SUPPORTING INFORMATION

Novel Carbazole/Fluorene Hybrids: Host Materials for Blue Phosphorescent OLEDs

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General. 9-Phenylcarbazole (**1**) and 9-fluorenone (**3**) were purchased from Aldrich and Acros Organics, respectively. 9-Phenyl-9-fluorenol (**2**) was either purchased from Acros or routinely prepared in on a 20-gram scale according to literature procedures.[1,2] The ^{1}H and ^{13}C NMR spectra were recorded on Varian UNITY 300 (300 MHz) and Bruker-DRX 300 (300 MHz) spectrometers. Mass spectra were obtained using a JEOL JMS-HX 110 mass spectrometer. Differential scanning calorimetry (DSC) was performed using a SEIKO EXSTAR 6000DSC unit at heating and cooling rates of 20 and 50 °C min^{-1}. Thermogravimetric analysis (TGA) was undertaken using a Perkin–Elmer TGA Pyris 1 instrument. The thermal stabilities of the samples were determined under nitrogen atmosphere by measuring their weight losses while heating them at a rate of 20 °C min^{-1}. UV–Vis spectra were measured using an HP 8453 diode-array spectrophotometer. Photoluminescence spectra were obtained using a Hitachi F-4500 luminescence spectrometer. The low-temperature phosphorescence spectra of the carbazole/fluorene hybrids were obtained using a composite spectrometer containing a monochromator (Jobin Yvon, Triax 190) coupled with a liquid nitrogen-cooled charge-coupled device (CCD) detector (Jobin Yvon, CCD-1024x256-open-1LS). The sample chamber was coupled to a static exchange gas continuous flow cryostate system (Oxford, OptistatCF) equipped with a temperature control unit (Oxford, ITC503), which allowed the temperature of the

sample to be controlled in the range 77–298 K when liquid nitrogen was used. The excitation wavelength was fixed at 355 nm; it was obtained through third harmonic generation of a fundamental pulse generated from a nanosecond Nd:YAG laser (Ekspla, NT342/1/UV) running at 10 Hz. The transient signal was collected by a PMT detector (Hamamatsu, R928) and the resulting temporal profile was recorded on a digital oscilloscope (LeCroy, LT372) connected to a PC via an IEEE-488 interface for data analysis. Cyclic voltammetry (CV) spectra were measured using a BAS 100 B/W electrochemical analyzer operated at a scan rate of 50 mV s^{-1}; the solvent was anhydrous CH_2Cl_2 and 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was the supporting electrolyte. The potentials were measured against an Ag/Ag^+ (0.01 M $AgNO_3$) reference electrode using ferrocene as an internal standard.

Common Procedure Used for the Synthesis of Carbazole/Fluorene Hybrids (CBZm-Fn). Eaton's reagent (7.7 wt% P_2O_5 in CH_3SO_3H) was added dropwise at 25 °C under a nitrogen atmosphere to a solution of 9-phenylcarbazole (**1**) or 9,9-bis(9-phenylcarbazol-3-yl)-fluorene (CBZ2-F1; synthesized as discussed below) and 9-phenyl-9-fluorenol (**2**) in CH_2Cl_2. The color of the solution changed to greenish blue immediately. Stirring was continued for 1 h and then the reaction mixture was washed sequentially with water (× 2), dilute aqueous sodium bicarbonate solution (×

1), and brine (× 2). The CH_2Cl_2 layer was separated and the aqueous layer was extracted with CH_2Cl_2 (× 2). The organic layers were combined, dried ($MgSO_4$), and evaporated under vacuum to provide a crude material that was subjected to purification (individual procedures are described with the experimental data of each compounds). The synthetic procedure for the preparation of compound CBZ2-F1 from **1** and 9-fluorenone (**3**) deviated slightly from the general procedure: an elevated temperature was required to activate the less-reactive carbonyl group of **3**. Details are given below with the respective experimental data of compounds CBZm-Fn.

