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Dibenzothiophene-*S*,*S*-dioxide derivatives containing triphenylamine and tetraphenylethene: Synthesis, aggregation-induced emission and electroluminescence

Aihui Liang^{a,*}, Sifan Hu^a, Zhiping Wang^a, Wenjing Zhou^a, Jiarong Xu^a, Mingzhong Cai^{a,**}, Dongge Ma^{b,***}

^a College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, 330022, PR China

^b State Key Laboratory of Luminescent Materials and Devices, Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology,

Guangzhou, 510640, PR China

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ABSTRACT

Several well-defined donor-acceptor (D-A) dibenzothiophene-*S*,*S*-dioxide (SO) derivatives possessing aggregation-induced emission (AIE) behaviour decorated by tetraphenylethene (TPE) and triphenylamine (TPA) were synthesized and characterized. The photophysical, thermal, electrochemical and electroluminescent (EL) properties, as well as the AIE property of the luminogens were discussed. All the luminogens show high thermal stability and exhibit good photoluminescence, and exhibit atypical AIE characteristic. Among the three OLEDs, the device of TPA–FSO–TPA showed the best performances with a V_{on} of 4.0 V, LE_{max} of 10.05 cd A⁻¹, EQE_{max} of 3.8% and L_{max} of 14,670 cd m⁻². Upon change of the operating voltage, the electroluminescent (EL) spectra of the devices based on TPA–FSO–TPA, TPA–FSO–TPE and TPE–FSO–TPE show negligible shift, indicating good device stability could be achieved in this system.

1. Introduction

In recent years, organic light-emitting diodes (OLEDs) have attracted considerable research interest due to their potential applications in large-area displays and solid-state lighting fields [1-7]. The development of efficient luminescent materials is the goal of both scientific and technological fields. However, an obstacle that has to be faced for traditional luminophors is the notorious aggregation-caused quenching (ACQ) effect: they show strong emission in dilute solution but become weaker even non-emissive in high concentration or condensed phases. The ACQ effect will massively destroy the performance and must be properly tackled when the traditional luminophores were used in optoelectronic devices, because they are commonly used as films or aggregates [8–11]. Various physical, chemical and engineering approaches have been adopted to alleviate this negative effect [12–19]. Nevertheless, most current methods to solve the problem are far from ideal, because the ACQ effect is alleviated at the expense of sacrificing other useful properties of the traditional luminophores. Aggregation-induced

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emission (AIE) pioneered by Tang et al., which is exemplified either no or weak luminescence in solution but exhibit strong luminescence in the aggregated state, is exactly the opposite behaviour to the ACQ effect [20,21]. The discovery of AIE molecular systems supplies a novel method to solve the problem of ACQ.

The benzothiophene-S,S-dioxide (SO) was demonstrated to be beneficial for increasing electron affinity and solid-state photoluminescence efficiency [22]. The SO moiety is conductive to promoting intramolecular charge-transfer (ICT) process and constructing donor-acceptor (D-A) materials for OLEDs as acceptor. However, the materials with SO moiety usually suffered from strong intermolecular interactions and exhibited sharp PL efficiency decline in solid states, which greatly degraded their electroluminescence properties [23]. As we know, tetraphenylethene (TPE) is a classical luminogen with intriguing AIE characteristic. TPE derivatives have been widely used in optical and electroactive materials due to their well-defined AIE properties, propeller-like molecular structure, good electron-donating property and high solid-state fluorescence quantum yields [24–27]. On the







^{*} Corresponding author.

^{**} Corresponding author.

^{***} Corresponding author.

E-mail addresses: lah14god@163.com (A. Liang), msdgma@scut.edu.cn (D. Ma).

other hand, triphenylamine (TPA) and its derivatives are mostly used in OLEDs as hole-transporting materials for their excellent luminescence properties, good electron-donating ability and hole transporting capability. Recently, TPA moiety was widely used in the construction of new AIE luminogens owing to its three phenyl rotors and the non-planar structure [28–30]. The rotational motion of the phenyl rings is beneficial for dissipating excited-state energy in solution and restricting the intramolecular rotation (RIR) in the solid-state.

