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Author Statement

All person have made substantial contributions to the work reported in manuscript, including Liang Cao, Lei Zhang, Jiasen Zhang, Dongjun Chen, performed data acquirement, data analysis and wrote the manuscript; Sheng Wang helped perform the analysis with constructive discussions; Qiang Wei revised the manuscript; Tao Wang, Shi-jian Su and Ziyi Ge contributed to the conception of the study.

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Bipolar Fluorophores Based on Intramolecular Charge-Transfer Moieties of Sulfone for Nondoped Deep Blue Solution-Processed Organic Light-Emitting Diodes

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ABSTRACT: Dipolar emitters exhibited excellent performance in organic light-emitting diode (OLED). However, these molecules had intramolecular charge-transfer (ICT) properties, which posed challenge to obtain deep blue emission. In this study, three fluorophores were designed by introducing carbazole and diphenylamine as electron donors and sulfone as electron acceptor due to their mild charge-accepting properties and twisted angles. These materials appeared almost in vertical angles of the dihedral configuration, and exhibited high thermal and electrochemical stability, suitable for solution-processed OLED. The solution-processed non-doped devices based on these three emitters were realized, where two emissions within the standard deep blue emission range were achieved with the Commission International e de l'Eclairage (CIE) coordinates of (0.16, 0.12) and (0.16, 0.15).

Keywords: intramolecular charge-transfer; bipolar fluorophores; deep blue; single layer, organic light-emitting diodes

1. Introduction

OLED have the advantages of self-luminance, low driving voltage, wide color gamut, wide viewing angle, ultra-thin and many more, therefore they are considered as the next generation of display technology [1-3]. For the fabrication of OLED, solution processing is preferred as it is suitable for large-scale processing of flexible devices at low cost. To realize full-color display of OLED, blue light-emitting materials are essential[4, 5]. However, these materials have deeper frontier molecular orbital (FMO) as compared to red and green light-emitting materials, which often resulted to poor performances. Dipolar materials with D-A structures have attracted tremendous attentions [6-12], because it can increase both hole and electron mobility[13, 14] to achieve 100% internal quantum efficiency with low efficiency roll-off[8, 15-17]. However, due to

the intramolecular charge-transfer (ICT) properties in dipolar materials, most of the emitters are designed with long wavelength, which pose a challenge to design deep-blue emitters.

In order to achieve deep blue emission, the D-A molecules need to have weak ICT effect and short conjugation length[13, 14, 18-32]. Therefore, in this work, three deep blue emitting compounds based on sulfone intramolecular charge-transfer type were designed and synthesized as shown in **Scheme 1**, which possessed two sulfonyl groups as electron acceptors (A) and carbazoles or triphenylamine as an electron donor (D). These D- π -A type molecules have ICT character with large dihedral angles and significant energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), which are both beneficial for generating short-wavelength emissions[33]. In addition, these fluorophores exhibited good photophysical, thermal, electrochemical and electroluminescence properties. Solution-processed non-doped OLED were then fabricated, in which two of it exhibited deep blue emission with CIE of (0.16, 0.15) and (0.16, 0.11).

2. Synthesis

2.1 Materials

(9-phenyl-9H-carbazol-3-yl)boronic acid, (4-(9H-carbazol-9-yl)phenyl)boronic acid, (4-(diphenylamino)phenyl)boronic 2,7-dibromo-9,9-dioctyl-9H-fluorene, acid, bis(pinacolato)diboron were purchased from TCI. Tetrakis(triphenylphosphine)palladium $(Pd(PPh_3)_4),$ bis(triphenylphosphine)palladium(II)dichloride(PdCl₂(PPh₃)₂) and 1,1'-bis(diphenylphosphino)ferrocenedichloropalladium(II) (PdCl₂(dppf)) were purchased from Shanxi Kaida Chemical Engineering Co., Ltd. Other reagents and solvents were purchased from Sinopharm Group Chemical Reagent Co., Ltd. The 1,4-dioxane was refluxed with sodium and benzophenone under argon atmosphere, then distilled. The synthetic routes of 6a, 6b and 6c were outlined in Scheme 1.



Scheme 1. The synthetic routes of 6a, 6b and 6c.

2.2 Synthesis

2.2.1 Synthesis of 2.2.1 3-(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)-9-phenyl-9H-carbazole (1a), 9-(4-(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)phenyl)-9H-carbazole (1b) and 4-(7-bromo-9,9-

dioctyl-9H-fluoren-2-yl)-N,N-diphenylaniline (1c)