9-Phenyl-3,6-bis(9-phenylfluoren-9-yl)carbazole (CBZ1-F2)**.** The general method was followed using **1** (511 mg, 2.1 mmol) and **2** (1.09 g, 4.2 mmol) in CH_2Cl_2 (10 mL) and Eaton's reagent (160 μL). The crude product was heated under reflux with *n*-hexane to provide a white precipitate, which was filtered, dried under vacuum and, recrystallized from acetone/*n*-hexane to yield CBZ1-F2 as a white crystalline solid (1.4 g, 92%). ^{1}H NMR ($CDCl_3$): δ 7.18–7.29 (m, 17H), 7.34–7.42 (m, 6H), 7.46–7.55 (m, 8H), 7.80 (d, J = 7.5 Hz, 4H), 7.85–7.86 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 65.5, 109.4, 119.7, 120.1, 123.1, 126.3, 126.5, 126.6, 126.8, 127.2, 127.3, 127.7, 128.1, 128.2, 129.7, 137.3, 137.5, 140.0, 146.7, 151.8. MS (*m*/*z*, FAB): $[M + 1]^+$ 724. HRMS (M^+, FAB): calcd. for $C_{56}H_{37}N$, 723.2926; found, 723.2931. Anal. Calcd. for $C_{56}H_{37}N$: C, 92.91; H, 5.15; N, 1.93. Found: C, 93.17; H, 5.36; N, 1.79.

9-Phenyl-3-(9-phenylfluoren-9-yl)carbazole (CBZ1-F1)**.** The general method was followed using **1** (1.46 g, 6.0 mmol) and **2** (0.78 g, 3.0 mmol) in CH_2Cl_2 (20 mL) and Eaton's reagent (150 μL). The crude product (2.2 g) was subjected to flash chromatography (SiO_2; gradient elution with *n*-hexane and EtOAc) to obtain a yellow solid, which was re-crystallized from *n*-hexane/CH_2Cl_2 to yield CBZ1-F1 (958 mg, 66%). The more-polar fractions yielded CBZ1-F2 as a white solid of (316 mg, 29%). ^{1}H NMR ($CDCl_3$): δ 7.15–7.43 (m, 15H), 7.47–7.57 (m, 6H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.91(s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 65.5, 109.6, 109.7, 119.4, 119.8, 120.2, 120.3, 123.1, 123.3, 125.9, 126.3, 126.6, 126.7, 126.9, 127.3, 127.4, 127.7, 128.2, 129.8, 137.5, 137.7, 139.7, 140.1, 141.1, 146.6, 151.8. MS (*m*/*z*, EI): [M^+] 483. HRMS (M^+, EI): calcd. for $C_{32}H_{25}N$, 483.1987; found, 483.1993. Anal. Calcd. for $C_{32}H_{25}N$: C, 91.89; H, 5.21; N, 2.90. Found: C, 91.62; H, 5.57; N, 2.93.

9,9-Bis(9-phenylcarbazol-3-yl)fluorene (CBZ2-F1)**.** Similar to the general method, Eaton's reagent (800 μL) was added under a flow of nitrogen to a solution of **1** (1.5 g, 6.1 mmol) and **3** (0.5 g, 2.8 mmol) in CH_2Cl_2 (5.0 mL); i.e., the reactants were dissolved in a minimum quantity of CH_2Cl_2. After the addition of Eaton's reagent, the reaction mixture was heated at 100 °C and the escaping CH_2Cl_2 was collected in a cold trap. (Although this reaction requires a higher temperature and neat

conditions, the reactants were dissolved in CH_2Cl_2 to ensure their uniform distribution in the reaction mixture prior to heating.) After heating at 100 °C for 30 min, the reaction mixture gradually became dry and thick as a result of the evaporation of CH_2Cl_2 and the formation of product. At this stage, methanol (20 mL) was added to the reaction mixture, which was then heated under reflux for 30 min to provide a white precipitate in a greenish-blue solution. The mixture was cooled to 25 °C and the methanol was decanted. This procedure was repeated one more time and then the precipitate was filtered and dried under vacuum to yield CBZ2-F1 as an amorphous white powder (1.3 g, 73%). ^{1}H NMR ($CDCl_3$): δ 7.17 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.19 (dd, *J* = 7.8, 2.1 Hz, 2H), 7.26–7.32 (m, 6H), 7.34–7.45 (m, 9H), 7.51–7.59 (m, 8H), 7.83 (d, *J* = 6.9 Hz, 2H), 7.95 (d, *J* = 7.8 Hz, 2H), 8.01 (d, *J* = 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 65.6, 109.6, 109.7, 119.5, 119.7, 120.2, 120.4, 123.1, 123.3, 125.8, 126.4, 126.8, 127.0, 127.3, 127.8, 129.8, 137.7, 138.3, 139.7, 140.1, 141.1, 152.5. MS (*m*/*z*, EI): (M^+) 648. HRMS (M^+, EI): calcd. for $C_{49}H_{32}N_2$, 648.2565; found, 648.2569. Anal. Calcd. for $C_{49}H_{32}N_2$: C, 90.71; H, 4.97; N, 4.32. Found: C, 90.67; H, 4.89; N, 4.63.