In this manuscript, we have synthesized three well-defined D-A structure SO derivatives by Pd(0)-catalyzed Suzuki cross coupling reaction. The photophysical, thermal, electrochemical and electroluminescent (EL) properties, as well as the AIE property of the resulting luminogens are discussed. All the luminogens show high thermal stability with a $T_{\rm d}$ above 300 °C and exhibit an absolute photoluminescence quantum yield above 60%. The device of TPA–FSO–TPA showed the best performances with a $V_{\rm on}$ of 4.0 V, LE_{max} of 10.05 cd A⁻¹ and $L_{\rm max}$ of 14,670 cd m⁻². The EL spectra of the devices based on TPA–FSO–TPA, TPA–FSO–TPE and TPE–FSO–TPE show negligible shift by changing the operating voltage, which indicate that good device stability could be achieved in this system.

2. Experimentals

2.1. Materials

3,7-Dibromodibenzothiophene-*S*,*S*-dioxide (1) [31], 4,4,5,5-tetramethyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,2-dioxaborolane (2) [32] and *N*-phenyl-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl) benzenamine (4) [33] were prepared according to the reported procedures. All reactions were performed under nitrogen. All solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated.

2.1.1. Synthesis of TPA-FSO-TPA

After degassing, Pd(PPh₃)₄ (58 mg) was added to the mixture of 3,7dibromodibenzothiophene-S,S-dioxide (374 mg, 1.0 mmol), N-phenyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) benzenamine (928 mg, 2.5 mmol), THF (60.0 mL) and aq. 2.0 M K₂CO₃ solution (20.0 mL). The mixture was heated to reflux with vigorously stirring for 18 h under an N2 flow protection. After cooling to room temperature (RT), the mixture was poured into water and extracted with dichloromethane (DCM). The organic layer was dried over anhydrous MgSO4 and evaporated to remove the solvent. The resulted crude product was purified by column chromatography on a silica gel (hexane/DCM = 20/1) to give TPA-FSO-TPA (569 mg) in a yield of 81%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.00 (s, 2H), 7.80 (s, 4H), 7.50 (d, J = 8.7 Hz, 4H), 7.34–7.27 (m, 8H), 7.15 (d, J = 7.4 Hz, 12H), 7.08 (t, J = 7.3 Hz, 4H). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 147.82, 147.66, 134.32, 132.62, 129.54, 128.01, 125.96, 124.15, 122.68. Anal. Calcd. for C48H34N2O2S: C, 82.02; H, 4.88; N, 3.99; S, 4.56; Found: C, 82.08; H, 4.86; N, 3.92; S, 4.52. HRMS (ESI): calcd for C47H36N2O2S: 702.8608, found 702.8612.

2.1.2. Synthesis of TPA-FSO-TPE

4,4,5,5-tetramethyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,2-dioxaborolane (1.38 g, 3.0 mmol), 3,7-dibromodibenzothiophene-*S*,*S*-dioxide (1.12 g, 3.0 mmol), Pd(PPh₃)₄ (69 mg), THF (70.0 mL) and aq. 2.0 M K₂CO₃ solution (20.0 mL) were added in a 150 mL flask. The mixture was heated to reflux for 16 h under argon atmosphere. After cooling to RT, the mixture was poured into brine and extracted twice with DCM. The combined organic layers were dried over MgSO₄ and the solvent was removed. The crude product was purified with column chromatography on silica gel (hexane/DCM = 20/1) to yield 1.01 g (58%) of **3** as yellow solid. ¹H NMR (400 MHz, CDCl₃) δ (ppm): ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 11.0 Hz, 2H), 7.83–7.72 (m, 3H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.19–7.09 (m, 11H), 7.09–7.00 (m,

6H).

After degassing, Pd(PPh₃)₄ (35 mg) was added to a mixture of 3 (938 mg, 1.5 mmol), N-phenyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) benzenamine (668 mg, 1.8 mmol), THF (50.0 mL) and aq. 2.0 M K₂CO₃ solution (20.0 mL). The reaction mixture was heated to reflux with vigorously stirring for 18 h under an N₂ flow protection. After cooling to RT, the mixture was poured into water and extracted with DCM (3 \times 30 mL). The combined organic layers were collected, dried over anhydrous MgSO4 and evaporated to remove the solvent. The resulted crude product was purified by column chromatography on silica gel (hexane/DCM = 13/1) to give TPA-FSO-TPE (948 mg) in a yield of 80%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.99 (d, J = 6.2 Hz, 2H), 7.80 (d, J = 5.7 Hz, 4H), 7.49 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.3 Hz, 2H), 7.30 (t, J = 7.9 Hz, 4H), 7.18–7.01 (m, 25H). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 147.29, 145.02, 144.15, 143.37, 141.75, 140.07, 138.73, 136.37, 132.04, 131.54, 131.26, 131.18, 130.02, 129.39, 127.80, 127.69, 127.44, 126.62, 126.55, 125.99, 124.78, 123.45, 123.02, 121.86, 121.71, 120.23, 119.74. Anal. Calcd. for C₅₆H₃₉NO₂S: C, 85.14; H, 4.98; N, 1.77; S, 4.06; Found: C, 85.12; H, 4.93; N, 1.79; S, 4.09. HRMS (ESI): calcd for C₅₆H₃₉NO₂S: 789.2072, found 789.2079.

