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Abstract

Three novel hole-transporting materials, 3,3'-(dibenzo[*b,d*]furan-2,8-diyl)bis(*N*,*N*-diphenylaniline) (BF-m-TPA), 4,4'-(dibenzo[*b,d*]furan-2,8-diyl)bis(*N*,*N*-diphenylaniline) (BF-p-TPA) and 4,4'-(dibenzo[*b,d*]furan-2,6-diyl)bis(*N*,*N*-diphenylaniline) (BF-2,6-TPA), were designed and synthesized. Owing to the rigid dibenzofuran core, these BF-TPA derivatives exhibited high thermal decomposition temperatures of over 395 °C and very high LUMO energy levels. Electroluminescent (EL) devices were fabricated using these three hole-transporting materials. The best device performance was obtained for BF-m-TPA, with the maximum luminance (L) of 15,230 cd/m², luminance efficiency (LE) of 56.5 cd/A, power efficiency (PE) of 13.3 lm/W, and external quantum efficiency (EQE) of 16.3%.

Keywords: dibenzofuran derivatives, triphenylamine based material, hole-transporting materials, green PhOLEDs, highly thermal stability.

1. Introduction

In this decade, organic light-emitting diodes (OLEDs) have attracted considerable interest due to their potential applications in flat panel displays and solid-state lighting.[1-4] Phosphorescent OLEDs (PhOLEDs) using iridium complexes as dopants have attracted extensive attention in recent years owing to their potential advantages of harvesting excitons from both the singlet and triplet energy states.[5-9] It is well demonstrated that carrier-transporting materials are crucial for enabling a balanced carrier transport for the electrodes. [10-12] Among carrier-transporting materials, the hole-transporting layer (HTL) is one of the key functional layers because it reduces the energy barrier between the anode and the emitting layer (EML), facilitating the injection of holes and their transport in devices.[13-16]

There has been extensive research for the development of remarkable hole-transport materials (HTMs) with the following properties. First, good hole mobility to enable the transfer of positive charge carriers from the anode to the emitting layer; [15] second, high electrochemical and thermal stability for high-temperature operations; [17,18] third, a suitable HOMO energy level to easy hole injection from anode to EML; fourth, a suitable LUMO energy level to block electron transfer from EML to HTL.[19-21] Dibenzofuran based on electron-rich moiety have been widely used for designing HTMs and host materials because of its high triplet energy and thermal stability, which make substituted dibenzofurans ideal materials for use in organic optoelectronic devices, including OLEDs, field-effect transistors, and photovoltaic cells. Triphenylamine (TPA) is a well-known hole-transporting functional group and matches well with the work function of anodes.[24,25] The lone pair electrons of N-atom of TPA is delocalized over the aromatic rings, leading to multiple resonance structures, making these structures strong electron donors and excellent HTMs.[26] Dibenzofuran is also a good electron donor; therefore, compounds containing both dibenzofuran and TPA are not only thermally stable but also have relatively high HOMO energy levels, which can lower the energy barriers for hole-transport, thereby enhancing hole mobility.

Hence, we synthesized three HTMs based on dibenzofuran as the core and TPA as the side group, and the thermal, optical, and electrochemical properties of these BF-TPA derivatives were compared according to the substitution position. Finally, the electroluminescent devices were fabricated using these BF-TPA derivatives as a hole-transporting material.

2. Experimental

2.1. Materials

Dibenzofuran, *N*-bromosuccinimide (NBS), 3-bromoiodobenzene, diphenylamine, 4-(diphenylamino)phenylboronic acid pinacol ester, 4-bromodibenzofuran, bis(pinacolato)diboron, tetrakis(triphenylphosphine)palladium(0), sodium *tert*-butoxide, tri*tert*-butylphosphine, tris(dibenzylideneacetone)dipalladium(0) and phenyliodine diacetate were purchased from Aldrich Chemical Co. and SEJINCI CO. Before use, all the solvents were purified and freshly distilled according to literature procedures.