(9-phenyl-9H-carbazol-3-yl)boronic acid (2.87g, 0.010 mol), 2,7-dibromo-9,9-dioctyl-9H-fluorene (6.58 g, 0.012 mol), PdCl₂(PPh₃)₂ (0.1 g), H₂O (5 ml) and K₂CO₃ (6g, 0.043 mol) were added to a 250 ml flask with 40 ml THF. The mixture was heated at 78 °C under argon atmosphere for 12h. After cooling down, the resulting mixture was extracted with CH₂Cl₂, and the organic layer was collected and dried with MgSO₄. The solvent was removed and purified by silica gel chromatography to obtain white solid, yield 95% (6.74 g). ¹H NMR (400 MHz, Chloroform-d) δ 8.40 (d, J = 1.5 Hz, 1H), 8.23 (d, J = 7.7 Hz, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.70 (ddd, J = 7.6, 6.0, 1.7 Hz, 2H), 7.66 - 7.55 (m, 6H), 7.52 - 7.47 (m, 4H), 7.47 - 7.41 (m, 2H), 7.36 - 7.27 (m, 1H), 2.20 - 1.89 (m, 4H), 1.24 - 1.02 (m, 20H), 0.80 (t, J = 7.0 Hz, 6H), 0.70 (s, 4H). ¹³C NMR (101) MHz, Chloroform-d) δ 153.24, 141.43, 138.63, 137.70, 133.81, 129.95, 127.56, 127.09, 126.34, 126.18, 125.60, 123.97, 121.70, 120.98, 120.43, 120.10, 120.04, 118.79, 110.04, 109.96, 55.53, 40.33, 31.79, 29.98, 29.22, 29.19, 23.78, 22.60, 14.06. The synthesis procedures of **1b** was similar to 1a. It was obtained as a white powder in yield of 90 %. 1b: 1H NMR (400 MHz, Chloroform-d) δ 8.17 (d, J = 7.8 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 7.9 Hz, 1H), 7.67 (d, J = 8.0 Hz, 3H), 7.63 (d, J = 1.6 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.49 (tdd, J = 5.2, 3.1, 1.4 Hz, 4H), 7.46 -7.39 (m, 2H), 7.31 (t, J = 7.4 Hz, 2H), 2.09 – 1.92 (m, 4H), 1.24 – 1.03 (m, 20H), 0.81 (t, J = 7.0 Hz, 6H), 0.69 (h, J = 6.0, 5.5 Hz, 4H). ¹³C NMR (101 MHz, Chloroform-d) δ 153.27, 151.27, 140.89, 140.55, 139.54, 130.09, 128.54, 127.37, 126.25, 126.21, 125.99, 123.48, 121.43, 121.24, 121.19, 120.37, 120.25, 120.02, 109.84, 55.61, 40.34, 31.79, 29.96, 29.20, 23.77, 22.62, 14.08. The synthesis procedures of 1c was similar to 1a. It was obtained as a yellow powder in yield of 87 %. 1c: ¹H NMR (400 MHz, Chloroform-d) δ 7.69 (d, J = 7.9 Hz, 1H), 7.54 (dd, J = 7.8, 3.2 Hz, 4H), 7.51 (s, 1H), 7.45 (d, J = 7.4 Hz, 2H), 7.31 – 7.23 (m, 4H), 7.16 (t, J = 7.2 Hz, 6H), 7.04 (t, J = 7.3 Hz, 2H), 1.95 (tt, J = 13.4, 6.7 Hz, 4H), 1.28 – 0.96 (m, 20H), 0.80 (t, J = 7.1 Hz, 6H), 0.70 – 0.58 (m, 4H). ¹³C NMR (101 MHz, Chloroform-d) δ 153.20, 151.03, 147.68, 147.21, 139.91, 138.90, 129.96, 129.30, 127.79, 126.15, 125.66, 124.42, 123.96, 122.98, 120.98, 120.91, 120.02, 55.48, 40.32, 31.77, 29.95, 29.20, 29.18, 23.72, 22.60, 14.06.

2.2.2 Synthesis of 3-(9,9-dioctyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren -2-yl)-9-phenyl-9H-carbazole (**2a**), 9-(4-(9,9-dioctyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-2-yl)phenyl)-9H-carbazole (**2b**), 4-(9,9-dioctyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan -2-yl)-9H-fluoren-2-yl)-N,N-diphenylaniline (**2c**)

1a (1.126g, 0.0016 mol), Bis(pinacolato)diboron (2g, 0.0078 mol), PdCl₂(dppf) (0.05 g) and KoAc (0.8g, 0.0081 mol) were dissolved in 1,4-dioxane. The reaction solution was stirred under 87°C for 4 h. After cooling down, the mixture was filtered through a short pad of silica with dichloromethane (DCM). The solvent was removed under reduced pressure, and the residue was further purified by silica gel chromatography to give a white solid (1.03 g), with yield of 85%. ¹H NMR (400 MHz, Chloroform-d) δ 8.41 (s, 1H), 8.23 (d, J = 7.7 Hz, 1H), 7.82 (dd, J = 9.9, 7.7 Hz, 2H), 7.78 (s, 1H), 7.76 – 7.67 (m, 3H), 7.67 – 7.56 (m, 5H), 7.49 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 4.0 Hz, 2H), 7.35 – 7.28 (m, 1H), 2.10 – 2.00 (m, 4H), 1.40 (s, 12H), 1.22 – 0.99 (m, 20H), 0.79 (t, J = 7.0 Hz, 6H), 0.70 (s, 4H). ¹³C NMR (101 MHz, Chloroform-d) δ 152.12, 150.17, 144.01, 141.42, 139.58, 137.73, 134.04, 133.83, 129.94, 128.89, 127.54, 127.09, 126.15, 125.67, 123.97, 123.54, 121.79, 120.45, 120.40, 120.09, 118.97, 118.83, 110.02, 109.95, 83.70, 55.26, 40.32,