2.1.3. Synthesis of TPE-FSO-TPE

To a mixture of 3,7-dibromodibenzothiophene-S,S-dioxide (374 mg, 1.0 mmol), 4,4,5,5-tetramethyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,2-dioxaborolane (1.15 g, 2.5 mmol), THF (60.0 mL) and aq. 2.0 M K₂CO₃ solution (20.0 mL), Pd(PPh₃)₄ (58 mg) was added after degassing. The mixture was heated to reflux with vigorously stirring for 24 h under an N₂ flow protection. After cooling to RT, the mixture was poured into water and extracted with DCM. The organic layer was dried over anhydrous MgSO4 and evaporated to remove the solvent. The resulted crude product was purified by column chromatography on silica gel (hexane/DCM = 25/1) to give TPE-FSO-TPE (684 mg) in a yield of 78%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.98 (s, 2H), 7.80 (s, 4H), 7.38 (d, J = 8.3 Hz, 4H), 7.17–7.09 (m, 22H), 7.09–7.01 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 144.2, 143.4, 143.3, 143.1, 141.7, 140.0, 138.5, 13 6.4, 132.1, 131.3, 129.9, 127.8, 127.6, 126.7, 126.6, 126.5, 126.1, 121.7, 120.4. Anal. Calcd. for C64H44O2S: C, 87.64; H, 5.06; S, 3.66; Found: C, 87.68; H, 5.08; S, 3.69. HRMS (ESI): calcd for C₆₄H₄₄O₂S: 876.3062, found 876.3069.

2.2. Measurements and characterization

¹H and ¹³C NMR spectra were recorded on a Bruker 400 spectrometer operating respectively at 400 and 100 MHz at room temperature. Chemical shifts were reported as δ values (ppm) relative to an internal tetramethylsilane (TMS) standard. High resolution mass spectrometry was acquired in positive Electrospray mode (ESI) on an LTQ Orbitrap XL instrument (Thermo Fisher Scientific). Elemental analyses were carried out with an Eurovector EA 3000 CHN instrument. Thermogravimetric analysis (TGA) was carried out on a Diamond TG/DTA instrument under a nitrogen atmosphere at a heating rate of 20 $^{\circ}$ C min⁻¹ and T_{d} was reported as the temperatures at 5% weight losses. UV-vis absorption spectra were measured on a HP 8453 spectrophotometer. PL spectra were recorded on an Instaspec IV CCD spectrophotometer (Oriel Co.) under 325 nm excitation of a HeCd laser. Cyclic voltammetry was carried out on a CHI660A electrochemical workstation in a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) in acetonitrile at a scan rate of 50 mV/s at room temperature under the protection of argon. A platinum electrode was used as the working electrode. A Pt wire was used as the counter electrode, and a calomel electrode was used as the reference electrode. The absolute photoluminescence quantum yield (Φ_{PL}) was measured with a Hamamatsu absolute PL quantum yield spectrometer equipped with an integrating sphere (Quantaurus-QY, C11347).



Scheme 1. Synthetic routes to TPA-FSO-TPA, TPA-FSO-TPE and TPE-FSO-TPE.

