS (ESI†). The thermogravimetric analysis (TGA) data reveal that all compounds possess good thermal stability with the decomposition temperature (T_d) of 412^{o}C (*p*-TFT), 374^{o}C (*mp*-TFT) and 437^{o}C (*m*-TFT) at 5 % weight loss, respectively.

Photophysical Properties

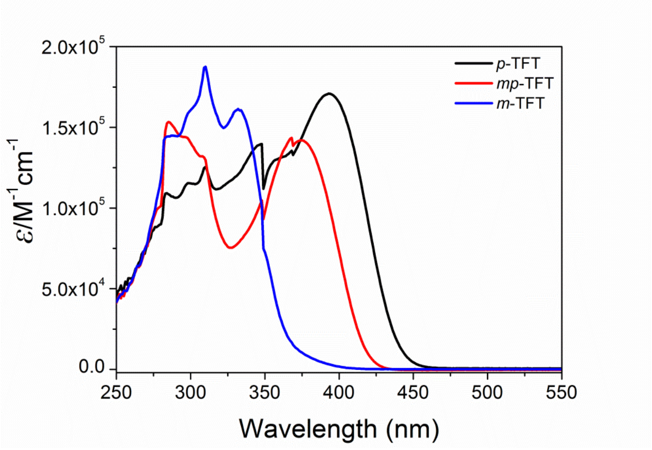


Figure 1. UV-vis absorption spectra of *p*-TFT, *mp*-TFT and *m*-TFT in CH$_2$Cl$_2$.

Figure 1 depicts the UV-vis absorption spectra of *p*-TFT, *mp*-TFT and *m*-TFT in CH$_2$Cl$_2$ (10^{-5} M), and the relevant data are listed in Table 1. All of the compounds show two clear absorption bands between 250 nm and 500 nm. The high-energy absorption bands are ascribed to the π-π* transitions of phenyls (triphenylamine, spirofluorene and triazine) while the low energy absorption bands are assigned to the intramolecular charge transfer (ICT) transition (from the donor unit to the accept unit).[22] Compared with *p*-TFT and *mp*-TFT, *m*-TFT has a relative weak ICT absorption character. Additionally, the absorption edges of *p*-TFT, *mp*-TFT and *m*-TFT occur obviously hypochromatic shifts in sequence. These phenomena imply that the degrees of π-conjugation of *p*-TFT, *mp*-TFT and *m*-TFT decrease successively (*p*-TFT > *mp*-TFT > *m*-TFT), which is caused by the changed interconnection position among triphenylamine, spirofluorene and triazine units.[35] As a consequence, the optical bandgaps of *p*-TFT, *mp*-TFT and *m*-TFT were evaluated to be 2.71, 2.88 and 3.07 eV, respectively.

To further investigate the effect of the linkage position on photoluminescent (PL) property, initially, the emission spectra of all compounds were measured in CH$_2$Cl$_2$ solution (10^{-5} M) with the excitation wavelength of 380 nm at room temperature. As shown in Figure 2a, all compounds present broad and structureless emission profiles in a range from deep blue to red region, assigning to the ICT transition state.[22,36] Compound *m*-TFT shows a deep blue emission centered at 406 nm. Conversely, *p*-TFT and *mp*-TFT display both high-energy emission (454 nm and 474 nm) and low-energy emission (627 nm and 629 nm), in which the long wavelength emissions are attributed to the solvatochromism effect (see below). Furthermore, the emissions of all compounds were measured in various solvents with different polarity (ESI†, CH$_2$Cl$_2$, THF, toluene and ethyl acetate). A remarkable solvatochromism effect was observed, which supports the charge transfer state in solution. The luminescent lifetimes (τ) for all compounds are in the nanosecond regime (Table 1), suggesting that the emission originates from fluorescence. Using 9,10-dibromoanthracene as a reference (Φ=0.89, in ethanol),[37] the photoluminescence quantum yields (Φ) of *p*-TFT, *mp*-TFT and *m*-TFT are evaluated to be 0.27, 0.15 and 0.11 in CH$_2$Cl$_2$ at room temperature, respectively.