2.2. Synthesis of 2,8-dibromodibenzofuran (1)

Dibenzofuran (5 g, 29.7 mmol) in DMF (20 mL) was poured dropwise solution of NBS (11.6 g, 68.3 mmol) in DMF (25 mL). This mixture was stirred at room temperature to precipitate the white compound (1), which was separated by filtration (3.8 g, 40 %). ¹H NMR (300 MHz, CDCl₃) δ 8.05 (s, 2H), 7.61 (d, 2H, *J* = 9.0 Hz), 7.47 (d, 2H, *J* = 9.0 Hz). ¹³C NMR (75 MHz, CDCl₃) δ 156.03, 129.21, 124.32, 124.18, 118.87, 111.81. HRMS (ESI, *m/z*): [M + H]⁺ calcd for C₁₂H₆Br₂O, 325.88; found 325.00. Elemental analysis; found: C, 44.14; H, 1.77 %; molecular formula C₁₂H₆Br₂O requires C, 44.21; H, 1.86; Br, 49.02; O, 4.91%.

2.3. Synthesis of 2-iodo-6-bromodibenzofuran (2)

In a 250 mL round-bottom three-neck flask under a nitrogen atmosphere, 4bromodibenzofuran (5 g, 20 mmol), iodine (2.57 g, 10 mmol), phenyliodine diacetate (3.259 g, 10 mmol), sulfuric acid (0.01 mL), acetic acid (15 mL) and acetic anhydride (15 mL) were placed, and stirred at room temperature for 10 h. The reaction mixture was washed with water, extracted with dichloromethane, and concentrated to give compound (2) (3.6 g, 47.7 %). ¹H NMR (300 MHz, CDCl₃) δ 8.27 (s, 1H), 7.85 (d, 1H, *J* = 6.0 Hz), 7.78 (d, 1H, *J* = 6.0 Hz), 7.66 (d, 1H, *J* = 9.0 Hz), 7.44 (d, 1H, *J* = 6.0 Hz), 7.25 (t, 1H, *J* = 7.5 Hz). ¹³C NMR (75 MHz, CDCl₃) δ 155.41, 153.41, 136.38, 130.79, 130.01, 126.80, 124.37, 124.33, 119.80, 114.14, 104.59, 86.35. HRMS (ESI, *m*/*z*): [M + H]⁺ calcd for C₁₂H₆BrIO, 371.86; found 372.00. Elemental analysis; found: C, 38.38; H, 1.48 %; molecular formula C₁₂H₆BrIO requires C, 38.64; H, 1.62; Br, 21.42; I, 34.02; O, 2.44%.

2.4. Synthesis of 2,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]furan (3)

The compound (1) (2.5 g, 7.7 mmol), bis(pinacolato)diboron (4.5 g, 17.7 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.45 g, 0.13 mmol) and potassium acetate (2.3 g, 23 mmol) were dissolved in 1,4-dioxane (50 mL) and stirred for 12 h at 110 °C. The reaction mixture was cooled to room temperature, extracted with dichloromethane (50 mL × 3), and dried over anhydrous MgSO₄. The crude product was subjected to flash column chromatography (dichloromethane : *n*-hexane = 1 : 2) to give compound (3) (1.1 g, 61 %). ¹H NMR (300 MHz, CDCl₃) δ 8.51 (s, 2H), 7.93 (d, 2H, *J* = 9.0 Hz), 7.58 (d, 2H, *J* = 9.0 Hz), 1.40 (s, 24H). ¹³C NMR (75 MHz, CDCl₃) δ 158.41, 133.72, 128.03, 123.83, 122.92, 111.07, 83.86, 24.94. HRMS (ESI, *m*/*z*): [M + H]⁺ calcd for C₂₄H₃₀B₂O₅, 420.23; found 420.30. Elemental analysis; found: C, 68.92; H, 7.04 %; molecular formula C₂₄H₃₀B₂O₅ requires C, 68.61; H, 7.20; B, 5.15; O, 19.04%.