9,9-Bis[3-(9-phenylfluoren-9-yl)-9-phenylcarbazol-6-yl]fluorene (CBZ2-F3). The general procedure was followed using a solution of CBZ2-F1 (300 mg, 460 μmol) and **2** (251 mg, 970 μmol) in CH_2Cl_2 (50 mL) and Eaton's reagent (100 μL).

The crude product was dissolved in a minimum quantity of ethyl acetate and added to methanol (100 mL) while stirring to obtain a white precipitate, which was filtered and dried under vacuum to yield CBZ2-F3 (480 mg, 92%). ^{1}H NMR ($CDCl_3$): δ 7.14–7.27 (m, 23H), 7.29–7.38 (m, 7H), 7.39–7.56 (m, 16H), 7.75 (d, *J* = 8.4 Hz, 4H), 7.78 (dd, *J* = 7.7, 2.0 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 65.49, 65.54, 109.38, 109.43, 119.6, 119.7, 120.1, 123.0, 123.1, 126.3, 126.3, 126.5, 126.8, 127.2, 127.3, 127.6, 128.07, 128.13, 129.7, 137.2, 137.6, 138.2, 139.9, 140.0, 146.7, 151.8, 152.3. MS (*m*/*z*, FAB): $[M + 1]^+$ 1129. HRMS ($[M + 1]^+$, FAB): calcd. for $C_{87}H_{57}N_2$, 1129.4522; found, 1129.4517. Anal. Calcd. for $C_{87}H_{56}N_2$: C, 92.52; H, 5.00; N, 2.48. Found: C, 92.01; H, 5.18; N, 2.80.

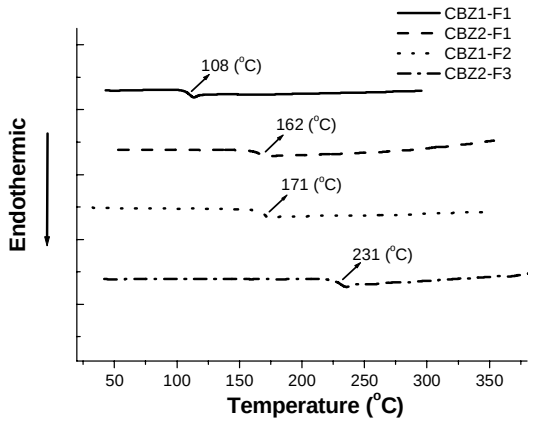

Figure S1: DSC thermograms of CBZm-Fn hybrids, recorded from the second heating scans.

