Electronic Supplementary Material for Journal of Materials Chemistry

# Novel Distyrylcarbazole Derivatives as Hole-Transporting Blue Emitters for Electroluminescent Devices

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## Details of experimental procedure and fabrication of light-emitting devices.

## Experimental Section

**General Procedures**. 2,7-Dibromo-9*H*-carbazole (**1**),[1] 2,2-diphenylvinyl bromide,[2] 3,6-dibromo-9-*p*-tolylcarbazole (**5**),[3] and 4,4′-bis(2,2-diphenylvinyl)-1,1′-biphenyl (**DPVBi**)[4] were synthesized as reported previously. The electron-transporting material, 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI),[5] was prepared according to reported procedures, and was sublimed twice before use. The solvents were dried according to standard procedures; all other reagents were used as received from commercial sources, unless otherwise stated. Differential scanning calorimetry (DSC) was performed (Seiko Exstar 6000DSC) at a heating rate 20 °C $\text{min}^{-1}$ and a cooling rate 40 °C $\text{min}^{-1}$. Samples were scanned from 30 to 320 °C, cooled to 0 °C, and then scanned again to 320 °C. The temperature ($T_g$) of the glass transition was determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken (DuPont TGA 2950 instrument). The thermal stability of samples under a nitrogen atmosphere was determined by measuring their loss of mass during heating at a rate 20 °C $\text{min}^{-1}$. We measured UV–visible spectra (HP 8453 diode-array spectrophotometer) and photoluminescence (PL) spectra (Hitachi F-4500 luminescence spectrometer). For cyclic voltammetry (CV) measurements (BAS 100 B/W electrochemical analyzer, we undertook oxidation and reduction measurements in anhydrous $CH_2Cl_2$ and anhydrous THF, respectively, containing $TBAPF_6$ (0.1 M) as the supporting electrolyte, at a scan rate 50 mV $s^{-1}$. The potentials were measured against an $Ag/Ag^+$ (0.01 M $AgNO_3$) reference electrode with ferrocene as an internal standard.

**2,7-Dibromo-9-isopropylcarbazole** (**2**). A mixture of 2,7-dibromo-9*H*-carbazole (**1**; 2.00 g, 6.15 mmol), 2-bromopropane (2.3 mL, 24.6 mmol), $K_2CO_3$ (3.40 g, 24.6 mmol) and NMP (20 mL) was heated at 75 °C for 12 h. The reaction mixture was added to water (300 mL) and the precipitate was collected on filtration. The product was purified by recrystallization from ethanol to give **2** (1.00 g, 44.3 %). $^1$H NMR (300 MHz, $CDCl_3$) δ 1.67 (d, *J* = 7.0 Hz, 6H), 4.85 (septet, *J* = 7.0 Hz, 1H), 7.31 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.64 (d, *J* = 1.6 Hz, 2H) 7.88 (d, *J* = 8.3 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 20.7, 47.2, 113.2, 119.4, 121.4, 121.7, 122.3, 140.3. HRMS [$M^+$]: calcd. for $C_{15}H_{13}N^{79}Br_2$ 364.9415, found 364.9407.

**2,7-Dibromo-9-*p*-tolylcarbazole** (**3**). A mixture of **1** (0.45 g, 1.38 mmol), 4-iodotoluene (1.52 g, 6.97 mmol), copper (0.12 g, 1.89 mmol), [18]crown-6 (25.0 mg, 0.09 mmol), $K_2CO_3$ (0.52 g, 3.77 mmol) and 1,2-dichlorobenzene (10 mL) was heated at 180 °C for 16 h. This mixture was filtered and concentrated under reduced pressure. The product was purified through column chromatography on silica gel with hexane as eluent to yield **3** (0.35 g, 59.6 %). $^1$H NMR (300 MHz, $CDCl_3$) δ 2.48 (s, 3H) 7.35 (d, *J* = 8.4 Hz, 2H), 7.37 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 1.6 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 21.4, 113.1, 120.0, 121.5, 121.6, 123.5, 127.0, 130.9, 133.8, 138.5, 142.1. HRMS [$M^+$]: calcd. for $C_{19}H_{13}N^{79}Br_2$ 412.9415, found 412.9413.

**2-(2,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (**4**). *n*-Butyllithium in hexane (2.5 M, 40 mL) was added slowly under nitrogen to a stirred solution of 2,2-diphenylvinyl bromide (13.0 g, 50.2 mmol) in THF (80 mL) at –78 °C and then the mixture was stirred further for 2 h. *n*-Butyl borate (30 mL, 111 mmol) was added at –78 °C before the mixture was warmed slowly to room temperature and stirred overnight. Water (50 mL) was added, followed by conc. HCl to acidify the mixture (to pH ~ 2), which was then stirred for 2 h. The reaction mixture was extracted with EtOAc and the combined organic phases were dried over $MgSO_4$. Concentration under reduced pressure gave 2,2-diphenylvinyl boronic acid, which, without further purification, was reacted with pinacol (8.50 g, 72.0 mmol) in benzene (100 mL) under reflux for 3 h to effect condensation by the azeotropic removal of the water formed. The mixture was concentrated under reduced pressure and the residue was purified by column chromatography (hexane/EtOAc) to afford **4** (7.53 g, 49%). $^1$H NMR (300 MHz, $CDCl_3$): δ 1.18 (s, 12H), 6.03 (s, 1H), 7.28–7.36 (m, 10 H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 24.7, 83.2, 127.6,127.7, 128.0, 128.1, 129.9, 141.9, 143.2, 159.9. HRMS [$M^+$]: calcd. for $C_{20}H_{23}BO_2$, 306.1791; found 306.1796.

