

Carbazole-Benzimidazole Hybrid Bipolar Host Materials for Highly Efficient Green and Blue Phosphorescent OLEDs

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Synthetic procedures and characterization data

Synthesis of CbzCBI

3-Bromo-9-phenyl-9*H*-carbazole (2.5 g, 7.76 mmol, 1.5 equiv) was dissolved in 20 mL of anhydrous THF under argon atmosphere and cooled to $-78\text{ }^{\circ}\text{C}$. *n*-butyllithium in hexane (5.17 mL, 8.28 mmol, 1.6 equiv) was added dropwisely and continue the stirring for 1 h at $-78\text{ }^{\circ}\text{C}$. ZnCl₂ (1.41 g, 10.35 mmol, 2.0 equiv) in 10 mL dry THF was added in one portion. After 30 min at $-78\text{ }^{\circ}\text{C}$, the reaction mixture was removed from the cooling bath and stirred at room temperature for 1 h. Pd(PPh₃)₄ (299 mg, 0.26 mmol, 5 mol%) and the 2-(4-bromophenyl)-1-phenyl benzimidazole **4** (1.0 equiv, 1.81 g, 5.17 mmol,) in 20 mL dry THF were added and heated to reflux for 48 h. The reaction mixture was then cooled to room temperature, quenched with water and extracted with brine and CH₂Cl₂. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel (CH₂Cl₂ / hexane) to provide the compound as a light-yellow solid (1.78 g, 67%). IR (KBr) ν 3054, 1592, 1495, 1451, 1318, 1232 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ 8.36 (s, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.27-7.70 (m, 22H). ¹³C-NMR (CDCl₃, 100 MHz): δ 152.25, 142.98, 142.84, 141.36, 140.61, 137.52, 137.34, 137.151, 132.19, 129.95, 129.93, 129.84, 128.62, 127.87, 127.58, 127.53, 126.94, 126.22, 125.26, 123.91, 123.37, 123.29, 123.01, 120.35, 120.16, 119.73, 118.78, 110.41, 110.08, 109.96; MS (*m/z*, FAB⁺) 511.3 (6); HRMS (*m/z*, FAB⁺) calcd for C₃₇H₂₅N₃ 511.2048, found 511.2049. Anal. calcd for C₃₇H₂₅N₃: C, 86.86; H, 4.93; N, 8.21; found: C 87.00, H 4.89, N 8.14.

Synthesis of CbzNBI

3-Bromo-9-phenyl-9*H*-carbazole (2.0 g, 6.21 mmol, 1.5 equiv) was dissolved in anhydrous THF (15 mL) under argon and the solution was cooled to $-78\text{ }^{\circ}\text{C}$. *n*-Butyllithium in hexane (4.14 mL, 6.62 mmol, 1.6 equiv) was then added dropwisely, the whole solution was stirred for 1h at $-78\text{ }^{\circ}\text{C}$, followed by addition of ZnCl₂ (1.13 g, 8.28 mmol, 2.0 equiv) in THF (10 mL). After 30 min at $-78\text{ }^{\circ}\text{C}$, the reaction mixture was removed from the cooling bath and stirred at room temperature for 1 h. Pd(PPh₃)₄ (243 mg, 0.21 mmol, 5 mol%) and the 1-(4-bromophenyl)-2-phenyl benzimidazole **5** (1.45 g, 4.14 mmol, 1.0 equiv) in 15 mL dry THF were added and heated to reflux for 48 h. The reaction mixture was then cooled to room temperature,

quenched with water and extracted with brine and CH₂Cl₂. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel (CH₂Cl₂ / hexane) to provide the compound as a light-yellow solid (1.32 g, 62%). IR (KBr) ν 3045, 1595, 1498, 1470, 1453, 1230 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ 8.43(s, 1H), 8.22 (d, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.59-7.71 (m, 7H), 7.29-7.52 (m, 13H). ¹³C-NMR (CDCl₃, 100 MHz): δ 152.37, 142.89, 142.19, 141.42, 140.65, 137.46, 137.26, 135.28, 131.78, 129.96, 129.51, 129.48, 128.43, 128.36, 127.64, 127.04, 126.35, 125.25, 123.99, 123.36, 123.29, 123.02, 120.34, 120.24, 119.81, 118.87, 110.59, 110.22, 110.03; MS (m/z, FAB⁺) 511.3 (11); HRMS (m/z, FAB⁺) calcd for C₃₇H₂₅N₃ 511.2048, found 511.2047. Anal. calcd for C₃₇H₂₅N₃: C, 86.86; H, 4.93; N, 8.21; found: C 86.83, H 5.05, N 8.16.