31.82, 30.04, 29.25, 29.21, 24.98, 24.90, 23.79, 22.61, 14.08. The synthesis procedures of **2b** was similar to **2a**. It was obtained as a white powder in yield of 91 %. **2b**: ¹H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, J = 7.6 Hz, 2H), 7.90 (d, J = 7.4 Hz, 2H), 7.84 (d, J = 6.7 Hz, 2H), 7.81 – 7.73 (m, 2H), 7.68 (d, J = 7.9 Hz, 4H), 7.50 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.2 Hz, 2H), 2.07 (s, 4H), 1.41 (s, 12H), 1.13 (d, J = 48.0 Hz, 20H), 0.86 – 0.75 (m, 6H), 0.68 (s, 4H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 140.91, 140.67, 133.88, 128.91, 128.56, 127.33, 125.98, 123.46, 121.49, 120.57, 120.34, 119.98, 119.14, 109.86, 83.75, 55.33, 40.30, 31.80, 30.00, 29.21, 29.19, 24.97, 24.88, 23.75, 22.61, 14.07. The synthesis procedures of **2c** was similar to **2a**. It was obtained as a yellow powder in yield of 89 %. **2c**: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, J = 7.6 Hz, 1H), 7.77 – 7.73 (m, 2H), 7.70 (d, J = 7.5 Hz, 1H), 7.58 – 7.51 (m, 4H), 7.31 – 7.23 (m, 4H), 7.16 (t, J = 7.0 Hz, 6H), 7.04 (t, J = 7.3 Hz, 2H), 2.07 – 1.92 (m, 4H), 1.39 (s, 12H), 1.21 – 0.98 (m, 20H), 0.79 (t, J = 7.1 Hz, 6H), 0.63 (s, 4H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 152.03, 150.13, 147.72, 139.85, 135.64, 133.82, 129.29, 128.84, 127.83, 125.46, 124.39, 124.01, 122.93, 120.99, 120.36, 118.96, 83.70, 55.20, 40.29, 31.79, 30.00, 29.22, 29.19, 24.97, 23.73, 22.60, 14.07.

2.2.3 Synthesis of 4,4'-sulfonylbis(bromobenzene) (3)

Diphenylsulfane (4 g, 0.021 mol) and Br₂ (9.95 g, 0.063 mol) were added into a flask to stir at room temperature for 6h. After that, 300 mL mixed solution of H₂O₂:CH₃COOH = 1:1 (v : v) was added to react for 10 h, and was further purified by silica gel column chromatography to give white solid, with yield of 73%. ¹H NMR (400 MHz, Chloroform-d) δ 7.81 – 7.76 (m, 4H), 7.68 – 7.63 (m, 4H). ¹³C NMR (101 MHz, Chloroform-d) δ 141.63, 133.18, 129.28, 127.66.

2.2.4 Synthesis of 3-(7-(4-((4-bromophenyl)sulfonyl)phenyl)-9,9-dioctyl-9H-fluoren-2-yl)-9-phenyl-9H-carbazole (**4a**), 9-(4-(7-(4-((4-bromophenyl)sulfonyl)phenyl)-9,9-dioctyl-9H-fluoren -2-yl)phenyl)-9H- carbazole (**4b**), 4-(7-(4-((4-bromophenyl)sulfonyl)phenyl)-9,9-dioctyl-9H -fluoren-2-yl)-N,N- diphenylaniline (**4c**)

Similar to the preparation of 1a, 2a (1.516g, 0.002 mol), 3 (1.13 g, 0.003 mol), PdCl₂(PPh₃)₂ (100 mg) and K_2CO_3 (1g, 0.007 mol) were dissolved in 30 ml THF and H_2O (5 ml). After that, white solid (0.76 g) was obtained, with yield of 41%. ¹H NMR (400 MHz, Chloroform-d) δ 8.41 (s, 1H), 8.24 (d, J = 7.7 Hz, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.6 Hz, 2H), 7.83 - 7.77 (m, 4H), 7.72 (d, J = 8.3 Hz, 2H), 7.69 – 7.63 (m, 4H), 7.63 – 7.53 (m, 5H), 7.50 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 3.7 Hz, 2H), 7.32 (dt, J = 8.0, 4.2 Hz, 1H), 2.15 – 1.97 (m, 4H), 1.21 – 1.01 (m, 20H), 0.77 (t, J = 7.0 Hz, 10H). ¹³C NMR (101 MHz, Chloroform-d) δ 152.00, 151.86, 140.42, 138.80, 137.68, 137.46, 132.63, 129.95, 129.16, 128.21, 128.00, 127.57, 127.09, 126.38, 126.20, 125.61, 123.98, 123.48, 121.77, 121.63, 120.42, 120.33, 120.19, 120.11, 118.82, 110.05, 109.97, 55.41, 40.39, 31.77, 29.98, 29.19, 29.17, 23.85, 22.58, 14.03. The procedure for synthesizing 4b was similar as above. It was obtained as a white powder in yield of 56 %. 4b: ¹H NMR (400 MHz, Chloroform-d) δ 8.17 (d, J = 7.7 Hz, 2H), 8.02 (d, J = 8.5 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 7.87 – 7.76 (m, 6H), 7.68 (q, J = 8.6, 8.1 Hz, 6H), 7.60 – 7.53 (m, 2H), 7.50 (d, J = 8.1 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.0 Hz, 2H), 2.07 (dd, J = 11.6, 4.0 Hz, 4H), 1.21 – 1.02 (m, 20H), 0.82 -0.65 (m, 10H). ¹³C NMR (101 MHz, Chloroform-d) δ 152.05, 151.99, 141.45, 140.88, 140.54, 139.65, 137.88, 132.64, 129.17, 128.55, 128.24, 128.05, 127.37, 126.48, 126.24, 125.99, 123.48, 121.69, 121.50, 120.52, 120.41, 120.38, 120.03, 109.83, 55.49, 40.39, 31.76, 29.96, 29.17, 23.84, 22.59, 14.04. The synthesis procedures of 4c was similar to 4a. It was obtained as a powder in yield of 54 %. 4c: ¹H NMR (400 MHz, Chloroform-d) δ 8.00 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.6