**2,7-Bis(2,2-diphenylvinyl)-9-isopropylcarbazole** (**DPVICz**). A mixture of **2** (1.00 g, 2.72 mmol), **4** (2.08 g, 6.79 mmol), aliquat 336 (274 mg), aqueous $K_2CO_3$ (2.0 M, 7.0 mL), and toluene (15 mL) was degassed; then tetrakis(triphenylphosphine)-palladium (31 mg, 2.68 μmol) was added in one portion under nitrogen. After heating at 105 °C for 2 h, the reaction mixture was poured into water (50 mL) and extracted with EtOAc (50 mL × 3). The organic extracts were dried ($MgSO_4$) and concentrated. The crude product was purified on recrystallization from EtOAc, followed by temperature-gradient sublimation to give **DPVICz** (1.08 g, 70.1 %). $^1$H NMR (300 MHz, $CDCl_3$) δ 1.17 (d, *J* = 7.0 Hz, 6H), 4.27 (septet, *J* = 7.0 Hz, 1H), 6.98–7.02 (m, 4H), 7.17 (s, 2H), 7.26–7.41 (m, 20H), 7.82 (d, *J* = 8.4 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 20.4, 46.0, 110.6, 119.6, 121.5, 122.0, 127.26, 127.34, 127.5, 128.2, 128.8, 129.3, 130.5, 134.5, 139.8, 141.0, 141.6, 143.5. HRMS [$M^+$]: calcd. for $C_{43}H_{35}N$ 565.2769, found 565.2766. Anal. Calcd for $C_{43}H_{35}N$: C, 91.29; H, 6.24; N, 2.48. Found: C, 91.31; H, 6.29; N, 2.20.

**2,7-Bis(2,2-diphenylvinyl)-9-*p*-tolylcarbazole** (**DPVTCz**). Using the procedure described for **DPVICz**, the reaction between **3** and **4**, followed by temperature-gradient sublimation, gave **DPVTCz** in 67.7% yield. $^1$H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 3H), 6.72 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 1.4 Hz, 2H), 7.01 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.07 (s, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.16–7.20 (m, 4H), 7.25–7.31 (m, 16H), 7.82 (d, *J* = 8.1 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 21.3, 110.8, 119.6, 121.9, 122.3, 126.0, 127.1, 127.4, 127.5, 128.2, 128.6, 129.1, 130.1, 130.6, 134.2, 135.2, 136.3, 140.7, 141.0, 142.1, 143.5. HRMS [$M^+$]: calcd. for $C_{47}H_{35}N$ 613.2769, found 613.2775. Anal. Calcd for $C_{47}H_{35}N$: C, 91.97; H, 5.75; N, 2.28. Found: C, 91.84; H, 6.07; N, 2.26.

**3,6-Bis(2,2-diphenylvinyl)-9-*p*-tolylcarbazole** (**3,6-DPVTCz**). Using the procedure described for **DPVICz**, the reaction between 3,6-dibromo-9-*p*-tolylcarbazole **5** and **4**, followed by temperature-gradient sublimation, gave **3,6-DPVTCz** in 51.6 % yield. $^1$H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3H), 7.00 (dd, *J* = 8.9, 1.8 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 7.14 (s, 2H), 7.24–7.40 (m, 24H), 7.57 (d, *J* = 1.8 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 21.2, 109.2, 121.4, 123.0, 126.6, 127.1, 127.2, 127.4, 127.7, 128.2, 128.7, 128.8, 129.5, 130.3, 130.5, 134.6, 137.3, 140.1, 140.4, 140.8, 143.7. HRMS [$M^+$]: calcd. for $C_{47}H_{35}N$ 613.2769, found 613.2767. Anal. Calcd for $C_{47}H_{35}N$: C, 91.97; H, 5.75; N, 2.28. Found: C, 91.63; H, 5.84; N, 2.14.

**Fabrication of Light-emitting Devices**. The devices were fabricated in the configuration ITO/emitting layer (65 nm) /TPBI (15 nm) / Mg:Ag (100 nm) / Ag (100 nm). The organic layer was grown by thermal sublimation under vacuum ($3 \times 10^{-6}$ torr). TPBI was used as an electron-transporting and hole-blocking layer to enhance charge recombination and exciton confinement.[6] A cathodic Mg:Ag (10:1, 100 nm) alloy was subsequently deposited by co-evaporation onto the TPBI layer, and an additional Ag protection layer (100 nm) was placed onto the alloy. The active area was 9 mm$^2$. The current–voltage–luminance characteristics (Keithley 2400 source meter, Newport 1835C optical meter equipped with an 818ST silicon photodiode) were measured under ambient conditions.

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