Synthesis of mCPCBI

1-(3-Bromocarbazolyl)-3-carbazolylbenzene **7** (1.8 g, 3.69 mmol, 1.5 equiv) was dissolved in 10 mL of anhydrous THF under argon atmosphere and cooled to -78 °C. *n*-butyllithium in hexane (2.46 mL, 3.94 mmol, 1.6 equiv) was added dropwisely and continue the stirring for 1 h at -78 °C. ZnCl₂ (671 mg, 4.92 mmol, 2.0 equiv) in 5 mL dry THF was added in one portion. After 30 min at -78 °C, the reaction mixture was removed from the cooling bath and stirred at room temperature for 1 h. Pd(PPh₃)₄ (243 mg, 0.12 mmol, 5 mol%) and 2-(4-bromophenyl)-1-phenyl benzimidazole **4** (859 mg, 2.46 mmol, 1.0 equiv) in 10 mL dry THF were added and the reaction mixture was heated to reflux for 48 h and then cooled to room temperature, quenched with water and extracted with brine and CH₂Cl₂. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel (CH₂Cl₂ / hexane) to provide the compound as a light-yellow solid (896 mg, 54%). IR (KBr) ν 3050, 1595, 1494, 1448, 1226 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ 8.37 (s, 1H), 8.18 (m, 3H), 7.94 (d, J = 0.8 Hz, 1H), 7.83-7.89 (m, 2H), 7.67-7.74 (m, 7H), 7.51-7.59 (m, 7H), 7.28-7.48 (m, 11H). ¹³C-NMR (CDCl₃, 100 MHz): δ 152.19, 142.96, 142.66, 141.06, 140.55, 140.29, 139.42, 139.16, 137.34, 137.12, 132.64, 131.26, 129.95, 129.86, 128.63, 127.99, 127.52, 126.96, 126.46, 126.15, 125.95, 125.70, 125.46, 125.20, 124.17, 123.61, 123.59, 123.30, 123.02, 120.58, 120.51, 120.45, 120.35, 119.74, 118.92, 110.42, 110.01, 109.87, 109.63; MS (m/z, FAB⁺) 676.3 (41); HRMS (m/z, FAB⁺) calcd for C₄₉H₃₂N₄ 676.2627, found 676.2625. Anal. calcd for C₄₉H₃₂N₄: C, 86.96; H, 4.77; N, 8.28; found: C 87.01, H 4.82, N 8.17.

Synthesis of mCPNBI

A double-neck flask containing 1-(4-bromophenyl)-2-phenyl benzimidazole **5** (2.0g, 5.73mmol, 1.0equiv), 9-(3-(9*H*-carbazol-9-yl)phenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole **9** (3.06 g, 5.73 mmol, 1.0 equiv), Na₂CO₃ (2.43 g, 22.9 mmol, 4.0 equiv) and Pd(PPh₃)₄ (199 mg, 0.17 mmol, 3 mol%) was equipped with a condenser and then evacuated and backfilled with argon. The flask was charged with degassed 1,2-dimethoxyethane (30 mL) and heated to reflux for 48 h. The reaction mixture was then cooled to room temperature, quenched with water and extracted with brine and CH₂Cl₂. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel (CH₂Cl₂ / hexane) to provide the compound as a light-yellow solid (1.32 g, 45%). IR (KBr) ν 3045, 1596, 1498, 1470, 1453, 1230 cm⁻¹. ¹H-NMR (acetone-d₆, 400 MHz): δ 8.52 (d, *J* = 8.0 Hz, 1H), 8.62 (t, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 4.0 Hz, 1H), 7.76–7.94 (m, 4H), 7.68–7.76 (m, 2H), 7.61–7.68 (m, 5H), 7.48–7.57 (m, 4H), 7.22–7.40 (m, 14H). ¹³C-NMR (CDCl₃, 100 MHz): δ 152.37, 142.90, 142.02, 141.16, 140.58, 140.37, 139.49, 139.15, 137.26, 135.42, 132.27, 131.30, 129.93, 129.53, 129.50, 128.46, 128.38, 127.68, 126.60, 126.17, 126.04, 125.73, 125.48, 125.25, 124.28, 123.63, 123.56, 123.39, 123.05, 120.68, 120.51, 120.48, 120.39, 119.83, 119.02, 110.58, 110.17, 109.96, 109.62; MS (*m/z*, FAB⁺) 677.3 (15); HRMS (*m/z*, FAB⁺) calcd for C₄₉H₃₂N₄ 676.2627, found 676.2628. Anal. calcd for C₄₉H₃₂N₄: C, 86.96; H, 4.77; N, 8.28; found: C 86.91, H 4.82, N 8.20.

Table S1. Crystal data for **CbzCBI**.

