



New carbazole-based bipolar hosts for efficient blue phosphorescent organic light-emitting diodes



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ABSTRACT

Four novel bipolar host materials, namely 9,9'-(4-(pyridin-2-yl)-1,3-phenylene)bis(9H-carbazole) (**2CzPy**), 9,9'-(4-(pyridin-2-yl)-1,3-phenylene)bis(3,6-di-*tert*-butyl-9H-carbazole) (**2TCzPy**), 5,5'-(4-(pyridin-2-yl)-1,3-phenylene)bis(5H-benzofuro[3,2-*c*]carbazole) (**2BFCzPy**) and 9,9''-(4-(pyridin-2-yl)-1,3-phenylene)bis(9-phenyl-9H,9'H-3,3'-bicarbazole) (**2PBCzPy**) were designed and synthesized. Within each host material, one pyridine group serving as electron-transporting unit and two identical electron-donating groups serving as hole-transporting motifs were attached to the central benzene ring. These two donor units are located ortho and para to pyridine group, respectively. The four compounds showed excellent thermal stability with the glass-transition temperature up to 192 °C and decomposed temperature up to 571 °C. These hosts possessed triplet energies over 2.80 eV, indicating that they could be used as suitable hosts for blue phosphorescent organic light-emitting diodes (PHOLEDs). The bis[2-(4,6-difluorophenyl)-pyridinato-C₂,N](picolinato)iridium(III) (Firpic) based PHOLEDs hosted by **2CzPy** and **2BFCzPy** exhibited high device performance with maximum external quantum efficiencies (EQEs) of 17.8% and 17.4%, respectively. More importantly, **2CzPy** exhibited a low efficiency roll-off at a brightness of 1000 cd m⁻² with an external quantum efficiency of 17.1% (3.9% roll-off). The results demonstrate that **2CzPy** could be a promising host for blue PHOLEDs.

1. Introduction

Since C. W. Tang and S. A. VanSlyke reported the invention of an organic electroluminescent device with a sandwich structure in 1987 [1], great progress has been made in organic light emitting diodes (OLEDs) related research areas over the past three decades [2–7]. OLEDs have lots of advantages such as wide angle of view, fast response, self-emitting, low power consumption, high contrast and capability of resisting bending. Currently, due to the development of OLED technology, a certain percentage of the liquid crystal display (LCD) and light-emitting diode (LED) market has been gradually taken over by OLED products. The organic materials in the light-emitting layer, namely host and dopant, play an important role in the determination of the device performance. The emissive material (dopant) has been developed rapidly and has attracted much attention. Conventional fluorescent materials can only utilize singlet exciton states, which can only theoretically reach 25% internal quantum efficiency. However, phosphorescent materials can utilize both singlet and triplet exciton states,

and they can approach 100% internal quantum efficiency theoretically [3]. Although thermally activated delayed fluorescent materials (TADF) can also reach 100% internal quantum efficiency [8–26], yet these materials currently are mainly for non-commercial use. So far the matrix and emitter materials for green and red phosphorescent OLEDs have been successfully developed [27–38], and are in commercial use today. Nevertheless, the development of high efficiency blue OLEDs is a pressing concern to realize commercial applications in display and solid-state lighting [39–45]. Furthermore, the performance of a blue emitting device is often inferior to these of green and red devices due to the intrinsic wide band gap of the blue emitting material. To obtain efficient blue PhOLEDs, the development of suitable host materials has become essential since these materials must have high triplet energies (E_T) and preferably with high hole- and electron-transport capability. High E_T values of the host materials can prevent endothermic energy transfers from the phosphorescent dopant to the host materials within a device, and host materials with bipolar properties can form excitons throughout the entire emitting layer [46,47]. Additionally, well-

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controlled energy levels for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a host material can reduce the barrier for charge injection from an adjacent hole- or electron-transport auxiliary layer to the emitting layer.