Compared to the PL spectra in solution, the emissions show distinctly bathochromic shifts (ca. 80-100 nm, see Table 1) in neat film owing to the planar structure of the triazine core. Notably, the decreased π-conjugation of *p*-TFT, *mp*-TFT and *m*-TFT leads to a hypochromatic shift of the onset of PL spectra both in solution and in neat film, which is also well matched with the change tendency of the absorption edge. The phosphorescence emission spectra measured in frozen toluene at 77 K are shown in Figure 3. Fine-structured emissions with large red shifts (80-100 nm) are observed for the compounds at low temperature. From the onset of the phosphorescent spectra, the triplet energy values of *p*-TFT, *mp*-TFT and *m*-TFT are evaluated to be 2.41, 2.46 and 2.58 eV, respectively.

Theoretical Calculations

The relationship between geometrical and electronic properties of these homologous series were carried out with density functional theory (DFT) using the B3LYP functional (Gaussian 09 program). The calculated highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of three compounds are depicted in Figure 4. The dihedral angles between the 2,4,6-tri(phenyl)-1,3,5-triazine and spirofluorene (or spirofluorene and triphenylamine) moieties are almost the same for these three compounds, which suggests that there is negligible effect of linkage position on the dihedral angles. Notably, it is distinctly different for the HOMO and LUMO distributions of all compounds. The spatially separated HOMO and LUMO distributions suggest that there is a large charge-transfer character in these compounds. The HOMOs of *p*-TFT and *mp*-TFT show the same pattern at the one of triphenylamine and spirofluorene units, while their LUMOs display different electron population. The LUMO of *p*-TFT is delocalized over the

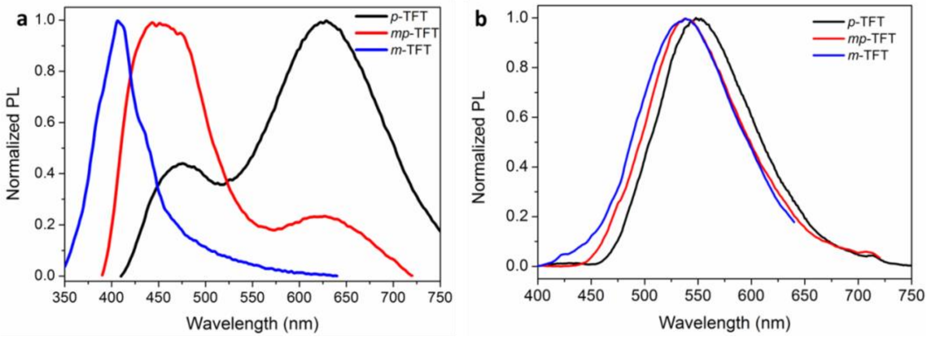


Figure 2. Normalized PL spectra of *p*-TFT, *mp*-TFT and *m*-TFT: (a) in CH_2Cl_2 solution; (b) in neat film.

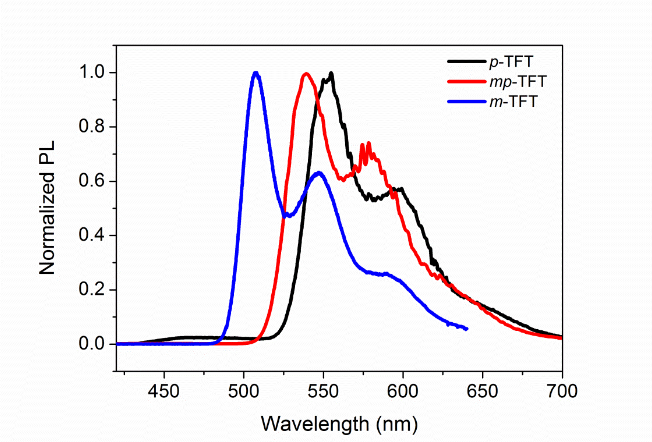


Figure 3. The phosphorescence spectra of *p*-TFT, *mp*-TFT and *m*-TFT measured in frozen toluene at 77 K.