2.5. Synthesis of 2,8-bis(3-bromophenyl)dibenzo[b,d]furan (4)

2,8-bis(3-bromophenyl)dibenzo[*b*,*d*]furan (4) was prepared by following a modified method of Suzuki coupling.[27] The compound (3) (1.6 g, 3.8 mmol), 3-bromoiodobenzene (2.38 g, 8.4 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.35 g, 0.3 mmol) were stirred in tetrahydrofuran (25 mL). Potassium carbonate solution (4M, 7 mL) and ethanol (8 mL) was added to the mixture, followed by vigorously stirring for 12 h at 80 °C. The reaction mixture was cooled to room temperature, extracted with dichloromethane (50 mL × 3), and dried over anhydrous MgSO₄. The crude product was subjected to flash column chromatography (ethyl acetate : *n*-hexane = 1 : 4) to give compound (4) (1.1 g, 61 %). ¹H NMR (300 MHz, CDCl₃) δ 8.19 (s, 2H), 7.86 (s, 2H), 7.72-7.62 (m, 6H), 7.54 (d, 2H, *J* = 9.0 Hz), 7.38 (t, 2H, *J* = 6.0 Hz). ¹³C NMR (75 MHz, CDCl₃) δ 156.24, 141.12, 136.68, 133.21, 131.47, 129.96, 126.78, 123.84, 122.97, 122.82, 119.20, 111.77. HRMS (ESI, *m/z*): [M + H]⁺ calcd for C₂₄H₁₄Br₂O, 478.18; found 478.94. Elemental analysis; found: C, 44.14; H, 1.77; O, %molecular formula C₂₄H₁₄Br₂O requires C, 44.21; H, 1.86; Br, 49.02; O, 4.91%. Elemental analysis; found: C, 60.32; H, 2.89 %; molecular formula C₂₄H₁₄Br₂O requires C, 60.28; H, 2.95; Br, 33.42; O, 3.35%.

2.6. Synthesis of 3,3'-(dibenzo[b,d]furan-2,8-diyl)bis(N,N-diphenylaniline) (BF-m-TPA)

Compound (4) (1 g, 2.1 mmol), P(t-Bu)₃ (0.021 g, 0.11 mmol), $Pd_2(dba)_3$ (0.058 g, 0.063 mmol), diphenylamine (0.9 g, 5.3 mmol), and sodium *tert*-butoxide (0.51 g, 5.3 mmol) were dissolved in toluene (20 mL). After the reaction mixture was stirred in a nitrogen atmosphere

for 20 h at 100 °C, it was cooled to room temperature. And then the reaction mixture extracted with dichloromethane (80 mL × 3) and dried over anhydrous MgSO₄. The crude product was subjected to flash column chromatography (ethyl acetate : *n*-hexane = 1 : 4) to give BF-m-TPA (1.2 g, 87 %). ¹H NMR (300 MHz, CDCl₃) δ 8.10 (s, 2H), 7.60 (t, 4H, *J* = 9.0 Hz), 7.45 (s, 2H), 7.38-7.28 (m, 12H), 7.20 (d, 8H, *J* = 9.0 Hz), 7.12-7.03 (m, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 156.24, 148.39, 147.85, 142.42, 136.18, 129.69, 129.30, 126.78, 124.62, 124.24, 123.08, 122.96, 122.82, 121.89, 119.20, 111.77. HRMS (ESI, *m/z*): [M + H]⁺ calcd for C₄₈H₃₄N₂O, 654.27; found 654.35. Elemental analysis; found: C, 87.79; H, 5.34; N, 4.29; O, 2.58%; molecular formula C₄₈H₃₄N₂O requires C, 88.04; H, 5.23; N, 4.28; O, 2.44%.

2.7. Synthesis of 4,4'-(dibenzo[b,d]furan-2,8-diyl)bis(N,N-diphenylaniline) (BF-p-TPA)[28]

A procedure identical to that for compound (4) was followed, using compound (1) (2 g, 6.1 mmol) and 4-(Diphenylamino)phenylboronic acid pinacol ester (5 g, 13.5 mmol). The obtained crude compound was purified by silica gel chromatography (ethyl acetate : *n*-hexane = 1 : 4) to give BF-p-TPA (2.67 g, 67 %). ¹H NMR (300 MHz, CDCl₃) δ 8.19 (s, 2H), 7.72-7.57 (m, 8H), 7.35-7.16 (m, 20H), 7.07 (t, 4H, *J* = 7.5 Hz). ¹³C NMR (75 MHz, CDCl₃) δ 156.03, 147.73, 147.04, 135.99, 135.31, 129.31, 128.05, 126.35, 124.82, 124.38, 124.16, 122.92, 118.68, 111.85. HRMS (ESI, *m/z*): [M + H]⁺ calcd for C₄₈H₃₄N₂O, 654.27; found 654.04. Elemental analysis; found: C, 87.71; H, 5.27; N, 4.32; O, 2.61%; molecular formula C₄₈H₃₄N₂O requires C, 88.04; H, 5.23; N, 4.28; O, 2.44%.