In this contribution, we report the design and synthesis of four bipolar hosts i.e. 9,9'-(4-(pyridin-2-yl)-1,3-phenylene)bis(9H-carbazole) (**2CzPy**), 9,9'-(4-(pyridin-2-yl)-1,3-phenylene)bis(3,6-di-*tert*-butyl-9H-carbazole) (**2TCzPy**), 5,5'-(4-(pyridin-2-yl)-1,3-phenylene)bis(5H-benzofuro[3,2-*c*]carbazole) (**2BFCzPy**) and 9,9''-(4-(pyridin-2-yl)-1,3-phenylene)bis(9-phenyl-9H,9'H-3,3'-bicarbazole) (**2PBCzPy**). The hosts were easily prepared by one-step aromatic nucleophilic substitutions reaction at high yields. Although the hosts can be considered as mCP derivatives, the rigid and large conjugation system could improve their thermal stabilities. The four materials are comprised of phenylpyridine unit and carbazole derivatives. Their photophysical properties, thermal stability, and electrochemical behaviors were fully investigated. The E_T of **2CzPy**, **2TCzPy**, **2BFCzPy** and **2PBCzPy** are higher than that of the typical blue phosphor FIrpic. Thus, we expect that these four materials might be suitable hosts for blue PHOLEDs [48–50]. The FIrpic based PHOLEDs hosted by **2CzPy** and **2BFCzPy** have been fabricated and exhibited high performance with maximum EQEs of 17.8% and 17.4% respectively. Especially, the blue devices hosted by **2CzPy** and **2BFCzPy** exhibit low efficiency roll-offs while keeping high efficiencies of 17.1% and 16.5% at 1000 cd/m², respectively.

2. Experiment section

All chemicals were purchased from either J & K Scientific, Alfa Aesar, Acros, or Strem chemicals, and were used without further purification. All air- and moisture-sensitive reactions were performed under a nitrogen atmosphere. Dry dichloromethane (DCM), tetrahydrofuran (THF), toluene and *N,N*-Dimethylformamide (DMF) were obtained from an Innovative Technology solvent purification system. 5H-benzofuro[3,2-*c*]carbazole was prepared according to the literature method [51].

Proton and carbon NMR spectra (¹H NMR and ¹³C NMR) were recorded in chloroform-*d* (CDCl₃) on a Agilent DD2-600 MHz NMR spectrometer. Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) was measured with a BRUKER ultrafleXtreme MALDI-TOF/TOF. UV-vis absorption spectra were measured on Cary 60 spectrometer (Agilent Technologies). PL spectra and phosphorescent spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA DSC 2010 unit at a heating rate of 10 °C/min under nitrogen. The glass transition temperatures (T_g) were determined from the second heating scan. Thermogravimetric analysis (TGA) was recorded on a TA SDT 2960 instrument at a heating rate of 10 °C/min under nitrogen. Temperature at 5% weight loss was used as the decomposition temperature (T_d). Cyclic voltammetry (CV) was carried out on a CHI600 voltammeter analyzer at room temperature with ferrocenium-ferrocene (Fc⁺/Fc) as the internal standard. The oxidative scans were performed using 0.1 M *n*-Bu₄NPF₆ (TBAPF₆) in dichloromethane (DCM) as the supporting electrolyte and a scan rate of 100 mV/s.

Device fabrication and measurements: OLED devices were fabricated by depositing materials on ITO-coated glass substrates (135 nm, 16 Ω per square, 3 cm × 3 cm × 0.7 cm) under high vacuum of 3 × 10⁻⁶ Torr. The active area of each device is 0.09 cm². The ITO glasses were ultrasonically cleaned by ethanol, acetone and deionized water for 10 min subsequently, and then exposed to UV-ozone for 15 min. The deposition rates were controlled at 2 Å/s for HAT-CN, 0.2–0.4 Å/s for Liq, 1–2 Å/s for other organic layers and 5–8 Å/s for Al anode. The electroluminescence (EL) spectra, the Commission International de l'Éclairage (CIE) coordinates, *J-L-V* curves, current efficiency (CE), and power efficiency (PE) of the devices were measured with a programmable spectra scan photometer (PHOTO RESEARCH, PR

655) and a constant current source meter (KEITHLEY 2400) at room temperature.

2.1. 9,9'-(4-(pyridin-2-yl)-1,3-phenylene)bis(9H-carbazole) (**2CzPy**)

