

## Spiro-Configured Bipolar Hosts Incorporating 4,5-Diazafluorene as the Electron Transport Moiety for Highly Efficient Red and Green Phosphorescent OLEDs

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### *Electronic Supplementary Information*

## Experimental Section

### Synthesis

The synthesis of **CSC** and **DSD** were reported previously.<sup>1</sup>

**Synthesis of TST.** The mixture of 4,5-diaza-2',7'-dibromo-9,9'-spirobifluorene<sup>1,2</sup> (500 mg, 1.67 mmol), di-*p*-tolylamine (1.23 g, 8.35 mmol), biphenyl-2-yl-dicyclohexylphosphane (150 mg, 0.43 mmol), palladium (II) acetate (46.5 mg, 0.21 mmol), and sodium *tert*-butoxide (700 mg, 7.28 mmol) was dissolved in *o*-xylene (15 ml). The mixture was refluxed for 48 h. The reaction mixture was quenched with water and extracted with dichloromethane, and then the combined organic solution was dried over MgSO<sub>4</sub>. The crude mixture was purified by column chromatography on silica gel (EtOAc/CH<sub>2</sub>Cl<sub>2</sub> = 1/5) to give compound **TST** (511 mg, 69% yield) as a white solid. Mp 285 °C (DSC); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz) δ 8.62 (dd, *J* = 4.8, 1.6 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.24 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.16 (dd, *J* = 8.0, 4.8 Hz, 2H), 6.94~6.90 (m, 10H), 6.79~6.76 (m, 8H), 6.36 (d, *J* = 1.6 Hz, 2H), 2.23 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 158.4, 149.9, 147.5, 146.9, 144.9, 144.1, 135.5, 132.6, 131.8, 129.8, 124.2, 123.6, 122.8, 119.9, 117.7, 61.5, 20.7. HRMS (*m/z*, FAB<sup>+</sup>) Calcd for C<sub>51</sub>H<sub>40</sub>N<sub>4</sub> 708.3253, found (*M* + H<sup>+</sup>) 709.3336, Anal. Calcd. For C<sub>51</sub>H<sub>40</sub>N<sub>4</sub>: C, 86.41; H, 5.69; N, 7.90. Found: C, 86.59; H, 5.58; N, 7.90.

**Synthesis of NSN.** The mixture of 4,5-diaza-2',7'-dibromo-9,9'-spirobifluorene (500 mg, 1.67 mmol), 1-naphthylphenylamine (1.37 mg, 6.25 mmol), biphenyl-2-yl-dicyclohexylphosphane (150 mg, 0.12 mmol), palladium (II) acetate

(46.5 mg, 0.21 mmol), and sodium *tert*-butoxide (700 mg, 7.28 mmol) was dissolved in *o*-xylene (15 ml). The mixture was refluxed for 48 h. The reaction mixture was quenched with water and extracted with dichloromethane, and then the combined organic solution was dried over MgSO<sub>4</sub>. The crude mixture was purified by column chromatography on silica gel (EtOAc/CH<sub>2</sub>Cl<sub>2</sub> = 1/5) to give compound NSN (520 mg, 66% yield) as a white solid. Mp 308 °C (DSC); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz) δ 8.56 (dd, *J* = 4.8, 1.2 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.69 (t, *J* = 8.0 Hz, 4H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.40~7.34 (m, 4H), 7.25 (td, *J* = 8.0, 1.2 Hz, 2H), 7.19~7.08 (m, 6H), 7.03 (t, *J* = 8.0 Hz, 4H), 6.89 (dd, *J* = 8.0, 2.4 Hz, 2H), 6.84~6.78 (m, 6H), 6.36 (d, *J* = 2.4 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 157.4, 149.4, 147.9, 146.6, 144.1, 143.0, 135.4, 135.1, 132.2, 130.5, 129.0, 128.4, 126.6, 126.5, 126.1, 126.0, 125.8, 124.0, 123.7, 122.1, 121.9, 120.1, 116.8, 116.7, 61.4. HRMS (*m/z*, FAB<sup>+</sup>) Calcd for C<sub>55</sub>H<sub>36</sub>N<sub>4</sub> 752.2940, found (*M* + H<sup>+</sup>) 753.3019, Anal. Calcd. For C<sub>55</sub>H<sub>36</sub>N<sub>4</sub>: C, 87.74; H, 4.82; N, 7.44. Found: C, 87.49; H, 4.82; N, 7.41.

### Device Fabrication and Measurement.

All chemicals were purified through vacuum sublimation prior to use. The OLEDs were fabricated through vacuum deposition of the materials at 10<sup>-6</sup> torr onto ITO-coated glass substrates having a sheet resistance of 15 Ω/sqr. The ITO surface was cleaned ultrasonically—sequentially with acetone, methanol, and deionized water—and then it was treated with UV-ozone. The deposition rate of each organic material was ca. 1–2 Å s<sup>-1</sup>. Subsequently, LiF was deposited at 0.1 Å s<sup>-1</sup> and then capped with Al (ca. 5 Å s<sup>-1</sup>) through shadow masking without breaking the vacuum. The *J–V–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 glovebox system. EL spectra were measured using a photodiode array (OTO SD1200).

### Time-of-Flight 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 the organic film was monitored *in situ* using a quartz crystal sensor and calibrated using a thin film thickness measurement system (K-MAC ST2000). A pulsed nitrogen tunable dye laser was used as the excitation light source (to match the absorption of the organic film) through the semitransparent electrode (Ag)–induced photogeneration 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 (Ag); it was then recorded using a digital storage oscilloscope. Depending on the polarity of the applied bias, the selected carriers (holes or electrons) were swept across the sample with a transit time of  $t_T$ . For an applied bias  $V$  and a sample thickness  $D$ , the applied electric field  $E$  is equal to  $V/D$ ; the carrier mobility is then given by the equation  $m = D/(t_T E) = D^2/(Vt_T)$  from which the carrier transit times,  $t_T$ , can be extracted from the intersection points of the two asymptotes to the plateau and tail sections in the double-logarithmic plots.

### Reference

- [1] K.-T. Wong, H.-F. Chen and F.-C. Fang, *Org. Lett.*, 2006, **8**, 3501.
- [2] K.-T. Wong, R.-T. Chen, F.-C. Fang, C.-C. Wu and Y.-T. Lin *Org. Lett.*, 2005, **7**, 1979.