2.3. OLEDs fabrication and measurements

The OLEDs were fabricated by the following procedure: ITO glass substrate with 10 Ω /sq of resistance was carefully pre-cleaned with detergent, rinsed in de-ionized water, dried in an oven, and finally treated with oxygen plasma for 5 min. Then, all organic materials were deposited with the rate of 1-2 Å/s in sequence at a high vacuum under a pressure less than 5×10^{-4} Pa. LiF and Al in another vacuum chamber (less than 5 \times 10⁻⁴ Pa) were deposited with the rates of 0.1 and 6 Å/s, respectively, weren't been exposed to the atmosphere. The thicknesses of these deposited layers and the evaporation rate of individual material were monitored in vacuum with quartz crystal monitors. The active device areas were 0.15 cm². The current density-voltage-luminance (J-V-L) data of the electroluminescent devices were obtained with a Keithley 2400 Source meter equipped with a calibrated silicon photodiode. The electroluminescent (EL) spectra were measured by JY SPEX CCD3000 spectrometer. All the measurements were carried out in ambient atmosphere.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic route to TPA–FSO–TPA, TPA–FSO–TPE and TPE–F-SO–TPE are shown in Scheme 1. 3,7-dibromodibenzothiophene-*S*,*S*-dioxide (1) [31], 4,4,5,5-tetramethyl-2-(4-(1,2,2-triphenylvinyl) phenyl)-1,3,2-dioxaborolane (2) [32] and *N*-phenyl-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) benzenamine (4) [33] were synthesized according to the reported procedures. The target products TPA–FSO–TPE was prepared by twice Suzuki cross coupling reaction in good yield. Firstly, the intermediate product (3) was obtained through the Pd-catalyzed Suzuki cross coupling reaction of 3,7-dibromodibenzothiophene-*S*,*S*-dioxide (1) with equimolar 4,4,5,5-tetramethyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,2-dioxaborolane (2) in the yield of 58%. Secondly, the compound **3** was reacted with 1.2 equiv of *N*-phenyl-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) benzenamine (4) at 80 °C to obtain yellow solid of TPA–FSO–TPE in 80% yield. Relative to TPA–FSO–TPE, the target products TPA–FSO–TPA and TPE–FSO–TPE were both easily synthesized through a one-step Suzuki coupling reaction of compound 1 with compound 4 and compound 2 in the yield of 81% and 78%, respectively. The chemical structures of TPA–FSO–TPA, TPA–FSO–TPE and TPE–FSO–TPE were fully characterized by NMR spectroscopy, elemental analysis and mass spectrometry. All synthesized products are readily soluble in common organic solvents such as THF, DCM, and chloroform at room temperature, but they are insoluble in water.

3.2. Photophysical properties

The photophysical properties of the three luminogens TPA-F-SO-TPA, TPA-FSO-TPE and TPE-FSO-TPE in THF solution were investigated. The UV-vis absorption and photoluminescence (PL) spectra of these luminogens at room temperature are shown in Fig. 1, and the relevant data are listed in Table 1. All the three luminogens showed two distinct absorption bands in THF solution: one of the bands whose peak at about 280 nm is attributed to the localized π - π * transition; the other band at longer wavelength between 325 nm and 400 nm are assigned to the intramolecular charge transfer (ICT) transition between the donor and acceptor units [34]. TPA-FSO-TPA, TPA-FSO-TPE and TPE-FSO-TPE in THF solution all displayed strong PL emission with the maximal peaks at 494 nm, 506 nm and 404 nm, respectively. Compared to TPA-FSO-TPA and TPA-FSO-TPE, TPE-FSO-TPE exhibited a hypsochromic shift with 90 nm and 102 nm, respectively. This is probably because of the higher energy transfer between the triphenyamine unit and the dibenzothiophene-S,S-dioxide unit than that of the tetraphenylethene unit and the dibenzothiophene-S,S-dioxide unit. Relative to TPA-FSO-TPE, TPA-FSO-TPA displayed a blue-shift emission with 12 nm, because of its symmetric structure. The absolute photoluminescence quantum yields (Φ_{PL}) for these targeted luminogens in THF solution were measured on an absolute PL quantum yield



Fig. 1. UV-vis absorption (a) and PL (b) spectra of TPA-FSO-TPA, TPA-F-SO-TPE and TPE-FSO-TPE.

spectrometer with an integrating sphere, and the data were summarized in Table 1. The values are recorded to be 87.5% for TPA–FSO–TPA, 89.4% for TPA–FSO–TPE and 60.8% for TPE–FSO–TPE.

3.3. Electrochemical properties

The electrochemical behaviour of these resultant compounds were studied by cyclic voltammetry (CV) measurement using ferrocene as the internal standard and the results are listed in Table 1. One quasi-reversible oxidization peak could be easily observed in the positive scan direction. The oxidization peaks with onset potentials of TPA–F-SO–TPA, TPA–FSO–TPE and TPE–FSO–TPE are 0.86, 0.83 and 0.82 eV, respectively. The energy levels of highest occupied molecular orbit (E_{HOMO}) are -5.66, -5.63 and -5.62 eV for TPA–FSO–TPA, TPA–F-SO–TPE and TPE–FSO–TPE, calculated from the empirical formula of $E_{\text{HOMO}} = -(4.8 + E_{\text{ox}})$. The energy band gap (E_{g}) was estimated from the onset wavelength of their UV–vis absorption. The lowest unoccupied

molecular orbital energy levels (E_{LUMO}) were calculated from E_{HOMO} and E_{g} , based on the equation of $E_{LUMO} = E_{HOMO} + E_{g}$. The E_{LUMO} of TPE–FSO–TPE is calculated to be -3.02 eV, while those of TPA–F-SO–TPA and TPA–FSO–TPE are -2.85 eV and -2.81 eV.