2.8. Synthesis of 4,4'-(dibenzo[b,d]furan-2,6-diyl)bis(N,N-diphenylaniline) (BF-2,6-TPA)

A procedure identical to that for compound (4) was followed, using compound (2) (1.7 g, 4.6 mmol) and 4-(diphenylamino)phenylboronic acid pinacol ester (3.9 g, 10.5 mmol). The obtained crude compound was purified by silica gel chromatography (ethyl acetate : *n*-hexane = 1 : 4) to give compound (6) (1.8 g, 60 %). ¹H NMR (300 MHz, CDCl₃) δ 8.17 (s, 1H), 7.95 (d, 1H, *J* = 6 Hz), 7.87 (d, 2H, *J* = 9 Hz), 7.72-7.58 (m, 5H), 7.45 (t, 1H, *J* = 9 Hz), 7.33-7.29 (m, 9H), 7.25-7.20 (m, 11H), 7.14-7.04 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 155.50, 153.78, 147.74, 147.64, 147.02, 135.97, 135.39, 130.03, 129.34, 128.07, 125.54, 124.78, 124.36, 124.18, 123.36, 122.67, 119.15, 118.66, 111.92. HRMS (ESI, *m/z*): [M + H]⁺ calcd for C₄₈H₃₄N₂O, 654.27; found 654.45. Elemental analysis; found: C, 88.04; H, 5.47; N, 4.25; O, 2.50%; molecular formula C₄₈H₃₄N₂O requires C, 88.03; H, 5.23; N, 4.28; O, 2.44%.

2.9. Instruments

¹H and ¹³C NMR spectra were recorded on Bruker-Spectrospin 300 MHz spectrometer, using CDCl₃ as the solvent. Chemical shifts are reported in parts per million (ppm) relative to residual CDCl₃ at 7.26 ppm (for ¹H NMR) and 77.0 ppm (for ¹³C NMR). UV-visible spectra were recorded on a Shimadzu UV/Vis spectrophotometer, while the photoluminescence spectra were measured using a PerkinElmer spectrofluoromater. Film thickness was measured using a TENCOR surface profiler. Thermogravimetric analyzer was performed on PerkinElmer Pyris 1 TGA with a heating scan rate of 10 °C/min from 40 to 800 °C under nitrogen. Cyclic voltammetry (CV, AMETEK VersaSTAT 3) was carried out at a potential scan rate of 50-100 mV s⁻¹ in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in acetonitrile under a N₂ atmosphere at room temperature. The potential was reported relative to a ferrocene/ferrocenium (Cp₂Fe/Cp₂Fe⁺) redox couple used as an internal reference. High resolution mass spectra were measured using a JEOL JMS-700 and elemental analyses using a Thermo Fisher Scientific Flash2000. Current density (I), voltage (V) and luminance (L) data were collected using a Keithley 236 source measurement unit. The CIE coordination was recorded using a PR-670 Spectra Scan Spectrophotomater.

2.10. Device fabrication

OLEDs were fabricated using BF-m-TPA, BF-p-TPA and BF-2,6-TPA as hole-transport materials. ITO glasses were ultrasonically cleaned sequentially with deionized water, acetone, and isopropanol, each for 15 min, and UV-ozone treated for 15 min. All of the organic layers were deposited on the pre-cleaned ITO glass. LiF and Al were evaporated on the ETL layer at a pressure of 5×10^{-7} Torr. Finally, all the devices were encapsulated using a glass cover and all deposition processes were conducted inside a nitrogen-filled glove box.