Hz, 2H), 7.77 (dd, J = 11.8, 8.1 Hz, 4H), 7.66 (d, J = 8.6 Hz, 2H), 7.59 – 7.50 (m, 6H), 7.29 (d, J = 7.6 Hz, 4H), 7.15 (d, J = 6.5 Hz, 6H), 7.04 (s, 2H), 2.01 (dd, J = 10.3, 5.8 Hz, 4H), 1.21 – 0.93 (m, 20H), 0.77 (t, J = 7.0 Hz, 6H), 0.73 – 0.55 (m, 4H). ¹³C NMR (101 MHz, Chloroform-d) δ 151.76, 147.66, 137.53, 132.63, 129.30, 129.15, 128.20, 127.99, 127.79, 126.37, 125.68, 124.43, 123.94, 122.99, 121.59, 120.97, 120.29, 120.19, 55.35, 40.37, 31.74, 29.95, 29.16, 23.79, 22.56, 14.02. 2.2.5 Synthesis of 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) -9H-carbazole (5)

Similar to the procedure for synthesizing **2a**, white solid of **5** (10.78 g, yield 82%) was obtained. ¹H NMR (400 MHz, Chloroform-d) δ 8.12 (t, J = 8.9 Hz, 2H), 8.02 (s, 1H), 7.88 (s, 1H), 7.66 (d, J = 7.5 Hz, 2H), 4.69 (tt, J = 10.2, 5.2 Hz, 1H), 2.33 (qt, J = 9.8, 4.7 Hz, 2H), 1.94 (ddt, J = 18.8, 10.3, 5.0 Hz, 2H), 1.39 (s, 24H), 1.29 – 1.04 (m, 24H), 0.82 (t, J = 7.0 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-d) δ 126.05, 120.03, 119.72, 115.44, 83.70, 83.50, 56.37, 33.84, 33.70, 31.77, 31.74, 29.48, 29.37, 29.32, 29.28, 29.20, 29.14, 26.78, 26.70, 24.95, 22.59, 14.06.

2.2.6Synthesisof3,3'-(((4,4'-(9-(heptadecan-9-yl)-9H-carbazole-2,7-diyl)bis(4,1-phenylenesulfonyl))bis(4,1-phenylene))bis(9,9-dioctyl-9H-fluorene-7,2-diyl))bis(9-phenyl-9H-carbazole)(**6a**),9,9'-((((4,4'-(9-(heptadecan-9-yl)-9H-carbazole-2,7-diyl))bis(4,1-phenylenesulfonyl))bis(4,1-phenylene))bis(9,9-dioctyl-9H-fluorene-7,2-diyl))bis(4,1-phenylene))bis(9H-carbazole)(**6b**)and4,4'-(((4,4'-(9-(heptadecan-9-yl)-9H-carbazole-2,7-diyl))bis(4,1-phenylenesulfonyl))bis(