Table 1. Photophysical data of *p*-TFT, *mp*-TFT and *m*-TFT

Compounds	$\lambda_{absorption}$/nm^a (10^5 M^{-1} cm^{-1})	λ_{em} /nm	λ_{em} /nm^d	τ /ns^e	T_d /°C^f	E_{ox} /V^g	E_{HOMO} /eV^h	E^{opt}_g /eV^i	Φ
***p*-TFT**	283 (1.09), 298 (1.16), 310 (1.25), 347 (1.40), 393 (1.71)	^{b}474 ^{b}629^{sh} ^{c}550	553, 598^{sh}	<5	412	0.39	5.19	2.71	0.27^j 0.043^k
***mp*-TFT**	285 (1.53), 297 (1.44), 309 (1.32), 347 (1.04), 374 (1.42)	^{b}454^{sh} ^{b}627 ^{c}538	539, 579^{sh}	<5	374	0.42	5.22	2.88	0.15^j 0.039^k
***m*-TFT**	282 (1.44), 298 (1.60), 310 (1.88), 332 (1.62)	^{b}406 ^{c}538	508, 547^{sh} 593^{weak}	10	437	0.46	5.26	3.07	0.11^j 0.007^k

Measure conditions: *a,b,e*) in toluene solution (10^{-5} M) at room temperature; *c*) in neat film at room temperature; *d*) in toluene solution (10^{-5} M) at 77 K; *f*) 5% weight loss in N_2; *g*) data collected from the maximum peak verse Fc/Fc^+; *h*) $E_{HOMO} = -(E_{ox} + 4.8)$ eV; *i*) evaluated from the UV-vis absorption spectra, $E^{opt}_g = 1240/\lambda_{absorption}$; *j*) Measured in CH_2Cl_2 solution; *k*) Measured in neat film.

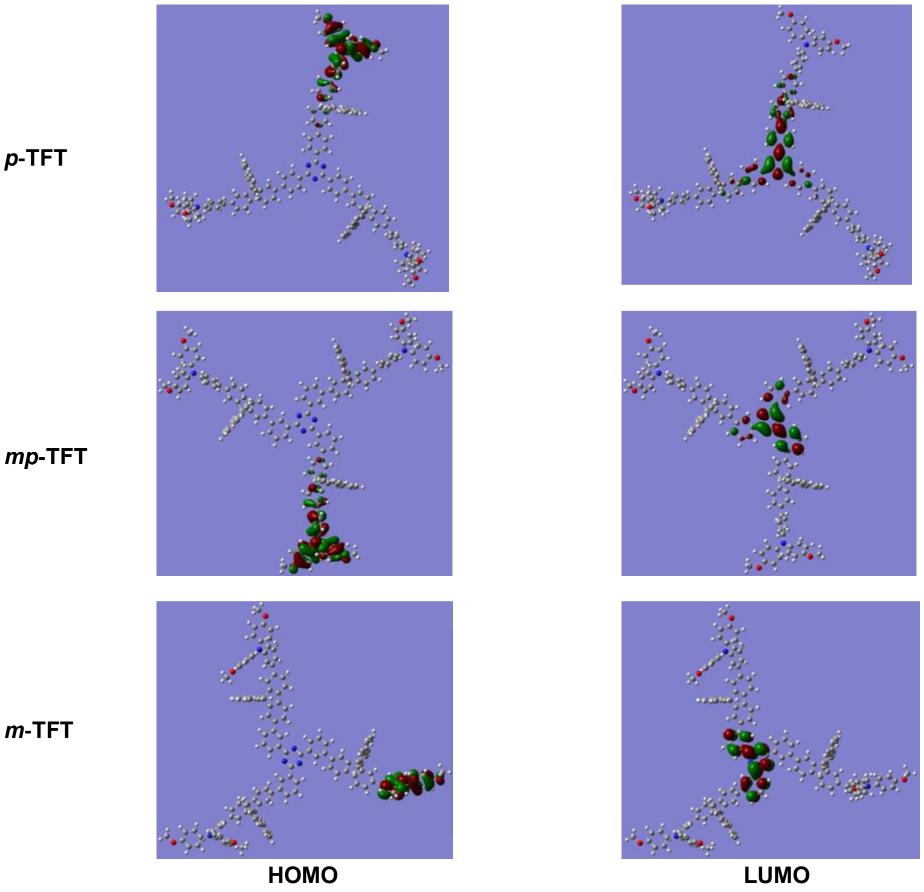


Figure 4. Molecular orbital distributions of *p*-TFT, *mp*-TFT and *m*-TFT.

