



Novel fluorene/indole-based hole transport materials with high thermal stability for efficient OLEDs



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ABSTRACT

A series of novel hole transport materials based on fluorene and indole were designed, synthesized and well characterized. The carbazole and triphenylamine groups, which have excellent charge carrier mobility and low ionization potential, were introduced by coupling reactions. Ultraviolet–visible (UV–vis) spectral, photoluminescence (PL) spectral, cyclic voltammetry (CV), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed to investigate the photophysical properties, thermal properties and electrochemical properties of these materials. The results implied that all these materials have excellent thermal stabilities with the 5% weight loss at 409–456 °C. The OLED devices based on the as-prepared materials were fabricated to investigate their hole transport ability. It turns out that device based on compound **c** exhibited the best performance with a maximum current efficiency of 3.74 cd/A and turn-on voltage at 4.0 V. The device performances indicated that the as-prepared materials can serve as highly efficient hole transport materials in OLED devices.

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1. Introduction

Organic light-emitting diodes (OLEDs) have drawn great academic and industrial attention since the pioneering work in 1980s by Tang et al. [1–4]. Numerous work has been done to improve the device efficiency and durability of OLEDs [5–7]. These works are mainly focused on the development of electroluminescent materials with better stability, high luminescence, and good film forming properties [8–10]. However, the hole transport materials are also crucial for the final performance of OLEDs [11,12]. Fluorene type materials, which have high thermal and morphological stabilities, ambipolar carrier transporting properties and high

fluorescent quantum efficiencies, are desirable semiconductor materials for organic optoelectronic devices, such as light-emitting diodes [13,14] photovoltaic cells [15,16] field-effect transistors [17,18]. Indole-based materials are widely used for OLED devices due to their extraordinary hole transporting properties and high triplet energy [19–21].

In this work, by combining the excellent properties of fluorene and indole, we designed and synthesized six compounds **a–f** for use as hole transport materials in OLEDs. We here introduce two substituent groups, carbazole and triphenylamine, into the N atom of indole moiety to adjust the charge carrier mobility and energy level of each compound, considering that carbazole and its derivatives have good carrier mobility, rigid structure, high triplet energy and high fluorescent quantum yield [22–24], while triphenylamine has low ionization and high charge carrier mobility [25–27]. All these target compounds were characterized by ¹H NMR, ¹³C NMR and high resolution mass spectrometry. The photophysical properties, thermal properties and electrochemical properties of these compounds were investigated by UV–vis spectra, PL spectra, cyclic voltammetry (CV), thermogravimetric

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analysis (TGA) and differential scanning calorimetry (DSC). Meanwhile, to investigate the hole transport ability, the OLED devices based on compounds **a–f** were fabricated with the following configuration: ITO/HTM (60 nm)/Alq₃ (50 nm)/LiF (1 nm)/Al.

2. General information

All the solvents and chemicals that we have used in the routes were purchased from Shanghai Taoe chemical technology Co., Ltd. and received without further purification. ¹H NMR spectra were recorded on a Bruker AT 400 spectrometer, using tetramethylsilane (TMS) as the internal standard material. The mass spectra were recorded on a Waters LCT Premier XE spectrometer. UV–vis spectra were obtained on a Varian Cary 200 spectrophotometer. Fluorescence spectra were obtained on a Perkin Elmer LS55 luminescence spectrophotometer. Cyclic voltammetry (CV) was carried out on a EG&G 283 voltammetric analyzer. The thermogravimetric analysis (TGA) were performed under a nitrogen atmosphere on a TGA instrument.