Cesium carbonate (6.68 g, 20.5 mmol) was added to a glass vial containing carbazole (0.68 g, 4.1 mmol) and 2-(2,4-difluorophenyl)pyridine (0.38 g, 2.0 mmol) in *N,N*-dimethylacetamide (DMA) (15 mL). The vial was sealed with a Teflon cap and the mixture was heated by the microwave reactor. The reaction mixture was kept at 190 °C for 23 h. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and water (100 mL) was added to the residue. The aqueous phase was extracted with DCM (3 × 100 mL). The combined organic phase was dried over Na₂SO₄, filtered, and concentrated under vacuum. The crude product was purified by silica gel column chromatography (DCM:PE = 2:1) to afford a white solid (0.88 g, 91%). ¹H NMR (600 MHz, CDCl₃) δ 8.65–8.62 (m, 1H), 8.34 (d, *J* = 8.3 Hz, 1H), 8.15 (d, *J* = 7.8 Hz, 2H), 8.08 (d, *J* = 7.7 Hz, 2H), 7.93 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.80 (d, *J* = 2.0 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.46 (td, *J* = 7.7, 0.9 Hz, 2H), 7.33 (dd, *J* = 17.5, 7.8 Hz, 4H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 2H), 7.09 (td, *J* = 7.8, 1.6 Hz, 1H), 6.98 (dd, *J* = 7.4, 4.9 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 155.31, 149.98, 140.81, 140.56, 139.51, 137.98, 136.42, 136.20, 133.54, 127.40, 127.23, 126.37, 123.86, 123.55, 122.66, 122.44, 120.60, 120.39, 110.00. MALDI-TOF-MS: *m/z*: calcd for [C₃₅H₂₃N₃]⁺: 485.189; found: 485.125. Anal. calcd for C₃₅H₂₃N₃ (%): C 86.57, H 4.77, N 8.65; found: C 86.38, H 4.77, N 8.54.

2.2. 9,9'-(4-(pyridin-2-yl)-1,3-phenylene)bis(3,6-di-*tert*-butyl-9H-carbazole) (**2TCzPy**)

2TCzPy was prepared with the similar procedure as for **2CzPy** (1.32 g, 93%). ¹H NMR (600 MHz, CDCl₃) δ 8.67–8.65 (m, 1H), 8.31 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 1.1 Hz, 2H), 8.06 (d, *J* = 1.3 Hz, 2H), 7.87 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.73 (d, *J* = 2.0 Hz, 1H), 7.50 (dt, *J* = 8.7, 5.2 Hz, 4H), 7.35 (dd, *J* = 8.6, 1.8 Hz, 2H), 7.16–7.11 (m, 3H), 6.98 (dd, *J* = 6.9, 5.3 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 1.47 (s, 18H), 1.43 (s, 18H). ¹³C NMR (151 MHz, CDCl₃) δ 155.58, 149.90, 143.49, 143.01, 139.89, 139.31, 138.90, 137.10, 136.91, 136.25, 133.33, 126.76, 126.44, 123.99, 123.84, 123.57, 122.91, 122.20, 116.48, 116.21, 109.40, 34.83, 32.13. MALDI-TOF-MS: *m/z*: calcd for [C₅₁H₅₅N₃]⁺: 709.440; found: 709.371. Anal. calcd for C₅₁H₅₅N₃ (%): C 86.27, H 7.81, N 5.92; found: C 86.37, H 7.53, N 6.03.

2.3. 5,5'-(4-(pyridin-2-yl)-1,3-phenylene)bis(5H-benzofuro[3,2-*c*]carbazole) (**2BFCzPy**)

2BFCzPy was prepared with the similar procedure as for **2CzPy** (1.18 g, 93%). ¹H NMR (600 MHz, CDCl₃) δ 8.64–8.62 (m, 1H), 8.59 (d, *J* = 7.6 Hz, 1H), 8.51 (d, *J* = 7.6 Hz, 1H), 8.40 (d, *J* = 8.3 Hz, 1H), 8.03 (dd, *J* = 8.3, 2.2 Hz, 1H), 8.01–7.98 (m, 2H), 7.96–7.94 (m, 1H), 7.93 (d, *J* = 2.1 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.73 (dd, *J* = 13.2, 8.1 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.55–7.52 (m, 1H), 7.44 (ddd, *J* = 11.6, 9.9, 3.5 Hz, 4H), 7.40–7.36 (m, 4H), 7.27 (s, 1H), 7.08–7.06 (m, 1H), 6.97–6.94 (m, 1H), 6.67 (d, *J* = 7.9 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 156.50, 156.38, 155.10, 151.35, 151.15, 150.08, 141.27, 141.05, 140.53, 140.32, 139.56 (s), 138.59 (s), 136.47 (s), 136.30 (s), 133.76 (s), 127.90 (s), 126.26 (s), 125.64, 125.10, 123.07, 122.88, 122.60, 121.56, 121.36, 121.23, 121.02, 119.8, 118.43, 117.23, 116.94, 111.88, 110.00, 109.89, 109.29, 108.92, 105.68, 105.52. MALDI-TOF-MS: *m/z*: calcd for [C₄₇H₂₇N₃O₂]⁺: 665.210; found: 665.138. Anal. calcd for C₄₇H₂₇N₃O₂ (%): C 84.79, H 4.09, N 6.31; found: C 84.57, H 4.25, N 6.03.

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