3. Results and discussion

3.1. Synthesis and structural characterization

The synthetic route used to prepare the BF-TPA derivatives is presented in Scheme 1. The BF-m-TPA was synthesized in one step through a Buchwald-Hartwig coupling reaction between compound (4) and diphenylamine and BF-p-TPA and BF-2,6-TPA were synthesized using the palladium-catalyzed Suzuki coupling reaction of the 2,8-dibromodibenzofuran and

2-iodo-6-bromodibenzofuran with 4-(diphenylamino)phenylboronic acid pinacol ester. The BF-TPA derivatives were purified by silica gel chromatography and obtained with over 60 % yield. The BF-TPA derivatives were characterized by ¹H NMR analysis, elemental analysis, and mass spectrometry analysis.

The thermal stability of hole-transport materials is very important for device fabrication and operation. The thermal characterization of BF-m-TPA, BF-p-TPA, and BF-2,6-TPA were studied using thermogravimetric analysis (TGA) in a nitrogen atmosphere. The five percent weight loss temperatures of BF-m-TPA, BF-p-TPA, and BF-2,6-TPA were 425, 441, and 396 \Box , respectively, indicating that the thermal stabilities were appropriate for electroluminescent devices.

To gain information about the three-dimensional conformations and electronic structures of BF-TPA derivatives, theoretical calculations were applied using density functional theory (DFT) through Gaussian software at B3LYP/6-31G(d) basis set. The molecular structure and electronic density distribution of BF-m-TPA, BF-p-TPA and BF-2,6-TPA are shown in Figure 1. In the materials synthesized, the triphenylamine units are linked at the 2,8- and 2,6-positions to the dibenzofuran core. The HOMO level of BF-m-TPA is populated on the TPA moieties, while the HOMO of BF-p-TPA and BF-2,6-TPA are distributed on the entire molecule and localized primarily on the peripheral TPA moieties. The LUMO levels of BF-m-TPA, BF-p-TPA, and BF-2,6-TPA are localized on dibenzofuran cores. No orbital overlap between the HOMO and LUMO is found in BF-m-TPA and the separation of HOMO and LUMO levels reveal their strong bipolar features.[29]

3.2. Optical and electrochemical properties

Figure 3 shows the UV-Vis and photoluminescence (PL) spectra of BF-m-TPA, BF-p-TPA and BF-2,6-TPA in dichloromethane solution and film state at room temperature, and the results are summarized in Table 1. The absorption maxima of BF-m-TPA, BF-p-TPA, and BF-2,6-TPA were observed at 300, 325, and 340 nm, respectively. The BF-TPA derivatives were showed the π - π * transition of around 250 nm and n- π * transition range of 300-350 nm. The introduction in the *para* position of the diphenylamine group led to a conspicuous red shift in BF-p-TPA and BF-2,6-TPA in comparison with BF-m-TPA. This result shows that introduction diphenylamine group of the *meta* position could cause a blue shift due to the short conjugation properties. The BF-TPA derivatives showed emission from UV to deep

blue at 403-425 nm in solution and 394-430 nm in film. The PL emission of BF-2,6-TPA was red-shifted compared to BF-m-TPA and BF-p-TPA. The solid state of BF-m-TPA exhibited emission ranging from 394 nm, which was significantly more blue-shifted than the solution state. This result is probably due to the change from the crystalline to amorphous state.[30] Phosphorescent emission peak from low temperature (at 77 K) PL measurement provided a high triplet energy of 2.67, 2.55, and 2.47 eV in BF-m-TPA, BF-p-TPA, and BF-2,6-TPA, respectively. The BF-TPA derivatives has a higher triplet energy than the 2.40 eV of Ir(mppy)₃. Thus, compounds can be used as an HTL material for green phosphorescent OLEDs.

The optical band gaps (ΔE_g) of BF-m-TPA, BF-p-TPA and BF-2,6-TPA deduced from the absorption edge of the absorption spectra were 3.70, 3.40, and 3.30 eV, respectively. In order to evaluate the redox behaviour of BF-TPA derivatives and access the HOMO energy levels, we performed cyclic voltammetry (CV) with respect to ferrocene as a standard. The BF-TPA derivatives revealed irreversible oxidation potentials at 0.83-0.91 V. The HOMO energy levels of BF-m-TPA, BF-p-TPA, and BF-2,6-TPA were 5.31, 5.30, and 5.23 eV, respectively. The LUMO levels were estimated from the HOMO levels and the values of optical band gaps by $E_{LUMO} = E_{HOMO} + \Delta E_g$. The resulting data are summarized in Table 1. The BF-m-TPA was exhibited a very high LUMO energy of 1.61 eV. This result suggested that it effectively blocked the electron transfer from EML to HTL.