whole 2,4,6-triphenyl-1,3,5-triazine core with some contributions from the spirofluorene unit. Conversely, the LUMO of *mp*-TFT is localized only on the 2,4,6-tri(phenyl)-1,3,5-triazine moiety. For *m*-TFT, the HOMO is localized at one of the triphenylamine units and the LUMO are distributed on the 1,3,5-triazine core with two phenyl rings. Obviously, the interconnection position in these star-shaped molecules has a significant influence on the electron density distributions of HOMO and LUMO.

Electrochemical Properties

The electrochemical properties of *p*-TFT, *mp*-TFT and *m*-TFT were investigated in CH_2Cl_2 solution by cyclic voltammetry (CV). All compounds show several irreversible oxidation waves in the range of 0-1.65 V (*vs* Fc/Fc^+, $E_{Fc/Fc+}$ = 0.15 V, ESI†). On the basis of the first oxidation potentials (Table 1), the HOMO energy levels are calculated to be -5.19, -5.22 and -5.26 eV for *p*-TFT, *mp*-TFT and *m*-TFT, respectively.[38] It is noted that the HOMO energy level is more stable with the decreased degree of π-conjugation ($E_{HOMO(p\text{-TFT})} < E_{HOMO(mp\text{-TFT})} < E_{HOMO(m\text{-TFT})}$). This change tendency agrees well with the calculation results. According to the HOMO energy levels and the optical band-gaps, the LUMOs of these compounds are evaluated to be -2.48 eV (*p*-TFT), -2.34 eV (*mp*-TFT) and -2.19 eV (*m*-TFT).

Electroluminescent Properties

To further explore the effect of interconnection position on the electroluminescent property, the devices based on *p*-TFT, *mp*-

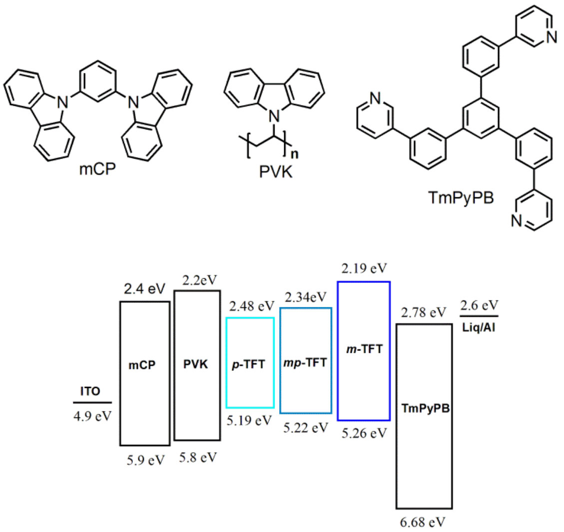


Figure 5. The molecular structure of the materials used in the device and the energy level diagram of the device.

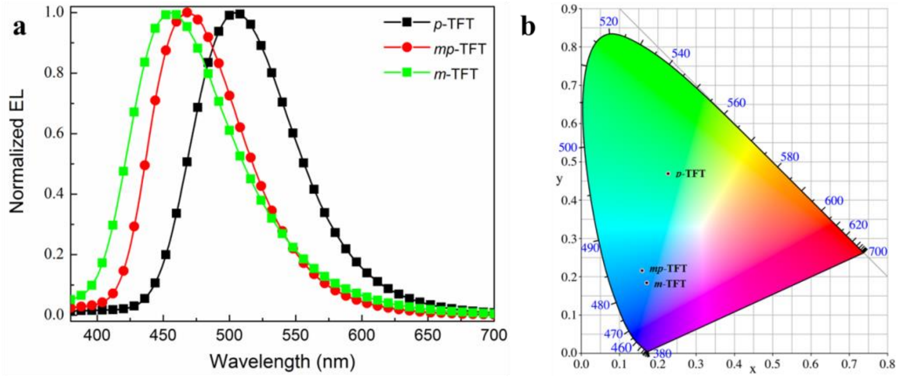


Figure 6. EL spectra (a) and CIE (b) coordinates of the devices.