Similar with the synthesis of **1a**, Pd(PPh₃)₄ (0.05 g) and additional ethanol were used (5 ml) under 85 °C for 24 h. After cooling down, the mixture was extracted with CH₂Cl₂, organic layer was dried by MgSO₄. The solvent was removed and subjected to silica gel column chromatography to give a white solid, with yield of 69%. Then product was recrystallized from ethanol and dichloromethane. (**6a**): ¹H NMR (400 MHz, CDCl₃) δ [ppm] 8.43 (s, 2H), 8.25 (d, J=7.76 Hz, 2H), 8.20 (dd, J=8.24, 12.32 Hz, 2H), 8.11 (d, J=8.20 Hz, 7H), 8.03 (q, J=8.40 Hz, 1H), 7.81-7.85 (m, 12H), 7.74 (d, J=8.24 Hz, 5H), 7.69 (s, 2H), 7.61-7.68(m, 9H), 7.58 (d, J=7.12 Hz, 4H), 7.50-7.53 (m, 4H), 7.46 (d, J=3.84 Hz, 6H), 7.32-7.36 (m, 2H), 4.65-4.68 (m, 1H), 2.31-2.35 (m, 2H), 1.95-2.15 (m, 10H), 1.09-1.18 (m, 64H), 0.76-0.81 (m, 26H). ¹³C NMR (400 MHz, CDCl₃) δ [ppm] 151.9, 151.8, 147.2, 146.7, 141.7, 141.5, 141.4, 140.4, 140.2, 139.9, 138.8, 137.6, 133.7, 129.9, 128.3, 128.2, 127.9, 127.5, 127.0, 126.3, 126.1, 125.5, 123.9, 123.4, 121.7, 121.6, 120.4, 120.3, 120.1, 120.0, 118.7, 110.0, 109.9, 55.4, 40.3, 33.7, 31.7, 31.6, 29.9, 29.3, 29.2, 29.1, 29.0, 26.7, 23.8, 22.5, 14.0. TOF-MS (m/z): Calcd: 2097.2; Found: 2097.4 (M⁺+1). Anal. Calcd (%) for C₁₄₇H₁₆₁N₃O₄S₂: C 84.16, H 7.73, N 2.00, O 3.05, S 3.06; Found: C, 84.14; H, 7.75; N, 2.02; O, 3.06; S, 3.08.

The synthesis procedures of **6b** was similar to **6a**. It was obtained as a white powder in yield of 74 %. **6b**: ¹H NMR (400 MHz, CDCl₃) δ [ppm] 8.23(s, 1H), 8.20 (d, J=7.76 Hz, 5H), 8.13 (d, J=8.2 Hz, 8H), 7.92 (d, J=8.44 Hz, 4H), 7.86 (t, J=7.64 Hz, 12H), 7.76 (s, 1H), 7.71 (t, J=7.84 Hz, 8H), 7.62 (d, J=7.96 Hz, 2H), 7.59 (s, 3H), 7.52 (d, J=8.16 Hz, 4H), 7.46 (t, J=7.16 Hz, 6H), 7.33 (t, J=6.96 Hz, 4H), 4.66-4.68 (m, 1H), 2.33-2.36 (m, 2H), 2.10 (d, J=6.16 Hz, 7H), 1.96-2.04 (m, 3H), 1.10-1.20 (m, 64H), 0.74-0.82 (m, 26H). ¹³C NMR (400 MHz, CDCl₃) δ [ppm] 152.0, 151.9, 147.2, 146.6, 141.3, 140.8, 140.5, 140.1, 139.9, 139.6, 138.0, 136.8, 128.5, 128.4, 128.2, 128.1, 127.9, 127.3, 126.4, 126.2, 125.9, 123.4, 121.6, 121.4, 120.5, 120.3, 120.0, 109.8, 55.4, 40.4, 33.7,

31.7, 29.9, 29.3, 29.2, 29.1, 26.8, 23.8, 22.5, 14.0; TOF-MS (m/z): Calcd: 2097.2; Found: 2097.4 (M⁺+1). Anal. Calcd (%): C₁₄₇H₁₆₁N₄O₄S₂: C, 84.16; H, 7.73; N, 2.00; O, 3.05; S, 3.06; Found: C, 84.12; H, 7.71; N, 1.98; O, 3.01; S, 3.04.

The synthesis procedures of **6c** was similar to **6a**. It was obtained as a faint yellow powder in yield of 70 %. **6c**: ¹H NMR (400 MHz, CDCl₃) δ [ppm] 8.20 (dd, J=8.28, 12.20 Hz, 2H), 8.10-8.12 (m, 8H), 7.84 (t, J=8.44 Hz, 8H), 7.78 (t, J=7.68 Hz, 4H), 7.75 (s, 1H), 7.55-7.60 (m, 13H), 7.47 (s, 2H), 7.29 (t, J=8.16 Hz, 8H), 7.18 (t, J=8.16 Hz, 12H), 7.06 (t, J=7.32 Hz, 4H), 4.63-4.67 (m, 1H), 2.31-2.35 (m, 2H), 1.95-2.05 (m, 10H), 1.06-1.18 (m, 64H), 0.79 (t, J=6.84 Hz, 18H), 0.70 (d, J=6.24 Hz, 8H). ¹³C NMR (400 MHz, CDCl₃) δ [ppm] 151.9, 151.7, 147.6, 147.2, 146.6, 141.5, 140.1, 140.0, 139.9, 139.0, 137.6, 135.3, 129.2, 128.3, 128.1, 127.9, 127.7, 126.3, 125.6, 124.4, 123.9, 122.9, 121.5, 120.9, 120.2, 120.1, 55.3, 40.3, 33.7, 31.7, 31.6, 29.9, 29.3, 29.2, 29.1, 26.7, 23.7, 22.5, 14.0; TOF-MS (m/z): Calcd: 2101.2; Found: 2101.4 (M⁺+1). Anal. Calcd (%): C₁₄₇H₁₆₅N₃O₄S₂: C, 83.99; H, 7.91; N, 2.00; O, 3.04; S, 3.05; Found: C, 84.01; H, 7.92; N, 1.98; O, 3.07; S, 3.07.

