Electronic Supplementary Information

Bipolar Material with Spiro-Fluorenyl Terminals: Synthesis, Characterization and Application for Enhancement of Electrophosphorescence

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Synthesis of Compounds 3, 4, 6 and 7.

9-(4-nitrophenyl)-9H-carbazole (3). A mixture of NaH (1.04 g, 40mmol) in 30 ml dimethyl sulfoxide (DMSO) was stirred at room temperature. To the mixture, carbazole (3.34 g, 20mmol) and 4-fluoronitrobenzene (2.94 g, 21 mmol) were added in sequence. The mixture was stirred at 140 °C for 12 h and then poured into a large amount of distilled water. The appearing precipitates were collected by filtration and recrystallized from ethyl acetate to afford 3 (63%). mp: 213 °C. ¹H NMR (CDCl₃, ppm): δ 8.47~8.44 (d, J = 8.8 Hz, 2H, Ar-H), δ 8.14~8.12 (d, J = 8 Hz, 2H, Ar-H), δ 7.78~7.75 (d, J = 9.2 Hz, 2H, Ar-H), δ 7.49~7.41 (m, 4H, Ar-H), δ 7.36~7.32 (t, 2H, Ar-H). Anal. Calcd. (%) for C₁₈H₁₃N₂O₂: C, 74.99; H, 4.20; N, 9.72. Found: C, 74.96; H, 4.26; N, 9.75.
Scheme 1 Synthetic procedures of bipolar monomer 8 and bipolar spiro-fluorene material FTzCz

**4-(9H-carbazol-9-yl)aniline (4).** The mixture of 3 (2.09 g, 7.25 mmol), 25 mg of Pd/C (palladium on activated charcoal, 10 mg), hydrazine monohydrate (1.50 g, 30.0 mmol) and 40 ml of ethanol was stirred at 90 °C for 12 h under nitrogen atmosphere. The Pd/C was separated by filtration. After stripping off ethanol under vacuum, it was purified by column chromatography (eluent: n-hexane/ethyl acetate) to afford 4 (95%). $^1$H NMR (DMSO-$d_6$, ppm): δ 8.18–8.17 (d, $J = 7.6$ Hz, 2H, Ar-H), δ 7.39–7.36 (t, 2H, Ar-H), δ 7.27–7.17 (m, 6H, Ar-H), δ 6.84–6.81 (d, $J = 8.4$ Hz, 2H, Ar-H), δ 5.44 (s, 2H, -NH$_2$). Anal. Calcd. (%) for C$_{18}$H$_{14}$N$_2$: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.40; H, 5.50; N, 10.74.
1,2-Bis(4-bromobenzoyl)hydrazine (6). To a two-neck glass reactor were added with 4-bromobenzoyl chloride (5: 6.59 g, 30 mmol), hydrazine monohydrate (0.72 g, 15 mmol), and 30 ml of N-methylpyrrolidone (NMP). The mixture was stirred at room temperature for 5 h, poured into a large amount of distilled water. The appearing precipitates were collected by filtration and recrystallized from DMSO and water to afford 6 (90%). mp > 250 °C. $^1$H NMR (DMSO-d$_6$, ppm):  $\delta$ 10.62 (s, 2H, -NH-), 7.85–7.83 (d, $J = 8.6$ Hz, 4H, Ar-H), 7.74–7.72 (d, $J = 8.4$ Hz, 4H, Ar-H). Anal. Calcd. (%) for C$_{14}$H$_{10}$Br$_2$N$_2$O$_2$: C, 42.24; H, 2.53; N, 7.04. Found: C, 42.19; H, 2.61; N, 7.05.

1,2-Bis((4-bromophenyl)chloromethylene)hydrazine (7). The mixture of 6 (3.20 g, 8.0 mmol), phosphorus pentachloride (3.84 g, 18.50 mmol), and 40 ml of toluene was stirred at 120 °C for 3 h under nitrogen atmosphere. After stripping off toluene under vacuum, the solid residue was washed twice with deionized water, dried in vacuo, and then recrystallized from ethanol and dichloromethane to afford 3 (53%). mp: 144-145 °C. $^1$H NMR (DMSO-d$_6$, ppm): $\delta$ 8.00–7.97 (d, $J = 8.5$ Hz, 4H, Ar-H), 7.81–7.78 (d, $J = 8.5$ Hz, 4H, Ar-H). Anal. Calcd. (%) for C$_{14}$H$_8$Br$_2$Cl$_2$N$_2$: C, 38.66; H, 1.85; N, 6.44. Found: C, 38.78; H, 1.90; N, 6.49.
Figure S1. $^1$H NMR spectrum of 8 in CDCl₃.

Figure S2. DSC trace of FTzCz recorded at a heating rate of 10 °C/min.
**Figure S3.** AFM images of blend films in different ratio of PVK and FTzCz coated on top of PEDOT:PSS layer.