Charge-carrier mobilities of BF-TPA derivatives were measured by the space-charge limited current (SCLC) method. Hole-only devices were fabricated with the following structure to hole transporting properties of BF-m-TPA, BF-p-TPA and BF-2,6-TPA; ITO/PEDOT:PSS (30 nm)/ BF-TPA derivatives (100 nm)/ MoO₃ (10 nm)/ Au (100 nm). Hole mobilities of BF-m-TPA, BF-p-TPA and BF-2,6-TPA were 2.48×10^{-4} cm² V⁻¹ s⁻¹, 2.53×10^{-6} cm² V⁻¹ s⁻¹ and 1.40×10^{-5} cm² V⁻¹ s⁻¹, respectively. According to the this result, it can be concluded that BF-m-TPA will fabricate more efficient device, because of fast hole mobility properties compared BF-p-TPA and BF-2,6-TPA.

3.3. Electroluminescent properties

To evaluate the performance of the BF-TPA derivatives as hole-transport layer, green phosphorescent OLEDs were fabricated using green emitter $Ir(mppy)_3$ as the dopant. The device configuration was ITO/NPB (20 nm)/HTL (30 nm)/CzTP + $Ir(mppy)_3$ (10 %, 40

nm)/TPBi (30 nm)/LiF (0.5 nm)/Al (500 nm) (HTL = BF-m-TPA: device 1, BF-p-TPA: device 2 and BF-2,6-TPA: device 3) and Figure 4 shows a device construction and HOMO/LUMO energy diagrams of the materials used. The performance of all devices are also shown in Figure 5. The corresponding device data are presented in Table 2. The EL spectra of devices based on BF-m-TPA, BF-p-TPA, and BF-2,6-TPA exhibit emission exclusively from 512 nm of Ir(mppy)₃. The three devices exhibit turn-on voltages of 6.3-8.0 V, maximum brightness of 10,244-15,230 cd/m², luminance efficiencies (LE) of 28.6-56.5 cd/A, and power efficiencies (PE) of 8.6-13.7 lm/W. Device 3, which used BF-2,6-TPA as the HTL, showed the lowest turn-on voltage among the three devices, which might be attributable to the suitable HOMO energy level of BF-2,6-TPA.

Device 1 using BF-m-TPA had the best result with a maximum luminance of $15,230 \text{ cd/m}^2$, PE of 13.3 lm/W, LE of 56.5 cd/A, and EQE of 16.3 %. Such high efficiency could be attributed to blocking electrons from EML to HTL, as a result of the high LUMO energy of BF-m-TPA. Another reason is that the triplet energy of BF-m-TPA was over 0.25 eV higher than of Ir(mppy)₃ (2.4 eV).[31] Device 1 presented pure Ir(mppy)₃ emission, while device 2 and device 3 exhibited an additional peak at 405 nm and 424 nm, respectively, which were recognized as the BF-p-TPA and BF-2,6TPA emissions, respectively. This phenomenon perhaps indicates that the BF-p-TPA and BF-2,6-TPA do not suite the energy level with the EML layer, causing the hole to not transfer well to EML, and thereby generating excitons in the HTL. Therefore, in future research, we will design a device in which the energy level is suited to BF-p-TPA and BF-2,6-TPA to fabricate a more efficient device and to observe its characteristics. Since the device configuration has not been optimized and the manufacturing environment is not good in the present work, it is expected that further performance can be improved by fine tuning the device structure and improving the manufacturing environment. Future studies will further investigate the life characteristics of the devices through fine tuning of the device.

