Electronic supplementary information

Solid-state highly fluorescent diphenylaminospirobifluorenylfumaronitrile red emitters for non-doped organic light-emitting diodes

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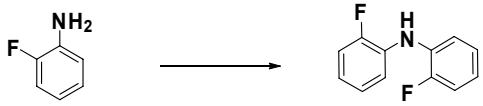
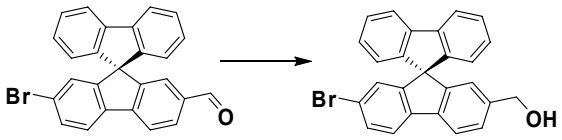
Synthesis and characterization

Bis(2-fluorophenyl)amine



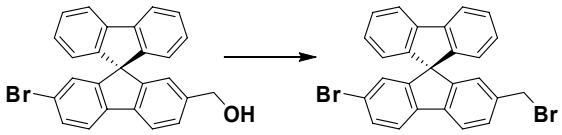
Under dry nitrogen atmosphere, a mixture of 1-bromo-2-fluorobenzene (16 g, 91 mmol), 2-fluoroaniline (10 g, 91 mmol), $Pd(OAc)_2$ (0.55 g, 2.4 mmol, 2.5 mol %), P(*t*Bu)$_3$ (0.99 g, 4.9 mmol, 5 mol %), and NaO*t*Bu (10.5 g, 11 mmol) in toluene (100 mL) was heated at 90 ^oC for 16 hours. After cooling to room temperature, saturated ammonium chloride solution was added to quench the reaction. The solution was extracted with ethyl acetate and dried over anhydrous $MgSO_4$. The solution was concentrated under reduced pressure and subjected to flash column chromatography (silica gel, ethyl acetate/hexanes: 1/20). A colorless liquid was obtained. Yield: 78% (16 g). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.31 (t, 2H, J = 8.2 Hz), 7.13 (t, 2H, J = 9.7 Hz), 7.07 (t, 2H, J = 7.8 Hz), 6.87-6.97 (m, 2H), 5.90 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 153.7 (d, J_{CF} = 240 Hz), 130.7 (d, J_{CF} = 11.3 Hz), 124.3, 121.6 (d, J_{CF} = 6.8 Hz), 118.2, 115.6 (d, J_{CF} = 19.5 Hz). FAB-MS: calcd MW 205.1, m/e = 205.1 (M^+). Anal. Found (calcd) for $C_{12}H_9F_2N$: C 70.19 (70.24), H 4.41(4.42), N 6.80 (6.83).

(2-Bromo-9,9'-spirobifluoren-7-yl)methanol



Under dry nitrogen atmosphere, $NaBH_4$ (1.1 g, 42 mmol) was added to a THF solution (70 mL) containing (2-Bromo-9,9'-spirobifluoren-7-yl)carxoaldehyde (6.0 g, 14 mol). The reaction was conducted at room temperature for 2 hours and then an excess amount of deionized water was added to quench the reaction. After three times of water extraction, the organic solution was dried over anhydrous $MgSO_4$. After the removal of drying agent, the solution was evaporated till dryness. A white solid was obtained and it was used in the next step of synthesis without further purification. Yield: 100% (6.0 g). ^{1}H NMR (400 MHz, $CDCl_3$) : δ (ppm) 7.84-7.77 (m, 3H), 7.67 (d, 1H, J = 8.1 Hz), 7.46 (dd, 1H, J = 6.3 Hz, J = 1.8 Hz), 7.39-7.35 (m, 3H), 7.11 (td, 2H, J = 8.7 Hz, J = 1.1 Hz), 6.82 (d, 1H, J = 1.7 Hz), 6.71-6.68 (m, 3H), 4.51 (d, 2H, J = 5.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.2, 149.2, 148.0, 147.9, 142.0, 141.4, 140.4, 140.2, 131.2, 128.3, 128.2, 127.5, 127.1, 127.0, 124.3, 122.8, 121.7, 121.5, 120.4, 65.4. FAB-MS: calcd MW 424.05; m/e = 424.0 (M^+). Anal. Found (calcd) for $C_{26}H_{17}BrO$: C 73.39 (73.42), H 4.01 (4.03).