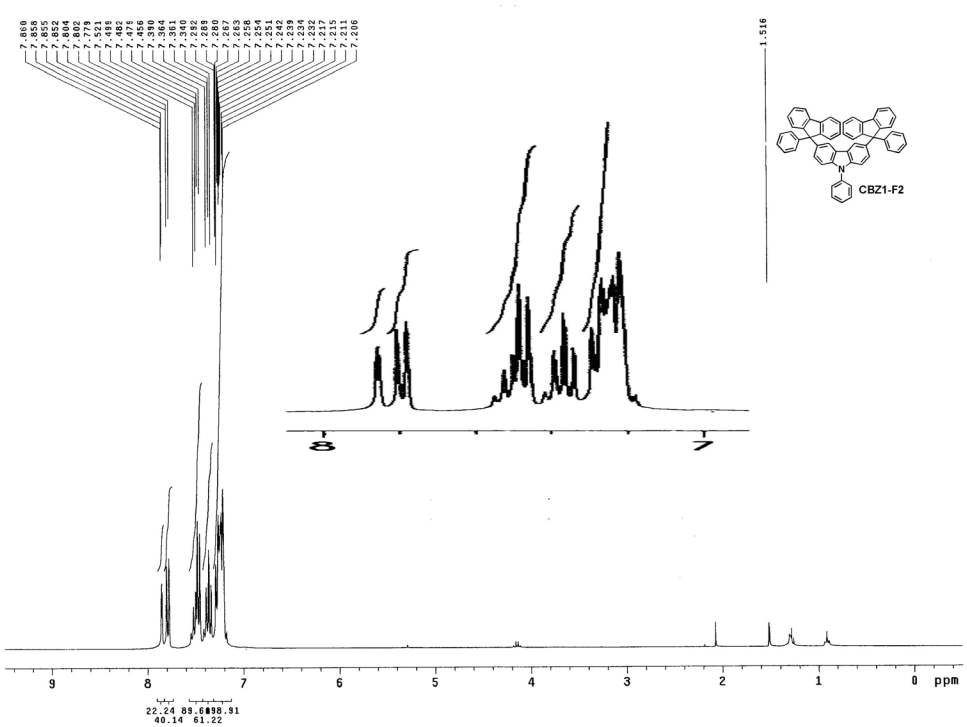

Figure S2: ^{1}H NMR of CBZ1-F2

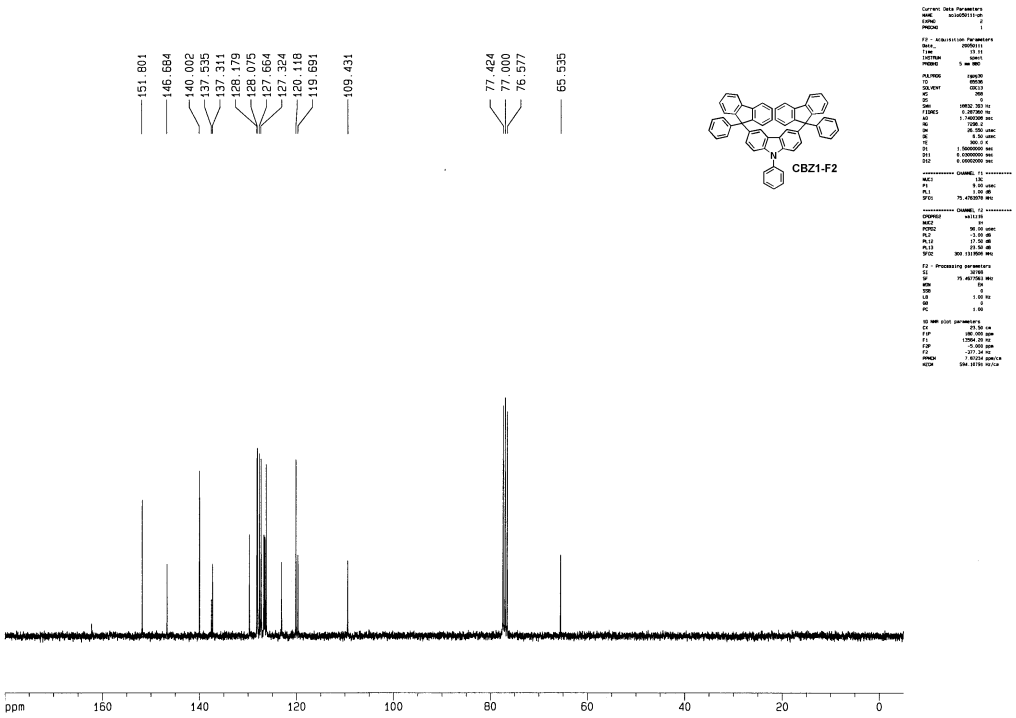

Figure S3: ^{13}C NMR of CBZ1-F2

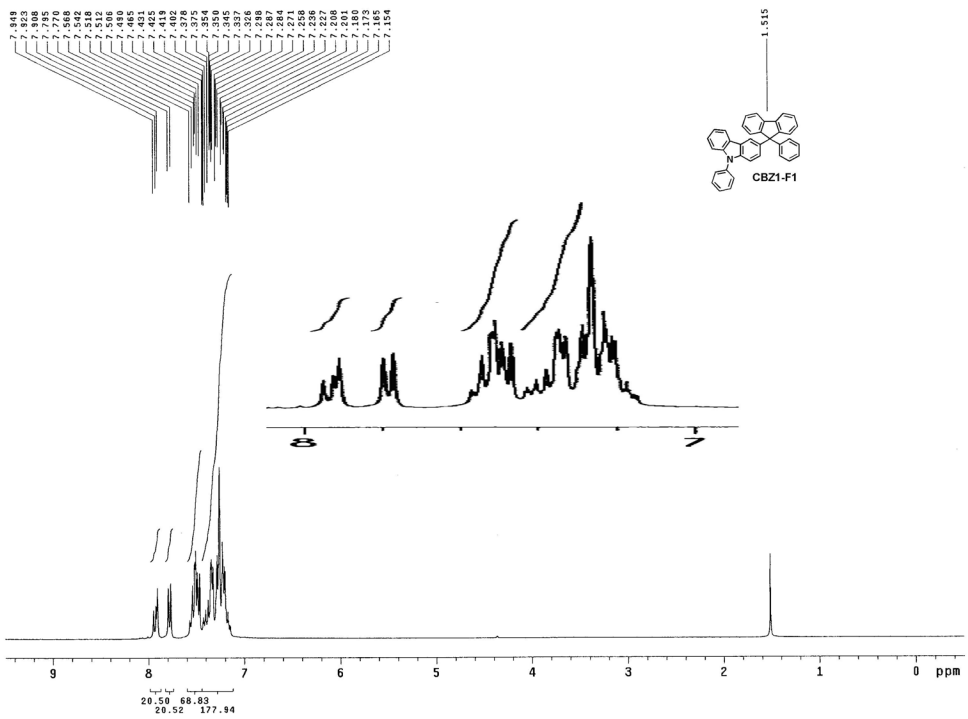

