

Electronic Supplementary Information

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

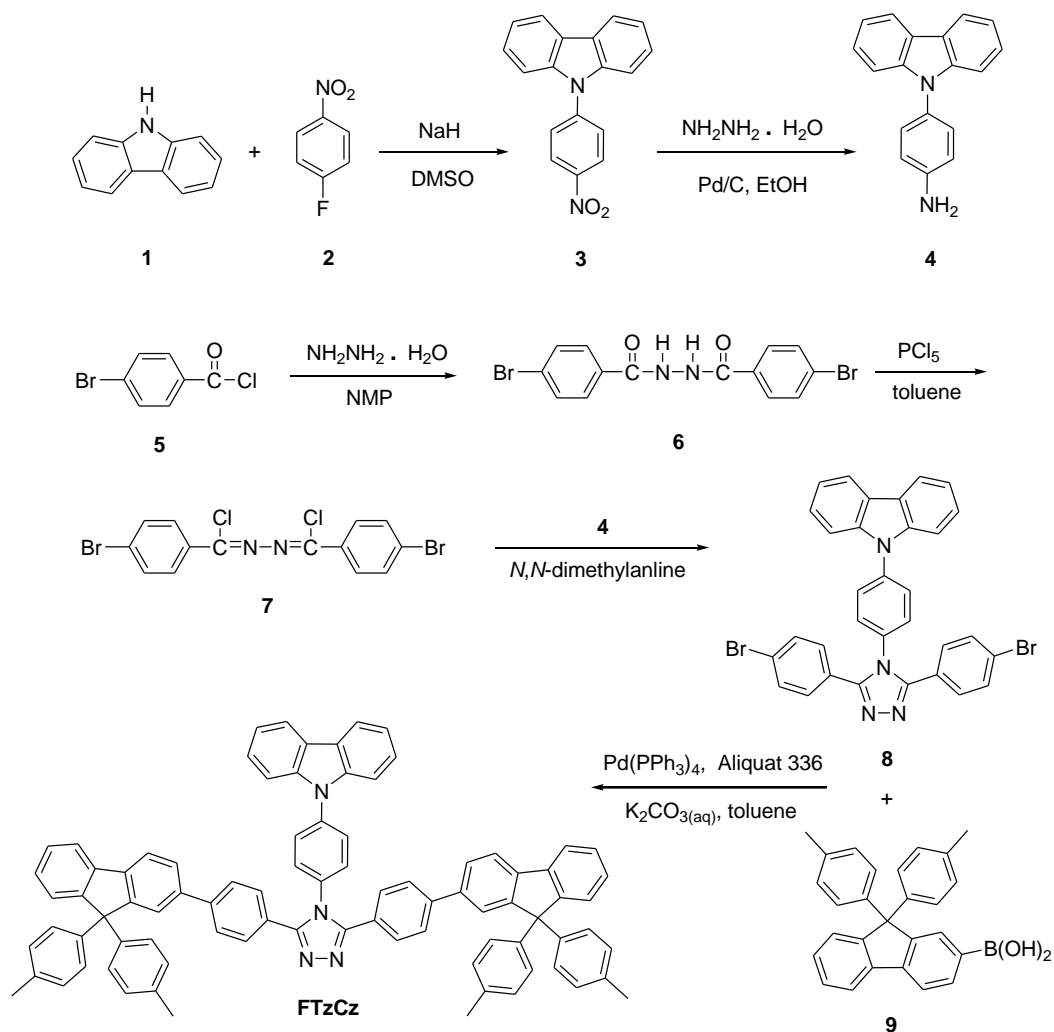
Chia-Shing Wu, Juin-Wei Wu and Yun Chen*

Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan

* Corresponding author. e-mail: yunchen@mail.ncku.edu.tw

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%). ¹H 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, -NH₂). Anal. Calcd. (%) for C₁₈H₁₄N₂: 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. ¹H NMR (DMSO-d₆, ppm): δ 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 C₁₄H₁₀Br₂N₂O₂: 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. ¹H NMR (DMSO-d₆, ppm): δ 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 C₁₄H₈Br₂Cl₂N₂: C, 38.66; H, 1.85; N, 6.44. Found: C, 38.78; H, 1.90; N, 6.49.