3.4. Thermal properties

The thermal properities of these compounds were investigated using the thermogravimetric analysis (TGA) under a stream of N₂ with a scanning rate of 20 °C/min. Their TGA curves are shown in Fig. 2 and their degradation temperatures (T_d) corresponding to 5% weight loss are listed in Table 1. The recorded T_d are 379 °C for TPA–FSO–TPA, 378 °C for TPA–FSO–TPE and 302 °C for TPE–FSO–TPE. The data suggest that all the luminogens have a high thermal stability, because of their rigid structure functionalized by tetraphenylethene and triphenylamine. Generally, good thermal properties are beneficial for the vacuum deposition processing and operating stability of OLED devices.

3.5. Aggregation-induced emission performances

In order to investigate the AIE properties of the luminogens TPA–FSO–TPA, TPA–FSO–TPE and TPE–FSO–TPE, a large amount of water was added to their THF solutions to make the luminous molecules undergo aggregation. The PL emission behaviour of the luminous molecules in THF/water solution with different water fractions were examined. As shown in Fig. 3, TPA–FSO–TPE dissolved in pure THF solution $(10^{-5} \text{ mol L}^{-1})$ displays the emission peak at 506 nm. As the water fraction (f_w) of the mixture was increased from 0% to 50%, TPA–FSO–TPE exhibited decreased fluorescent intensity and the emission peak showed a red-shift at the same time. In particular, at f_w of 50%, more than 90% of its fluorescent intensity was quenched and a 25 nm bathochromic shift could be observed. This may be because the twisted intramolecular charge-transfer (TICT) effect of TPA–FSO–TPE became stronger while the polar of mixed solvent of THF/water gradually strengthened by increasing the fraction of polar water [35–37].



Fig. 2. TGA curves of TPA–FSO–TPA, TPA–FSO–TPE and TPE–FSO–TPE under nitrogen atmosphere.

Table 1

Photophysical, electrochemical and thermal data of TPA-FSO-TPA, TPA-FSO-TPE and TPE-FSO-TPE.

Compound	λabs [a] (nm)	$\lambda PL[a]$ (nm)	$\Phi_{ m PL}$ (%)	<i>E</i> ox[b] (V)	Ered (V)	HOMO (eV)	LUMO (eV)	Eg (eV)	<i>T</i> d (°C)
TPA-FSO-TPA	280, 373	494	87.5	0.86	-1.99	-5.66	-2.81	2.85	379
TPA-FSO-TPE	279, 388	506	89.4	0.83	-1.98	-5.63	-2.82	2.81	378
TPE-FSO-TPE	279, 345	404	60.8	0.82	-2.20	-5.62	-2.60	3.02	302

[a] Measured in THF solution at room temperature. [b] Measured in a solution of Bu4NPF6 (0.1 M) in acetonitrile at a scan rate of 50 mV/s at room temperature.



Fig. 3. PL spectra of TPA–FSO–TPE in THF/water mixtures with different water fractions.



Fig. 4. EL spectra of TPA-FSO-TPA, TPA-FSO-TPE and TPE-FSO-TPE.

Afterwards, f_w was increased continuously from 60% to 80%, the fluorescence intensity promptly enhanced and the emission peak displayed a blue-shift due to the aggregation-induced emission enhancement (AIEE). But by further increasing f_w to 90%, the emission intensity of TPA–FSO–TPE in the THF/water mixtures became weaker. This is probably because TPA–FSO–TPE has different aggregate morphology when f_w is 90% [38,39]. TPA–FSO–TPA and TPE–FSO–TPE exhibited the similar AIE behaviour to TPA–FSO–TPE (Fig. S2, ESI[†]).