3. Synthesis

3.1. 5-(4-(9-Phenyl-9H-fluoren-9-yl)phenyl)-1H-indole (**1-2**)

In a 50 mL one-necked round-bottomed flask, 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (**1-1**) (2.40 g, 10 mmol), 9-(4-bromophenyl)-9-phenyl-9H-fluorene (4.40 g, 11 mmol), K₂CO₃ (2.70 g, 20.0 mmol), H₂O (4 mL) and Pd(PPh₃)₄ (40 mg) were dissolved in 20 mL 1,4-Dioxane and the mixture was refluxed under N₂ for 5 h. After the reaction was finished, the solvent was removed under vacuum, and the mixture was cooled to room temperature and 20 mL H₂O was poured into the mixture, followed by extraction with CH₂Cl₂ (25 mL × 3). The solvent was removed in vacuum and then recrystallized from methanol to afford a white solid (2.85 g, 80%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.14 (s, 1H), 7.96 (d, *J* = 7.4 Hz, 2H), 7.76 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.1 Hz, 3H), 7.34 (m, 4H), 7.29 (m, 3H), 7.18 (t, *J* = 8.4 Hz, 4H), 6.45 (s, 1H).

3.2. 9-Phenyl-3-(5-(4-(9-phenyl-9H-fluoren-9-yl)phenyl)-1H-indol-1-yl)-9H-carbazole (**a**)

In a 50 mL one-necked round-bottomed flask, **1-2** (0.50 g, 1.15 mmol), 4-bromo-*N,N*-diphenylaniline (0.5 g, 1.56 mmol), *t*-BuOK (0.2 g, 1.78 mmol), Pd(OAc)₂ (30 mg) and X-Phos (90 mg) were put into 30 mL *o*-xylene. The mixture was refluxed under N₂ for 5 h, and after the reaction was complete, the solvent was removed under vacuum and 20 mL H₂O was poured into the mixture, followed by extraction with CH₂Cl₂ (25 mL × 3). The solvent was removed under vacuum and then recrystallized from methanol to afford a white solid (0.50 g, 64%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.87 (d, *J* = 1.4 Hz, 1H), 7.66 (d, *J* = 3.2 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 3H), 7.51 (t, *J* = 7.9 Hz, 4H), 7.47–7.41 (m, 3H), 7.35 (t, *J* = 7.9 Hz, 6H), 7.27 (ddd, *J* = 6.7, 6.3, 2.4 Hz, 3H), 7.19 (d, *J* = 8.2 Hz, 4H), 7.15 (d, *J* = 8.8 Hz, 2H), 7.12–7.07 (m, 6H), 6.71 (d, *J* = 2.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) 151.28, 147.56, 146.39, 146.01, 144.00, 140.57, 140.18, 135.47, 133.99, 133.29, 129.56, 129.40, 128.62, 128.47, 128.21, 127.74, 127.46, 127.09, 126.62, 126.26, 125.12, 124.46, 124.33, 123.18, 121.91, 120.17, 119.35, 110.74, 103.51, 65.26. HRMS (*m/z*): [M+H]⁺ calcd for C₅₁H₃₇N₂, 677.2957; Found [M+H]⁺: 677.2939. Anal. calcd for C₅₁H₃₆N₂: C, 90.5; H, 5.36; N, 4.14; Found: C, 90.54; H, 5.38, N, 4.08%.

3.3. 9-Phenyl-3-(5-(4-(9-phenyl-9H-fluoren-9-yl)phenyl)-1H-indol-1-yl)-9H-carbazole (**b**)

Compound **b** was synthesized by the same procedure as described above for compound **a** using **1-2** and 3-bromo-9-phenyl-9H-carbazole. Yield: 73%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.51 (d, *J* = 1.4 Hz, 1H), 8.37 (d, *J* = 7.5 Hz, 1H), 7.97 (d, *J* = 7.4 Hz, 2H), 7.91 (s, 1H), 7.77–7.67 (m, 5H), 7.67–7.56 (m, 5H), 7.56–7.46 (m, 5H), 7.43 (t, *J* = 7.2 Hz, 3H), 7.30 (ddd, *J* = 18.7, 14.0, 7.1 Hz, 6H), 7.19 (d, *J* = 7.9 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) 151.33, 146.06, 143.95, 141.66, 140.72, 140.20, 139.53, 137.42, 136.27, 133.19, 132.45, 130.06, 129.52, 129.43, 128.49, 128.23, 127.82, 127.77, 127.48, 127.14, 126.67, 126.64, 126.29, 124.01, 123.26, 122.92, 121.90, 120.57, 120.30, 120.19, 119.36, 116.75, 110.69, 110.50, 110.14, 103.20, 65.29. HRMS (*m/z*): [M+H]⁺ calcd for C₅₁H₃₅N₂, 675.2800; Found [M+H]⁺: 675.2800. Anal. calcd for C₅₁H₃₄N₂: C, 90.77; H, 5.08; N, 4.15; Found: C, 90.88; H, 5.02, N, 4.10%.