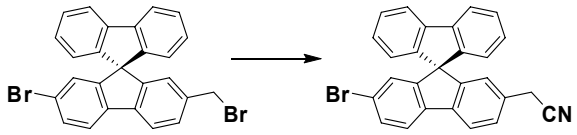
2-Bromo-7-(bromomethyl)-9,9'-spirobifluorene



Under dry nitrogen atmosphere, PBr_3 (1.6 mL, 17 mmol) was added drop wise to a dichloromethane solution (100 mL) containing (2-bromo-9,9'-spirobifluoren-7-yl)methanol (6.0 g, 14 mmol) at ice-bath cooling temperature (~0 ^{O}C). The solution was allowed to warm up slowly (within 1 hour) to room temperature and the reaction solution was further stirred for another 5 hours.

An excess amount of deionized water was added to quench the reaction. After three times of water extraction, the organic solution was dried over anhydrous $MgSO_4$. After the removal of drying agent, the solution was evaporated till dryness. An off-white solid was obtained and it was used in the next step of synthesis without further purification. Yield: 99% (6.8 g). ^{1}H NMR (400 MHz, $CDCl_3$) : δ (ppm) 7.86-7.76 (m, 3H), 7.67 (d, 1H, *J* = 8.2 Hz), 7.48 (dd, 1H, *J* = 6.3 Hz, *J* = 1.8 Hz), 7.43-7.35 (m, 3H), 7.15-7.10 (m, 2H), 6.83 (d, 1H, *J* = 1.7 Hz), 6.73-6.70 (m, 3H), 4.31 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 147.7, 141.9, 142.0, 140.3, 138.1, 131.3, 129.5, 128.4, 128.3, 128.2, 128.1, 127.5, 124.8, 124.3, 121.7, 121.6, 120.6, 120.4, 120.3, 33.7. FAB-MS: calcd MW 485.96; m/e = 485.9 (M^+). Anal. Found (calcd) for $C_{26}H_{16}Br_2$: C 63.89 (63.96), H 3.34 (3.30).

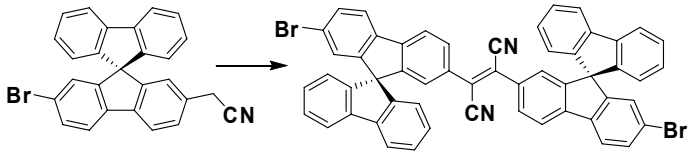
2-(2-Bromo-9,9'-spirobifluoren-7-yl)acetonitrile



Under dry nitrogen atmosphere, NaCN (0.92 g, 18.7 mmol) was added to a dry DMSO solution (125 mL) containing 2-bromo-7-(bromomethyl)-9,9'-spirobifluorene (6.1 g, 12.5 mmol). The solution was thoroughly stirred and heated at 80 ^{o}C for 12 hours. After cooling to room temperature, the solution was evaporated till dryness under vacuum. The solid residue was re-dissolved in dichloromethane and the solution was extracted with saturated NaCl solution. The organic solution was dried over anhydrous $MgSO_4$. After the removal of drying agent, the solution was evaporated till drynesss. The product was subjected to purification by flash column chromatography (silica gel, dichloromethane/hexanes : 2/3). A white solid was obtained. Yield: 50% (2.7 g). ^{1}H NMR (400 MHz, $CDCl_3$) : δ (ppm) 7.85-7.79 (m,

3H), 7.68 (d, 1H, *J* = 8.2 Hz), 7.48 (dd, 1H, *J* = 8.1 Hz, *J* = 1.8 Hz), 7.40-7.34 (m, 3H), 7.12 (t, 2H, *J* = 8.0 Hz, *J* = 1.0 Hz), 6.83 (d, 1H, *J* = 1.7 Hz), 6.69 (d, 2H, *J* = 7.6 Hz), 6.60 (s, 1H), 3.56 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 147.5, 141.9, 140.9, 140.0, 131.3, 130.0, 128.5, 128.3, 128.2, 128.0, 127.6, 124.2, 124.0, 122.1, 121.7, 121.0, 120.5, 120.4, 117.9, 112.23, 23.7. FAB-MS: calcd MW 433.05; m/e = 433.0 (M^+). Anal. Found (calcd) for $C_{27}H_{16}BrN$: C 74.49 (74.66), H 3.78 (3.71), N 3.16 (3.22).