TFT or *m*-TFT with the configuration of ITO/PEDOT:PSS (30 nm)/mCP:PVK:compounds (80:10:10, 30 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al were fabricated. The molecular structure of the host matrix and electronic transport material and the energy level diagrams of the device are shown in Figure 5.

The electroluminescence (EL) spectra of the devices doped with *p*-TFT, *mp*-TFT or *m*-TFT at 10 V are shown in Figure 6a. All the devices display the emission spectra with broad and structureless emission centered at 504 nm (λ_{onset} = 424 nm), 468 nm (λ_{onset} = 403 nm) and 455 nm (λ_{onset} = 387 nm) for *p*-TFT, *mp*-TFT and *m*-TFT, respectively, suggesting that there is a complete energy transfer from the host matrix to the dopant (Figure 6a). The commission international de L'Eclairage (CIE) coordinates of (0.23, 0.47), (0.16, 0.22) and (0.17, 0.18) (Figure 6b) are observed for the *p*-TFT, *mp*-TFT and *m*-TFT doped devices, respectively. From the luminance-voltage-current density (*L*-*V*-*J*) curves (Figure 7), the *p*-TFT based device possesses a low turn-on voltage (a voltage for the luminance of 1 cd/m^2) of 4 V with a maximum luminance of 10150 cd/m^2 at 14 V (369 mA/cm^2). Compared to the *p*-TFT based device, the *mp*-TFT and *m*-TFT based devices give the relatively higher turn-on voltages of 5.0 and 5.5 V respectively. In addition, the devices based on *mp*- TFT and *m*-TFT show the inferior performance with a maximum luminance of 4238 cd/m^2 at 15 V (373 mA/cm^2) and 1241 cd/m^2 at 14 V (353 mA/cm^2), respectively. This result can be explained by the increased energy barrier for electron injection at the TmPyPB/dopant interface leading to an unmatched LUMO energy level.

The current density-current efficiency (*CE*) and current density-external quantum efficiency (*EQE*) characteristics of the devices are shown in Figure 8. The maximum *CE* and *EQE* of the OLED based on *p*-TFT are 6.2 cd/A and 2.3 %, respectively. The efficiencies were drastically reduced to 2.0 cd/A (CE) and 1.2 % (*EQE*) for the *mp*-TFT based device and 0.7 cd/A (CE) and 0.5 % (*EQE*) for the *m*-TFT based device. The *EQE* of the *p*-TFT based device is 2 times and 4 times higher than that of the *mp*-TFT and *m*-TFT based devices, respectively. Obviously, it is clearly demonstrated that the interconnection position plays a significant role on the device performance.

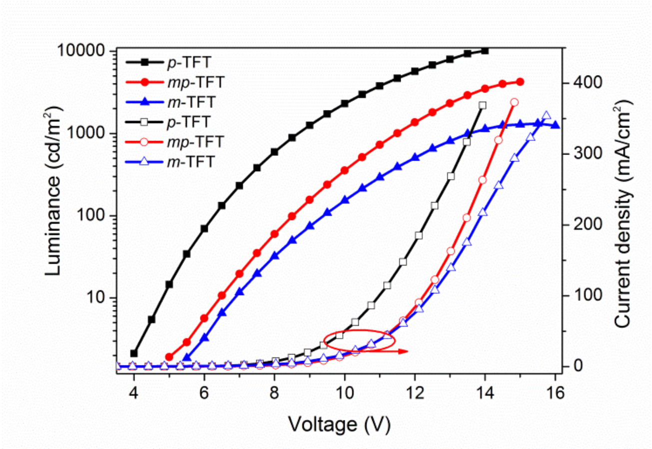


Figure 7. Luminance-voltage-current density (*L*-*V*-*J*) characteristics of the devices.