3. Results and discussion

3.1 Synthesis

1a, 1b and 1c were prepared from Suzuki Coupling, and then subjected to Miyaura boration to obtain the precursor of 4. Diphenylsulfane was brominated and oxidized to give 4,4'-sulfonylbis (bromobenzene), which was then reacted quantitatively with intermediate 2 to produce 3. Finally, 2 equivalents of 4 and 1 equivalents of 5 were coupled to yield the target product 6 via Suzuki. After recrystallization for several times, these fluorescence materials were utilized as emitters without sublimation. Thanks to their large alkyl chains, these emitters exhibited good solubility and film-forming ability in conventional organic solvents like chloroform, THF and so on, which were suitable for fabrication through spin-coating.

3.2 Photophysical properties

The UV-vis absorption and photoluminescence (PL) spectra of **6a**, **6b** and **6c** in solution and film are shown in **Fig. 1**. The maximum UV absorption of these materials in the film state were peaked at 359 nm, 355 nm, 374 nm, respectively, which could be attributed to ICT transition and the result of π - π * transitions. Compared with absorption in solution, the UV absorption spectra in film state showed a slight bathochromic-shift, similar to previously reported literatures[34]. By the on-tail of the absorption curves, band gaps (E_g) of these compounds were calculated to be 3.01, 3.08 and 2.94 eV as shown in **Table 1**. The fluorescence emission peaks in film state were found at 447nm, 428nm and 468nm, respectively. From the fluorescence spectra, **6a** and **6b** showed deep blue emissions as shown in **Fig. 1**. It should be noted that these materials showed hypsochromic shift by 24 nm, 9 nm and 62 nm from DCM solution to thin film state. The hypsochromic shift could be attributed to the highly twisted configurations between the donor and acceptor in solution state and strong intermolecular π - π stacking in film state.



Fig. 1. a).The normalized UV-Vis absorption spectra in DCM of **6a**, **6b** and **6c**; b). The normalized UV-visible absorption spectrum in film states; c). The PL spectrum in DCM; d). The PL spectrum in film states.

Photoluminescence quantum yields (PLQYs) for **6a**, **6b**, **6c** were listed in **Table 1**. Among the three, **6b** showed the highest PLQYs with 50.4% at film state. However, when compared to solution state, all the PLQYs of **6a 6b** and **6c** in film state were lower, which could be attributed to the concentration quenching of common fluorescence materials. The fluorescence spectra of three emitters (**Fig. 2**) were slightly bathochromically-shifted with the increase of solvent polarity (from non-polar solvent such as toluene to polar solvents such as THF and DCM), indicating the weak ICT characteristics for the excited states of the three emitters. Compared to **6a** and **6c**, **6b** showed better stability in deep blue emission with different polar solvents. This was mostly attributed to the tail end of molecule structure that had smaller dipole moment than the others. The time-resolved photoluminescence (TRPL) spectra of the three emitters were measured and different decay life of three emitters were clearly observed in **Fig. S32**. It was found that **6b** had a fairly longer life (τ_{6b} : 15.2 ns) than **6c** (τ_{6c} : 7.7 ns) and **6a** (τ_{6a} : 4.7 ns).



Fig. 2. Normalized PL spectra measured in toluene (TOL), chlorobenzene (CB), tetrahydrofuran (THF), trichloromethane (CHF), dichloromethane (DCM) of a) **6a**, b) **6b** and c) **6c**.

Table 1. The thermal, photophysical and electrochemical properties of the 6a, 6b and 6c emitters

Compounds	T_g/T_d	$\lambda_{max}Abs^{a,b}$	$\lambda_{max} P L^{a,b}$	PLQY ^{a,b}	HOMO/LUMO ^c	HOMO/LUMO ^d	$E_{\rm g}^{\ e,f}$
	(°C)	(nm)	(nm)	(%)	(eV)	(eV)	(eV)
6a	103.68/416.7	353/359	471/447	74.8/45.9	-4.95/-1.94	-5.21/-1.80	3.01/3.41
6b	106.79/417.8	347/355	437/428	79.2/50.4	-5.24/-2.16	-5.34/-1.88	3.08/3.46
бс	92.52/426.9	363/374	530/468	69.3/39.4	-4.94/-2.00	-4.94/-1.81	2.94/3.13

a. The maximum UV-vis absorption peaks and PL spectra in DCM.

b. The maximum UV-vis absorption peaks and PL spectra in thin film.

c. Calculated from the formula HOMO = - $(4.40 + E_{ox})$ (eV), LUMO = HOMO + E_g (eV).

d. Calculated by Gaussian 03 software at the B3LYP/6-31G (d, p) level.

e. $E_g = 1240/\lambda$ (λ is the wavelength of the on-set of the UV-vis absorption spectrum)

f. E_g calculated by Gaussian 03 software at the B3LYP/6-31G (d, p) level).