CbzCBI	
empirical formula	C ₃₇ H ₂₅ N ₃
formula weight	511.60
	0.25 × 0.20 × 0.15
crystal dimensions	
crystal system	monoclinic
space group	P2 ₁ /n
<i>a</i> (Å)	14.0207(2)
<i>b</i> (Å)	9.87210(10)
<i>c</i> (Å)	19.5803(3)
α (deg)	90
β (deg)	106.189(2)
γ (deg)	90
cell volume (Å ³)	2602.72(6)
<i>Z</i>	4
density (calc) (g cm ⁻³)	1.306
<i>F</i> (000)	1072
temperature (K)	120(2)
wavelength (Å)	1.54178
no. of reflns collected	10117
no. of indep reflns (<i>R</i> _{int})	4751 (0.0166)
<i>R</i> (<i>F</i>), <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0362, 0.1153
<i>R</i> (<i>F</i>), <i>wR</i> ₂ (all data)	0.0424, 0.1212

Experimental procedures for the physical properties measurements

Cyclic Voltammetry

The oxidation potentials were determined in CH₂Cl₂ solutions (1.0 mM) containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte at a scan rate of 100 mV s⁻¹ using CHI 619B potentiostat. The reduction potentials were determined in DMF solutions (1.0 mM) containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). A glassy carbon electrode and platinum wire were used as the working and counter electrodes, respectively. All potentials were recorded versus Ag/AgCl (saturated) as a reference electrode. The ferrocenium/ferrocene redox couple in DMF/TBAP occurs at a value of $E_{o'}$ of +0.51 V for oxidation and in CH₂Cl₂/TBAPF₆ at +0.45 V for reduction, with respect to Ag/AgCl (saturated).

Physical Measurements

Thermogravimetric analysis (TGA) was performed under nitrogen using a TA instrument Dynamic Q500 thermogravimetric analyzer. The sample was heated from 50 °C to 800 °C with a heating rate of 10 °C /min. Differential scanning calorimeter (DSC) studies were carried out under nitrogen using a LT-modulated DSC 2920 differential scanning calorimeter. The sample was heated from 30 °C to 300 °C with a heating rate of 10 °C /min. Steady state spectra were recorded from both solutions and solid films prepared through vacuum (2×10^{-6} torr) deposition on a quartz plate (1.6 × 1.0 cm). Absorption spectra were recorded using a U2800A spectrophotometer (Hitachi). Fluorescence spectra were recorded at 300 K and phosphorescence spectra at 77 K using a Hitachi F-4500 spectrophotometer, with excitation at the absorption maxima. The experimental HOMO energy levels were determined using a Riken AC-2 photoemission spectrometer (PES); the LUMO energy levels were estimated by subtracting the optical energy gap from the measured HOMO energy level.

TOF Mobility Measurements

The samples for the TOF measurements were prepared through vacuum deposition in the configuration glass/Ag (30 nm)/organic (2–3 μm)/Al (150 nm); they were then placed inside a cryostat and maintained under vacuum. The thickness of organic film was monitored in situ with

a quartz crystal sensor and calibrated through thin film thickness measurement (K-MAC ST2000). A pulsed nitrogen laser used as the excitation light source through the transparent electrode (ITO) induced photo-generation of a thin sheet of excess carriers. Under an applied dc bias, the transient photocurrent was swept across the bulk of the organic film toward the collection electrode (Al) and then recorded using a digital storage oscilloscope. Depending on the polarity of the applied bias, selected carriers (holes or electrons) were swept across the sample with a transit time t_T . With an applied bias V , a sample thickness D , and an applied electric field E equal to V/D , the carrier mobility was given using the formula $\mu = D/(t_T E) = D^2 / (V t_T)$ from which the carrier transit time, t_T , was extracted from the intersection point of two asymptotes to the plateau and the tail sections in double-logarithmic plots.

OLED Device Fabrications

All chemicals were purified through vacuum sublimation prior to use. The OLEDs were fabricated through vacuum deposition of the materials at 10^{-6} torr onto ITO-coated glass substrates having a sheet resistance of $15 \Omega \text{ sq}^{-1}$. The ITO surface was cleaned ultrasonically—sequentially with acetone, MeOH, and deionized water and then it was treated with UV-ozone. A hole-injection layer (PEDOT: PSS) was spin-coated onto the substrates and dried at $130 \text{ }^\circ\text{C}$ for 30 min to remove residual water. Organic layers were then vacuum-deposited at a deposition rate of ca. $1\text{--}2 \text{ \AA s}^{-1}$. Subsequently, LiF was deposited at 0.1 \AA s^{-1} and then capped with Al (ca. 5 \AA s^{-1}) through shadow masking without breaking the vacuum. The $I\text{--}V\text{--}L$ characteristics of the devices were measured simultaneously using a Keithley 6430 source meter and a Keithley 6487 picoammeter equipped with a calibration Si-photodiode in a glove box. EL spectra were measured using a photodiode array (OTO SD1200) with a spectral range from 300 to 1100 nm and a resolution of 1.5 nm.