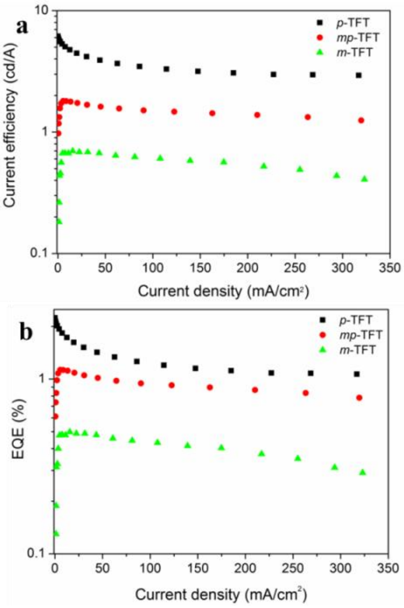


Figure 8. Current density-current efficiency (a) and current density-external quantum efficiency (b) characteristics of devices.

Conclusions

In summary, three star-shaped D-π-A isomers based on the triazine, spirofluorene and triphenylamine units were successfully designed and prepared. All target compounds showed a good thermal stability. Through modification the interconnection position among the building blocks, these isomers can exhibit tunable emission colors from deep blue to green in solution owing to a different degree of π-conjugation. In addition, these compounds possessed clearly different HOMO and LUMO distributions in the ground state and energy gap evidenced by theory calculation and cyclic voltammetry. The OLEDs employing these isomers as the emissive dopants were fabricated, and the *p*-TFT based OLEDs offered a highest *EQE* of 2.3 % and CE of 6.2 cd/A. Therefore, we believe that the molecular engineering described in this research could pave the way to the development of novel blue emitter featuring D-π-A framework.

Experimental Section

Experimental Section

Materials and Measurement

4-bromoiodobenzene, 3-bromoiodobenzene, 2,7-dibromofluorenone, 4-bromobenzonitrile and 3-bromobenzonitrile are commercial from Energy Chemical Company Ltd. Other reagents were purchased from *J&K* Chemical and Aladdin companies. All reactions were carried out under N_2 atmosphere. Compound 2a, 2b, 3 and 5b were prepared via the previous work.[22,31] ^{1}H NMR and ^{13}C NMR spectra were acquired using a Bruker Dex-400 NMR instrument using $CDCl_3$ as a solvent. Mass spectra (MS) were recorded on a Bruker Autoflex MALDI-TOF instrument using dithranol as a matrix. The UV-vis absorption and photoluminescence (PL) spectra were measured with a Varian Cray 50 and Perkin-Elmer LS50B luminescence spectrometer, respectively. Lifetimes were measured with Edinburgh analytical instrument (FLS920 fluorescence spectrometer) in degassed toluene at room temperature. Solutions of 9,10-dibromoanthracene in ethanol (Φ=0.89) were used as a reference. The equation $\Phi_s = \Phi_r(\eta_s^2 A_r I_s/\eta_r^2 A_s I_r)$ was used to calculate the quantum yields. The Φ in neat film was collected by EdinburghInstruments FLS980. Thermogravimetric analysis (TGA) was carried out with a NETZSCH STA449 from 25°C to 600°C at a 20°C/min heating rate under N_2 atmosphere. Electrochemical property was evaluated by cyclic voltammetry with three typical electrodes in degassed CH_2Cl_2 solution with a rate of 100 mV/s. The CV system employed Bu_4NPF_6 as electrolyte. Platinum disk is used as the working electrode, platinum wire is regarded as the counter electrode and silver wire is used as the reference electrode. Ferrocenium/ferrocen (Fc/Fc^+) was used as the internal standard compound.