3.4. 4-(9,9-Diphenyl-9H-fluoren-4-yl)-1H-indole (**2-2**)

Compound **2-2** was synthesized by the same procedure as described above for compound **1-2** using **1-1** and 4-bromo-9,9-diphenyl-9H-fluorene. 90%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.28 (s, 1H), 7.62 (s, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.46–7.40 (m, 2H), 7.37 (dd, *J* = 12.3, 7.6 Hz, 2H), 7.33–7.22 (m, 7H), 7.21–7.13 (m, 6H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.53–6.47 (m, 1H).

3.5. 4-(4-(9,9-Diphenyl-9H-fluoren-4-yl)-1H-indol-1-yl)-*N,N*-diphenylaniline (**c**)

Compound **c** was synthesized by the same procedure as described above for compound **a** using **2-2** and 4-bromo-*N,N*-diphenylaniline. Yield: 77%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.77–7.72 (m, 2H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.64–7.58 (m, 2H), 7.45 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.42–7.33 (m, 3H), 7.33–7.22 (m, 4H), 7.22–7.14 (m, 7H), 7.14–7.07 (m, 6H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.77 (d, *J* = 3.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) 151.89, 151.60, 147.59, 146.46, 140.46, 139.09, 137.42, 135.51, 134.04, 133.14, 130.17, 129.44, 129.29, 128.63, 128.37, 128.13, 127.15, 127.01, 126.89, 126.59, 125.98, 125.21, 124.82, 124.53, 124.34, 123.92, 123.42, 123.24, 121.46, 110.45, 103.54, 65.03. HRMS (*m/z*): [M+H]⁺ calcd for C₅₁H₃₇N₂, 677.2957; Found [M+H]⁺: 677.2957. Anal. calcd for C₅₁H₃₆N₂: C, 90.5; H, 5.36; N, 4.14; Found: C, 90.63; H, 5.26, N, 4.11%.

3.6. 3-(4-(9,9-Diphenyl-9H-fluoren-4-yl)-1H-indol-1-yl)-9-phenyl-9H-carbazole (**d**)

Compound **d** was synthesized by the same procedure as described above for compound **a** using **2-2** and 3-bromo-9-phenyl-9H-carbazole. Yield: 85%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.60 (d, *J* = 2.0 Hz, 1H), 8.40 (d, *J* = 7.7 Hz, 1H), 7.83 (d, *J* = 3.2 Hz, 1H), 7.79 (d, *J* = 1.1 Hz, 1H), 7.74 (dt, *J* = 12.3, 5.1 Hz, 6H), 7.62–7.56 (m, 2H), 7.53–7.49 (m, 1H), 7.45 (td, *J* = 5.7, 3.0 Hz, 2H), 7.42–7.34 (m, 3H), 7.34–7.23 (m, 8H), 7.19 (dd, *J* = 13.0, 7.6 Hz, 5H), 7.07–7.03 (m, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 3.1 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) 151.92, 151.63, 146.35, 141.71, 140.53, 139.57, 139.24, 137.45, 136.30, 133.04, 132.53, 130.21, 130.08, 129.49, 129.16, 128.39, 128.18, 127.84, 127.17, 127.01, 126.92, 126.70, 126.58, 125.99, 124.79, 124.09, 123.89, 123.49, 123.32, 122.97, 121.44, 120.60, 120.34, 116.83, 110.56, 110.38, 110.17, 103.23, 65.06. HRMS (*m/z*): [M+H]⁺ calcd for C₅₁H₃₅N₂, 675.2800; Found [M+H]⁺: 675.2780. Anal. calcd for C₅₁H₃₄N₂: C, 90.77; H, 5.08; N, 4.15; Found: C, 90.91; H, 5.93, N, 4.16%.

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