3.2 Thermal properties

The thermal properties of **6a**, **6b** and **6c** were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere at 10 K.min⁻¹ as shown **in Fig. 3**. The thermal decomposition temperature (T_d) at 5% weight loss of the three materials **6a**, **6b** and **6c** were higher than 400 °C. The three materials also had high glass transition temperatures (T_g) of 103.68 °C, 106.79 °C and 92.52 °C respectively. The high thermal stability can usually be attributed to the high contains of polar groups of sulfone, and rigid aromatic rings and aromatic systems [38, 39]. The higher T_d and T_g of the materials enabled better stability during OLED's working time.



Fig. 3. TGA a) and DSC b) curves of 6a, 6b and 6c;

3.3 Theoretical calculations and electrochemical properties

To further explore the molecules' geometry and electronic density distributions, Gaussian 03 program at the B3LYP/6-31G (d, p) level was applied to calculate electronic structure and the FMO. The characteristic results were listed in **Table 1**. The HOMO of these molecules was mainly located on the fluorene, triphenylamine or carbazole units, while the LUMO was almost distributed on the sulfone and carbazole molecules. Note that the separation of HOMO and LUMO distribution would reduce the communication of electron donor and acceptor, beneficial to form blue emitting.



6c HOMO (566) -4.946 eV

6c LUMO (567) -1.809 eV

Fig. 4. HOMO and LUMO energy levels of 6a, 6b and 6c calculated from Gaussian 03

Meanwhile, the geometrical configuration of the three molecules (**6a**, **6b** and **6c**) were compared, as shown in **Fig. 5**. **6a** and **6b** had larger twist angle for the alkyl chain and sulfone moieties twist angles approached 90° , favorable for reducing the overlapping of FMO and increasing the molecule's solubility. In addition to the sulfone moiety, there was almost 90° dihedral angle between the triphenylamine terminal group and the molecular body of **6c**, which could inhibit the molecular aggregation in the solid state and also reduce the red-shifting effect owing to ICT.





Fig. 5. Molecular geometry modeling of 6a, 6b and 6c.

To study the practical electrochemical behavior of **6a**, **6b** and **6c**, cyclic voltammetry (CV) curves were shown in **Fig. 6**. Based on the initial oxidation sites E_{ox} (0.55eV, 0.84eV and 0.54eV), the HOMO energy levels were estimated to be -4.95 eV, -5.24 eV and -4.94 eV via the empirical equation HOMO = (E_{ox} + 4.40) eV. Meanwhile, the LUMOs were estimated from HOMO and Eg, which were calculated to be -2.34 eV, -2.56 eV and -2.40 eV. The DFT results showed the HOMO

energy levels at -5.21eV, -5.34eV, -4.49-eV, due to the same molecule core, the similar LUMO energy levels of **6a**, **6b** and **6c** be found at -1.80 eV, -1.88 eV, -1.81 eV respectively, Compared with DFT results, experimental measurement values showed smaller energy gap. This different most probably attributed to the fact that DFT calculation was conducted on single molecules, while the experiments were conducted on the emitters in solution. In spite of the differences in DFT and experiment results, both of them showed the same consequence that 6a, 6b had deeper HOMO energy levels and 6c had smallest Eg in these emitters. Compareing the energy gap of **6a** and **6b**, **6b** with larger energy gap almost attributed to the different bond positions of 9-phenyl-9*H*-carbazole. The triphenylamine made **6c** to show shallower HOMO and narrower energy gap which promoted fluorescence wavelength red shift to 530 nm. In other words, the deeper HOMO and larger energy gap are significant for the design of deep blue fluorescence emitter.



Fig. 6. Cyclicvoltammetry characteristics of 6a, 6b and 6c

3.4 Electroluminescent (EL) properties

The electroluminescence performance of these materials was evaluated by fabricating OLED through spin coating method. The device structure was ITO / PEDOT: PSS (30nm) / emissive layer (EML) (50nm) / 2,4,6-tris(biphenyl-3-yl)-1,3,5-triazine (T2T) (50nm) / LiF (1nm) / Al (100nm). Among them, ITO and Al served as anode and cathode, PEDOT: PSS as hole injection and transport layer, and the synthesized blue-emitting materials as EML layer. Meanwhile, T2T was selected as electron transport and hole blocking layer and LiF as the electron injection layer. The energy levels of each layer are shown in **Fig. 7 a**). The non-doped devices based on these three emitters showed standard blue emission peaks at 454 nm, 444 nm and 474 nm with the CIE of (0.16, 0.12), (0.16, 0.15) and (0.16, 0.27), respectively. In addition, those devices showed quite stable electroluminescence at different luminance from 0.1 to 100 cd.m⁻².