Devices fabrication and characterization

All devices employing *p*-TFT, *mp*-TFT and *m*-TFT as the dopant were fabricated by solution-processed approach. In these OLEDs, PEDOT:PSS was spin-coated onto ITO substrate, which is utilized as the hole injection layer. The blend of mCP and PVK was used as the host matrix. 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 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: ITO/PEDOT:PSS (30 nm)/mCP:PVK:compounds (80:10:10, 30 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al

Synthesis of 5a

A mixture of 4a (1.2 g, 2.2 mmol) and bis(pinacolato)diboron (1.9 g, 7.3 mmol), CH_3COOK (0.6 g, 6.6 mmol) and 1,1'-Bis(diphenylphosphino) ferrocene palladiumdichloride (102 mg) were dissolved in 50 mL 1,4-dioxane was refluxed for 24 h. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2 (3×20 mL). The organic phase was collected and washed with water (3×20 mL), dried with anhydrous Na_2SO_4. The solvent was removed under vacuum, and then the residue was purified by column chromatography with petroleum ether (PE)/CH_2Cl_2 (1:1) as an eluent to get the compound 5a, white solid, 1.1 g, yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78 (d, *J* = 8 Hz, 6H), 8.03 (d, *J* = 8.4 Hz, 6H).

General synthesis procedure for compound 6a and 6b

To a dry round bottom flask was added compound 2a or 2b (1 eq), compound 3 (1 eq), *tetrakis*(triphenylphosphine)palladium (0.04 eq), potassium carbonate solution (2 M, 15 mL) and THF (50 mL). The mixture 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 for three times and dried with anhydrous Na_2SO_4. The solvent was removed *via* rotary evaporator under vacuum, and then the residue was purified by column chromatography with PE/CH_2Cl_2 (4:1) as an eluent to get the compound 6a and 6b.

6a: light green solid, 0.71 g, yield: 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 7.2 Hz, 4H), 7.69 (d, *J* = 7.6 Hz 1H), 7.56 (s, 1H), 7.49-7.36 (m, 6H), 7.13 (t, *J* = 7.2 Hz, 4H), 6.99-6.76 (m, 10H), 3.77 (s, 6H). TOF-MS (EI, m/z): [M^+] cal. for $C_{45}H_{32}BrNO_2$ 698.653, found 699.328.

6b: light green powder, 0.65 g, yield : 48%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 9.2 Hz, 2H), 7.78 (d, *J* = 6.4 Hz 1H), 7.68 (d, *J* = 6.8 Hz, 1H), 7.47-7.38 (m, 4H), 7.11-7.01(m, 8H), 6.83-6.75 (m, 10H) 3.79 (s, 6H). TOF-MS (EI, m/z): [M^+] cal. for $C_{45}H_{32}BrNO_2$ 698.653, found 699.174.

General Synthesis procedures for p-TFT, mp-TFT and m-TFT

A mixture of compound 6a or 6b (1 eq), 5a or 5b (1 eq), *tetrakis*(triphenylphosphine)palladium (0.04 eq), potassium carbonate solution (2 M, 10 mL) and THF (50 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 Na_2SO_4. The solvent was removed via rotary evaporator under vacuum, and then the residue was purified by column chromatography to get the target compounds.

***p*-TFT:** yellow solid, 0.24 g, yield: 48%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.63 (d, *J* = 8.0 Hz, 6H), 7.94-7.87 (m, 12H), 7.72 (d, *J* = 8.0 Hz, 3H), 7.59 (d, *J* = 8.0 Hz, 9H), 7.39 (t, *J* = 7.5 Hz, 6H), 7.24 (d, *J* = 8.0 Hz, 6H), 7.13 (t, *J* = 7.5 Hz, 6H), 7.03-7.0 (m, 15H), 6.89-6.83 (m, 15H), 6.79 (d, *J* = 9.0 Hz, 12H), 3.78 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.14, 155.89, 150.08, 149.97, 148.78, 148.17, 141.93, 141.71, 140.93, 139.86, 139.80, 135.06, 132.91, 129.31, 128.06, 127.95, 127.59, 127.24, 126.55, 126.35, 124.39, 122.79, 122.15, 120.83, 120.56, 120.42, 120.21, 114.75, 66.22, 55.61. TOF-MS (EI, m/z): [M^+] cal. for $C_{156}H_{108}N_6O_6$ 2161.836, found 2161.275.