Figure S4: ^{1}H NMR of CBZ1-F1

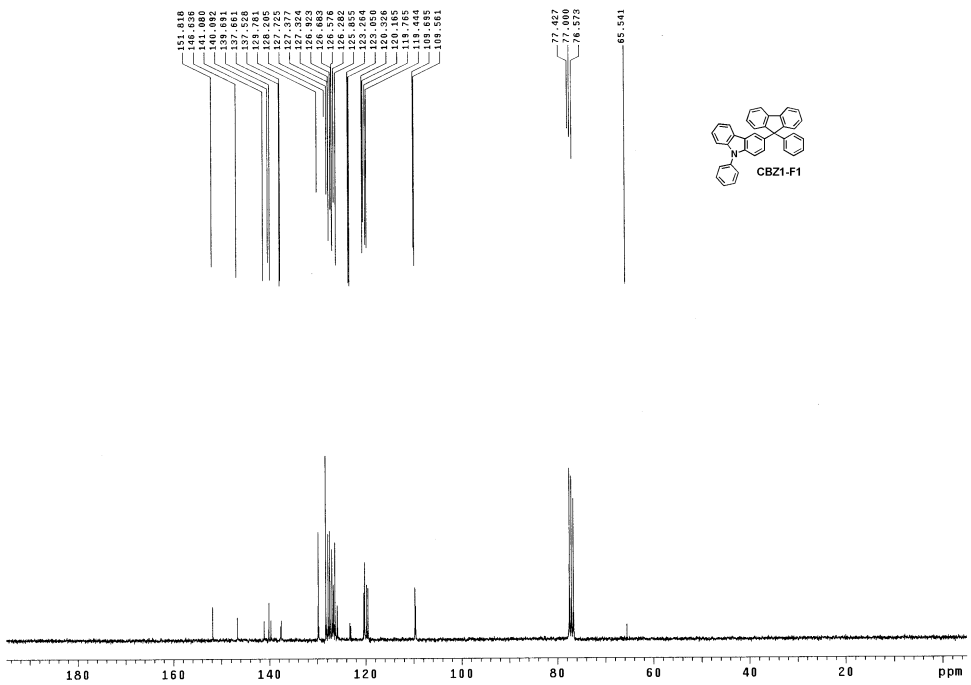

Figure S5: ^{13}C NMR of CBZ1-F1

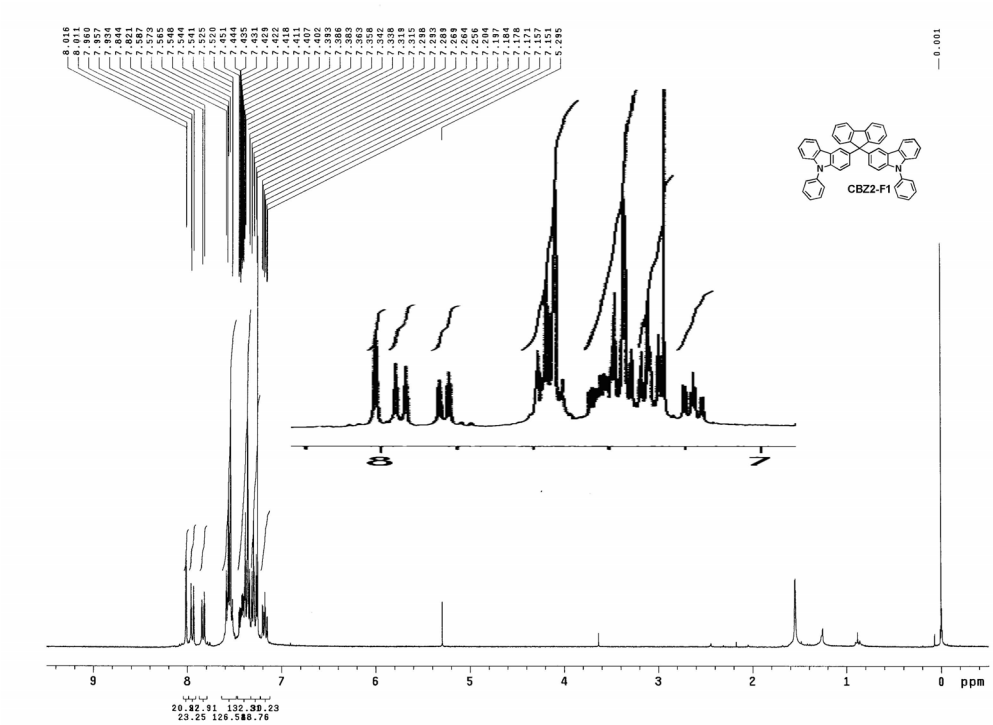

Figure S6: ^{1}H NMR of CBZ2-F1

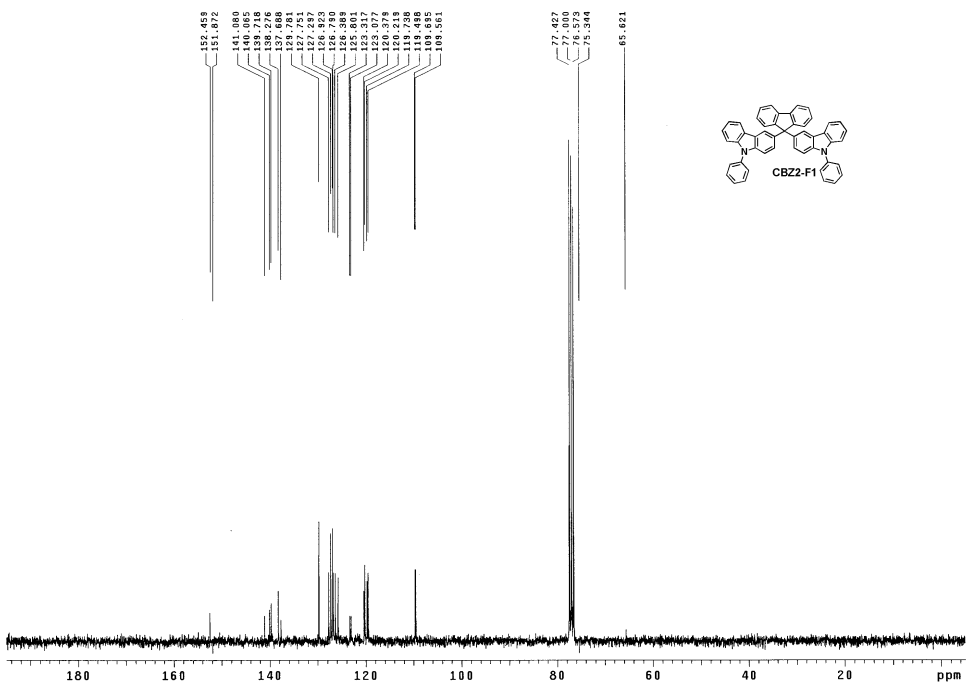