The charge mobility as a key parameter that can evaluate the performance of devices. Here, the space charge limited current (SCLC) method was employed to calculate the charge mobility of the single carrier devices. Herein, two types of single carrier devices configuration were fabricated, ITO / PEDOT: PSS (30nm) / EML(50nm) / LiF (1nm) / Al (100nm) as hole-only devices (H-type)

and ITO / EML(50nm) / (T2T) (50nm) / LiF (1nm) / Al (100nm) as electron-only devices (E-type), the current density dependence of voltage ($J^{1/2}$ -V) curves is presented in **Fig. S33**. The hole mobility (μ_h) and electron mobility (μ_e) of the three emitters are calculated by fitting the Mott-Gurney square law.

$$J_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_e \frac{V^2}{L^3}$$

where ε_0 (8.855 × 10⁻¹² F/m) is the permittivity of free space, ε_r is the relative dielectric constant of the three materials (typically \approx 3), L is the thickness of film. V is the applied voltage and J is current density across device. The μ_h of **6a**, **6b** and **6c** were calculated to be 1.28×10^{-4} cm² V⁻¹ s⁻¹, 1.51×10^{-4} cm² V⁻¹ s⁻¹ and 1.17×10^{-4} cm² V⁻¹ s⁻¹, while μ_e of **6a**, **6b** and **6c** were calculated to be 1.05×10^{-5} cm² V⁻¹ s⁻¹, 9.77×10^{-5} cm² V⁻¹ s⁻¹ and 7.2×10^{-5} cm² V⁻¹ s⁻¹. Obviously, devices based on the three emitters have showed high μ_h than μ_e , mostly attributed to delocalized π electron density of donor and acceptor.



Fig. 7. a) Diagram of the non-doped blue light-emitting device and electroluminescence (EL) spectra of **6a** (b), **6b** (c) and **6c** (d) devices at different current density.

Compared with PL spectra in film states, a bathochromic-shift of more than 10 nm was observed in the EL spectra. And this redshift could be explained by the increased thickness through spin coating process[35, 36]. The current density-voltage-luminance (J-V-L) curves are plotted in **Fig. 8** a). The turn-on voltages of the devices based on **6a**, **6b** and **6c** devices were 6.2, 7.3, 6.1 V, indicating that the most facile charge injection took place in **6b** based devices mostly due to the planar configuration of **6b** emitters. Meanwhile, the device brightness was increased by increasing the voltage with the maximum brightness of 2354.1 cd/cm², 1226.2 cd/cm² and 2457.2 cd/cm². as shown in **Fig. 8**. **a**) and **Table 2**. The external quantum efficiency (EQE) of **6a**, **6b** and **6c** were 0.71%, 0.42% and 0.65%, which also showed that there was no obvious efficiency roll-off by increasing current density. However, the OLED did not show high efficiency, which might be attributed to the effects of aggregation-caused quenching[37]. Another possible reason was that these emitters could not take advantage of the triplet excitons like what other materials did such as TADF and TTA materials [38-40].



Fig. 8 a) Normalized EL Spectra; b). Current density-voltage-luminance (J-V-L) curves; c). Current efficiency (CE) curves; d). EQE characteristics of OLED based on the three non-doped emitters.

	 a	CT		FOF	amh			At 100 cd/m ²			At 1000 cd/m ²			
Daviass	V _{on} -	CE _{max}	PE _{max}	EQE _{max}	CIE-	λ _{max} EL	v	CE	PE	EQE	v	CE	PE	EQE
Devices	(v)	(cd/A)	(111/W)	(70)	(x,y)	(nm)	(V)	(cd/A)	(lm/W)	(%)	(V)	(cd/A)	(lm/W)	(%)
Α	6.2	2.67	1.19	0.71	0.16,0.15	454	9.0	2.67	0.93	0.71	12.2	1.85	0.47	0.50
В	7.3	1.01	0.61	0.42	0.16,0.12	448	10.9	0.79	0.23	0.26	15.4	0.55	0.11	0.18
С	6.1	3.36	1.36	0.65	0.16,0.27	489	8.8	3.36	1.20	0.65	11.6	2.68	0.73	0.52

Table. 2. The EL parameters of devices of 6a (A), 6b (B) and 6c (C)

a) Recorded at the luminance of 1 cd/m^2 ;

b) Recorded at the current of 10 mA/m^2

4. Conclusions

Three bipolar fluorophores based on the electron acceptor of sulfone moieties with intramolecular charge transfer properties were designed and synthesized. The three materials had a highly distorted spatial geometry and separation of the electron density distribution. The dihedral angle was close to 90° in the molecular configuration containing sulfone moieties, especially in **6c** containing triphenylamine end group. These fluorophores exhibited deep-blue photoluminescence, good thermal stability and reversible electrochemical behaviors, and therefore were applied into OLED with deep-blue electroluminescence. Solution-processed non-doped OLED were subsequently fabricated, two of which exhibited deep blue emission with CIE of (0.16, 0.15) and (0.16, 0.11). Those devices showed stable deep-blue emission and marginal roll-off, highlighting the potential of our newly synthesized deep blue emitters.

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Highlights

- ۸ Two deep-blue electroluminescence were designed and synthesized which with the CIEx,y of (0.16, 0.12) and (0.16, 0.15)
- ▲ These materials appeared almost vertical angles of the dihedral configuration.
- ▲ These materials exhibited high thermal and electrochemical stability.
- ▲ The OLED devices of this article were fabricated through solution-process with nondoped

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Dear Editor,

We solemnly declare there are no conflicts of interest to all authors

Best regards.

Sincerely yours,

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