mp*-TFT*: yellow powder, 0.24 g, yield: 46%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.79 (s, 3H), 8.50 (d, *J* = 8.0 Hz, 3H), 7.98 (d, *J* = 8.0 Hz, 3H), 7.93 (d, *J* = 7.5 Hz, 3H), 7.85 (d, *J* = 8.0 Hz, 6H), 7.77 (dd, *J* = 1.0 Hz, 7.5 Hz, 3H), 7.61 (dd, *J* = 8.0 Hz, 13.5 Hz, 6H), 7.47 (t, *J* = 7.5 Hz, 3H), 7.36 (t, *J* = 7.5 Hz, 6H), 7.25 (t, *J* = 8.5 Hz, 3H), 7.11 (t, *J* = 7.5 Hz, 6H), 7.05-7.0 (m, 15H), 6.91 (s, 3H), 6.86 (t, *J* = 7.5 Hz, 12H), 6.79 (t, *J* = 8.5 Hz, 12H), 3.78 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.48, 155.87, 150.07, 149.96, 148.85, 148.13, 141.93, 141.47, 141.29, 140.94, 140.34, 139.96, 136.51, 132.96, 128.99, 128.03, 127.90, 127.59, 127.28, 126.52, 124.42, 122.82, 122.21, 120.86, 120.46, 120.17, 114.74, 66.23, 55.60. TOF-MS (EI, m/z): [M^+] cal. for $C_{156}H_{108}N_6O_6$ 2161.836, found 2161.233.

***m*-TFT:** yellow powder, 0.21 g, yield : 42%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.78 (s, 3H), 8.49 (d, *J* = 7.5 Hz, 3H), 7.97 (d, *J* = 7.5 Hz, 3H), 7.87 (dd, *J* = 8.0 Hz, 16.5 Hz, 9H), 7.77 (d, *J* = 7.5 Hz, 3H), 7.63 (d, *J* = 7.5 Hz, 3H), 7.50-7.47 (m, 6H), 7.37 (t, *J* = 7.5 Hz, 6H), 7.12-7.02 (m, 27H), 6.88-6.78 (m, 27H), 3.79 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.50, 155.70, 150.12, 149.84, 149.16, 148.71, 141.94, 141.46, 141.29, 141.13, 140.64, 136.52, 131.33, 129.25, 129.03, 128.02, 127.93, 127.57, 127.29, 127.09, 126.47, 124.39, 122.88, 120.57, 120.41, 120.16, 120.01, 119.72, 114.74, 66.21, 55.60. TOF-MS (EI, m/z): [M^+] cal. for $C_{156}H_{108}N_6O_6$ 2161.836, found 2161.073.

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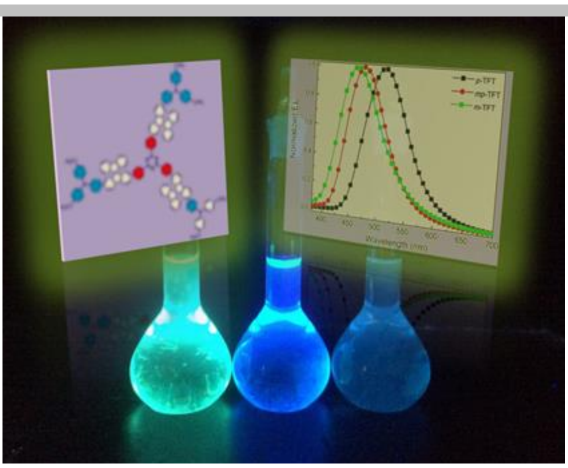
Table of Contents

Three star-shaped D-π-A isomers based on 1,3,5-triphenyl-2,46-triazine, spiro-fluorene and triphenylamine moieties, *p*-TFT, *mp*-TFT and *m*-TFT, were synthesized and prepared *via* elaborately engineering the interconnection position among the building block units. The structure-property relationship of these isomers was systematically explored by experiment and theory calculation.



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Engineering The Interconnection Position of Star-Shaped D-π-A Molecules Based on Triazine, Spirofluorene and Triphenylamine Moieties for Color Tuning from Deep blue to Green