4. Conclusions

We have successfully synthesized BF-m-TPA, BF-p-TPA, and BF-2,6-TPA as holetransporting materials containing dibenzofuran and triphenylamine. Their thermal, photophysical, electrochemical, and electroluminescent properties have been investigated. The BF-TPA derivatives have a high thermal stability of over 395 \Box . They also have high

LUMO energy levels of over 1.93 eV. The BF-TPA derivatives were fabricated as holetransporting materials in green phosphorescent OLEDs. The fabricated OLEDs of the BF-m-TPA showed the best performance with a current efficiency of 56.6 cd/A, luminance of 15,230 cd/m², power efficiency of 13.3 lm/A, and EQE of 16.3 % compared to compounds with introduction at the para position. This indicated that BF-m-TPA had a higher triplet energy and a more suitable band diagram with EML compared to BF-p-TPA and BF-2,6-TPA.

. w BF-p-TPA

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Scheme 1. Synthetic procedure of the BF-TPA derivatives

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Figure Captions

Figure 1. Calculated HOMO and LUMO distributions of (a) BF-m-TPA, (b) BF-p-TPA and (c) BF-2,6-TPA.

Figure 2. TGA curves of a) BF-m-TPA, (b) BF-p-TPA and (c) BF-2,6-TPA.

Figure 3. (a) Absorption and (b) photoluminescence spectras of BF-TPA derivatives in dichloromethane and film.

Figure 4. Device structure and HOMO/LUMO energy levels of the materials used for OLEDs.

Figure 5. (a) Electroluminescence spectra, (b) voltage-current density-luminance, (c) current density-luminance efficiency-power efficiency and (d) luminance-EQE of three devices.

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Fig. 5

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		Emissi	on	A D	OV	т	Б	Б	HOMO	LIMO	Б
	Absorption	$\lambda_{\max}(n)$	m)	ΔΔ.	QY		\mathbf{E}_{t}				E _g
	λ_{\max} (nm)	solution ^a	film	(nm)	(%0)	(□)	(ev)	(v)	(ev)	(ev)	(ev)
BF-m-TPA	300	403	394	103	38	425	2.67	0.91	5.31	1.61	3.70
BF-p-TPA	325	403	410	78	43	441	2.55	0.90	5.30	1.90	3.40
BF-2,6-TPA	340	425	430	80	81	396	2.47	0.83	5.23	1.93	3.30

Table 1. Photophysical and electrochemical properties for BF-TPA derivatives.

^a All data were measured in CH₂Cl₂ solution

^b T is the temperature at 5 % weight loss

^cEstimated from the onset of the phosphorescence spectrum.

^dLUMO levels were derived via eq. E_g=HOMO - LUMO

 $^{e}\Delta E_{g}$ collected by UV-Vis spectrophotometer

	Turn-on	LE _{max}	PE _{max}	L _{max}	EQE	EL	CIE
	voltage(V)	(cd/A) ^a	(lm/W) ^a	$(cd/m^2)^a$	$(\%)^{a}$	(nm) ^a	$(\mathbf{x},\mathbf{y})^{\mathrm{a}}$
Device 1	8	56.5	13.3	15230	16.3	512	0.31, 0.61
Device 2	7.2	28.6	8.6	10738	8.4	512	0.28, 0.62
Device 3	6.3	46.5	13.7	10244	13.5	512	0.31, 0.61

Table 2. Device performances based on BF-TPA derivatives

^aValues indicate maximum efficiency.

13.5

Dibenzofuran derivatives with meta- and para-triphenylamine substituents as hole-transporting materials in organic lightemitting devices

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Highlights

- Three hole-transporting materials based on dibenzofuran and triphenylamine were developed.

- The BF-TPA derivatives were showed highly LUMO energy.
- Green phosphorescent OLEDs using the hole transporting materials were fabricated.
- Green PhOLED with BF-m-TPA had the best result with a maximum LE of 56.5 cd/A.

AUTHORSHIP STATEMENT

Manuscript title: <u>Dibenzofuran derivatives with - and para-triphenylamine substituents as hole-transporting</u> materials in organic light-emitting devices

All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing, or revision of the manuscript. Furthermore, each author certifies that this material or similar material has not been and will not be submitted to or published in any other publication before its appearance in the *Dye and Pigments*.

Authorship contributions

Please indicate the specific contributions made by each author (list the authors' initials followed by their surnames, e.g., Y.L. Cheung). The name of each author must appear at least once in each of the three categories below.

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Declaration of interests

 \boxtimes 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.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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