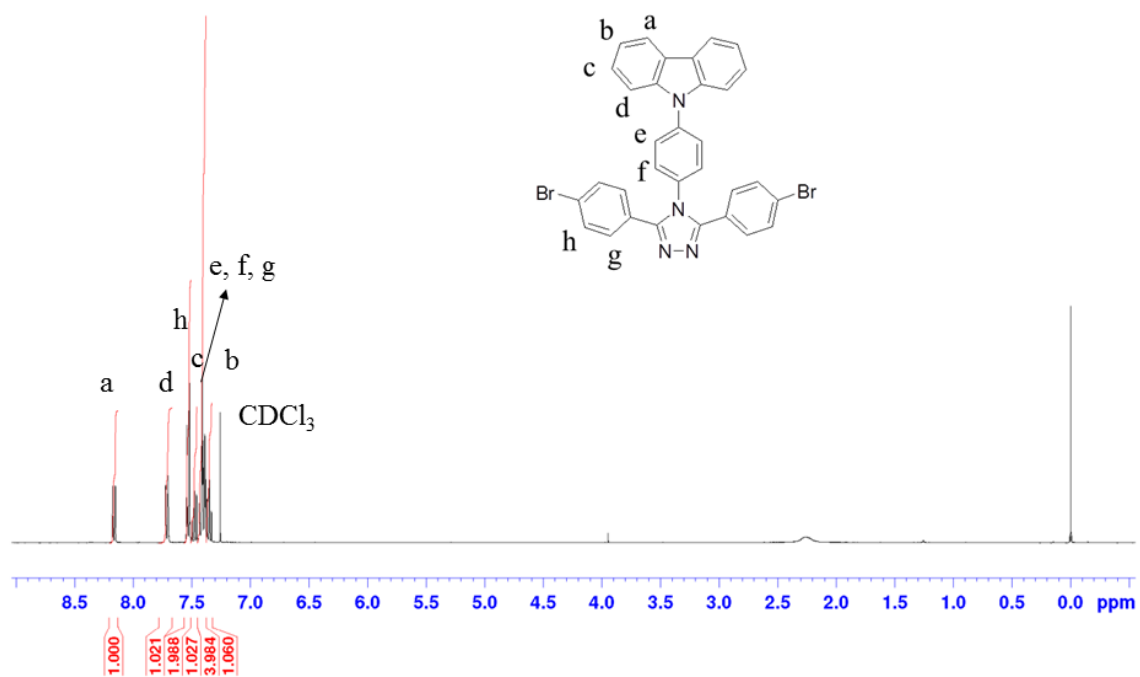


Figure S1. ^1H NMR spectrum of **8** in CDCl_3 .

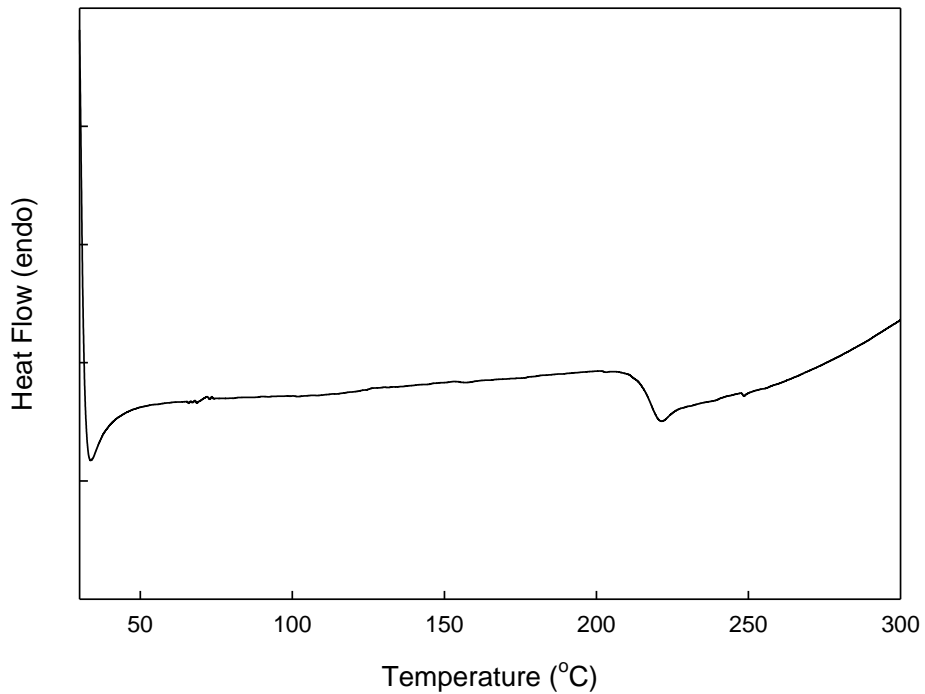


Figure S2. DSC trace of **FTzCz** recorded at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$.

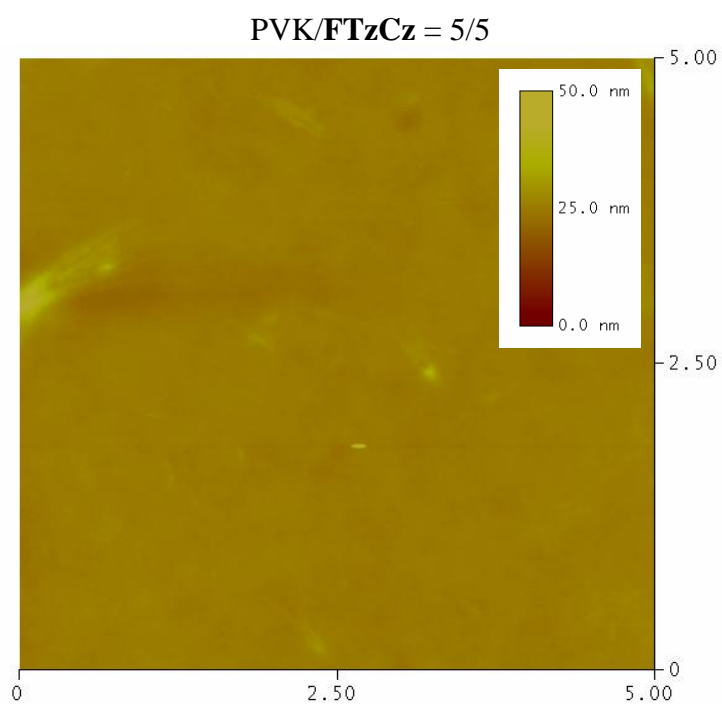


Figure S3. AFM images of blend films in different ratio of PVK and **FTzCz** coated on top of PEDOT:PSS layer.