Figure S7: ^{13}C NMR of CBZ2-F1

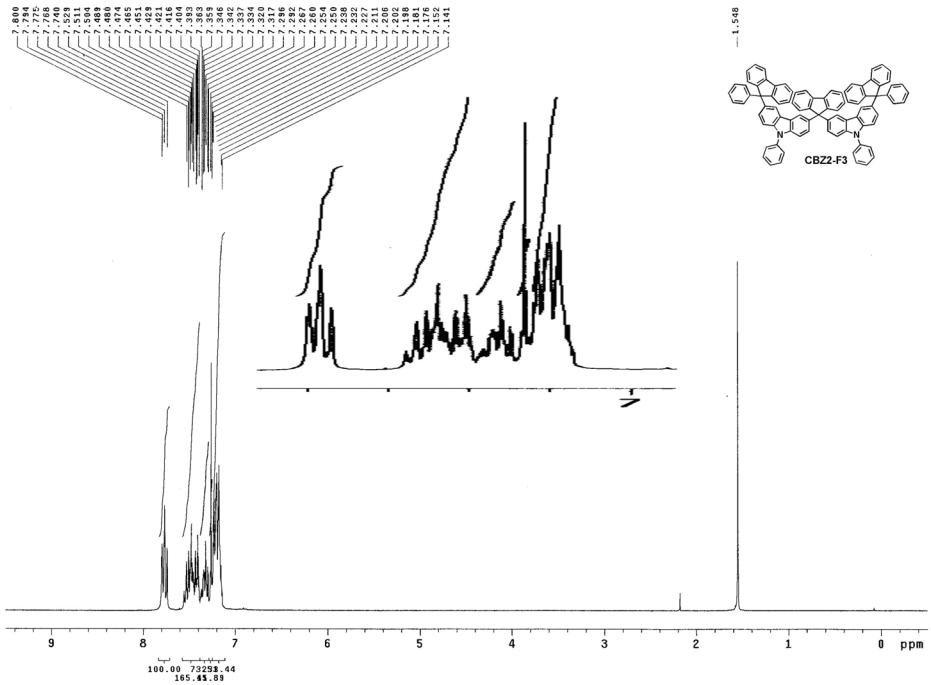

Figure S8: ^{1}H NMR of CBZ2-F3

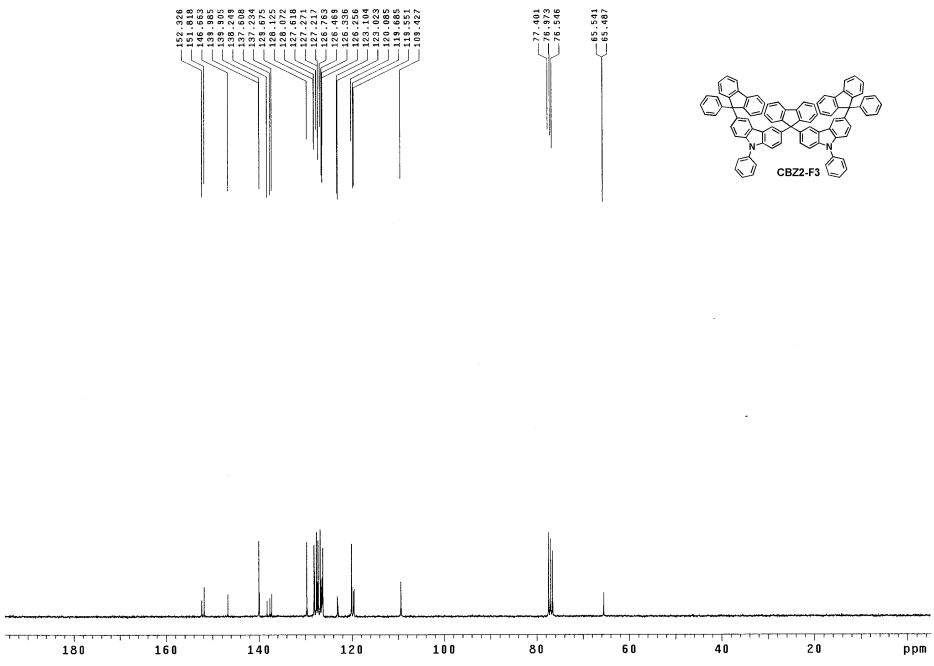

Figure S9: ^{13}C NMR of CBZ2-F3

References:

1. Bolton, R.; Mguni, R. S.; Williams, G. H. *J. Chem. Soc. Perkin Trans. 2* **1986**, 405.

2. Goerner, R. N., Jr.; Cote, P. N.; Vittimberga, B. M. *J. Org. Chem.* **1977**, *42*, 19.