3.6. Electroluminescent devices

To further understand the electroluminescent properties of the luminogens, we fabricated OLEDs using TPA–FSO–TPA, TPA–FSO–TPE and TPE–FSO–TPE as emitters with the configuration of ITO/HATCN (15 nm)/TAPC (50 nm)/TCTA (5 nm)/2,6DCzPPy:luminogens(10%, 20 nm)/TPBi(40 nm)/LiF(1 nm)/Al, where HATCN, TAPC, TCTA, 2,6DCzPPy and TPBi are dipyrazino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile, 1,1-bis[(di-4-tolylamino)phenyl]cyclo-hexane, 4,4',4"-tris(*N*-carbazolyl)triphenylamine, 2,6-bis[3-(9*H*-carbazol-2-9yl)phenyl]pyridine and 1,3,5-tris(*N*-phenylbenzimidazol-2-yl) benzene, respectively. In the OLEDs, ITO substrate was used as an anode, HATCN as a hole-injection layer, TAPC and TCTA as hole-transporting



Fig. 5. The EQE-brightness (EQE–*L*) characteristics (a) and current density-voltage (J-V) characteristics (b) of TPA–FSO–TPA, TPA–FSO–TPE and TPE–FSO–TPE.

Table 2
The EL performances of TPA-FSO-TPA, TPA-FSO-TPE and TPE-FSO-TPE.

Device	V _{on} [a] (V)	PE _{max} (lm W ⁻¹)	EQE _{max} (%)	$L_{\rm max}$ (cd m ⁻²)	LE _{max} (cd A ⁻¹)	CIE (x, y)
TPA-FSO-TPA	4.0	7.52	3.80	14,670	10.05	(0.216, 0.494)
TPA-FSO-TPE	4.2	3.59	3.16	4987	5.10	(0.174,
TPE-FSO-TPE	3.8	2.00	2.04	948	2.42	(0.167, 0.180)

[a] The turn-on voltage at which luminescence reach 1 cd m^{-2} .

layers, 2,6DCzPPy as host material doped by the resulting luminogens, composing a light-emitting layer (EML), TPBi as an electron-transporting/hole-blocking layer, LiF as an electron-injection layer, Al as a cathode. The EL spectra of the three luminogens are shown in Fig. 4. TPA–FSO–TPA, TPA–FSO–TPE and TPE–FSO–TPE displayed blue emission with a maximal emitting peak at ca. 491 nm, 481 and 453 nm, respectively. The Commission Internationale de L'Eclairage (CIE) coordinates of TPA–FSO–TPA, TPA–FSO–TPE and TPE–FSO–TPE are located at (0.216, 0.494), (0.174, 0.326) and (0.167, 0.180), respectively. Fig. 5 shows the external quantum efficiency–brightness characteristics (EQE–L) and voltage–current density (V–J) of the devices with these luminogens, and the relevant data are presented in Table 2.

Fig. 6. The EL spectra of TPA–FSO–TPA, TPA–FSO–TPE and TPE–FSO–TPE at different voltages.

Among the three luminogens, the device of TPA-Se-TPA exhibited the best device performance with a turn-on voltage (V_{on}) of 4.0 V, a maximal luminous efficiency (LE_{max}) of 10.05 cd A^{-1} , external quantum efficiency (EQE_{max}) of 3.8%, power efficiency (PE_{max}) of 7.52 l m W⁻¹ and a maximum luminance (L_{max}) of 14,670 cd m⁻². In order to investigate the EL stability of the three luminogens, the EL spectra of the devices with TPA–FSO–TPA, TPA–FSO–TPE and TPE–FSO–TPE was measured under

different applied voltages. As shown in Fig. 6, it can be seen that all the EL spectra of the three luminogens exhibit little shift, while the driving voltages increasing from 4 V to 8 V. Therefore, the OLEDs based on the resulting luminogens exhibited stable emission under different operating voltages.

4. Conclusions

In summary, we have successfully developed three well-defined luminogens with D-A structure via covalently binding electron-rich TPA and TPE moieties to an electron-deficient SO core by Pd(0)catalyzed Suzuki cross coupling reaction in high yield. All the three luminogens show high thermal stability and absolute photoluminescence quantum yield, and exhibit atypical aggregation induced emission feature. Among the three OLEDs, the device of TPA–FSO–TPA showed the best performances with a V_{on} of 4.0 V, LE_{max} of 10.05 cd A⁻¹, EQE_{max} of 3.8% and L_{max} of 14,670 cd m⁻². Upon change of operating voltage, the EL spectra of the devices based on TPA–FSO–TPA, TPA–F-SO–TPE and TPE–FSO–TPE show negligible shift, indicating good device stability could be achieved in this system.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2020.108526.

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