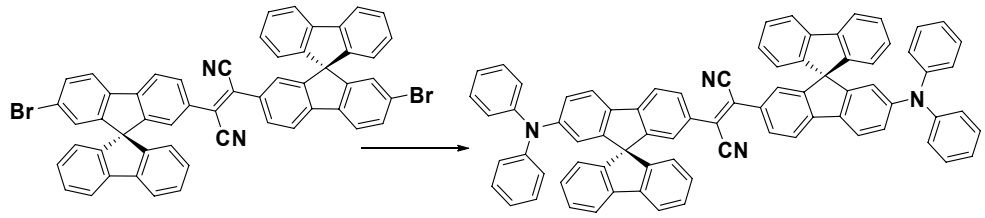
2,3-Bis(2-bromo-9,9'-spirobifluoren-7-yl)fumaronitrile



Under dry nitrogen atmosphere, iodine (1.2 g, 4.6 mmol) was added to a dry solution of diether ether and THF (40 and 20 mL) containing 2,3-bis(2-bromo-9,9'-spirobifluoren-7-yl)fumaronitrile (2.0 g, 4.6 mmol) at -78 ^{o}C. A 3 M methanol solution (1.29 mL) containing sodium methoxide (0.57 g, 10.5 mmol) was added dropwise to the reaction solution. After 30 minutes of stirring, the reaction was quenched by the addition of a mixture (1:3 in volume) of 2 N HCl aqueous solution and methanol. Formation of bright yellow precipitate was observed. The solid was isolated by filtration and dried under reduced pressure. Yield: 96% (1.9 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84-7.65 (m, 3H), 7.55-7.49 (m, 2H), 7.36-7.20 (m, 3H), 7.09 (t, 2H), 6.78 (d, 1H, *J* = 1.6 Hz), 6.51 (d, 2H, *J* = 7.6 Hz), 6.44 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 151.9, 149.4, 146.6, 141.8, 139.0, 131.4, 130.1, 129.6, 128.7, 128.3, 128.2, 127.7, 125.2, 125.0, 124.0, 123.4, 122.5, 120.8, 120.4, 120.2, 1.25. FAB-MS: calcd MW 862.06, m/e =

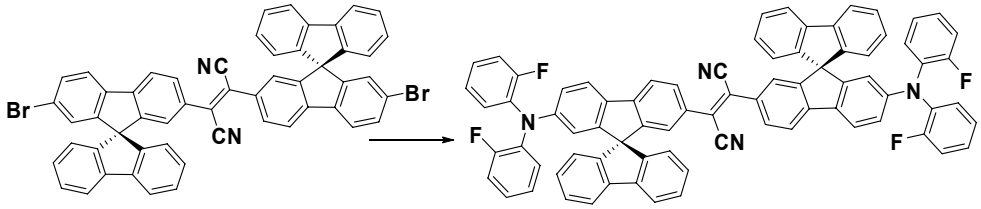
862.1 (M^+). Anal. Found (calcd) for $C_{54}H_{28}Br_2N_2$: C 74.98 (75.01), H 3.22 (3.26), N 3.25 (3.24).

2,3-Bis(2-(diphenylamino)-9,9'-spirobifluorene-7-yl)fumaronitrile

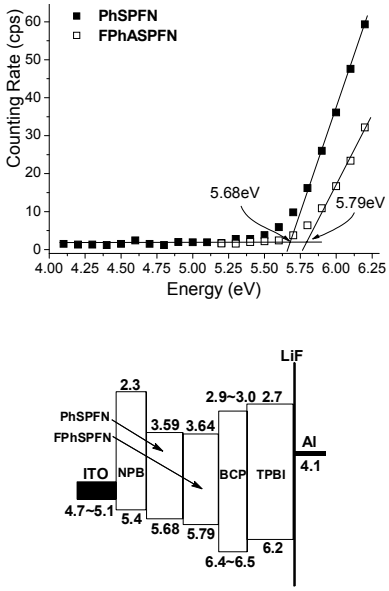


Under dry nitrogen atmosphere, a mixture of 2,3-bis(2-(diphenylamino)-9,9'-spirobifluorene-7-yl)fumaronitrile (1.8 g, 2.1 mmol), diphenylamine (0.85 g, 4.8 mmol), cesium carbonate (1.6 g, 4.8 mmol), palladium acetate (0.024 g, 0.10 mmol), P(*t*Bu)$_3$ (0.10 mL, 0.42 mmol), and dry xylenes (10 mL) was heated at 120 ^{o}C for 12 hours. The reaction was quenched by an excess amount of saturated sodium chloride solution. The solution was extracted with dichloromethane. The organic solution was dried over anhydrous $MgSO_4$. After the removal of drying agent, the solution was evaporated till drynesss. The product was subjected to purification by flash column chromatography (silica gel, dichloromethane/hexanes: 2/3). A brown-red solid was obtained. Yield: 90% (1.96 g). ^{1}H NMR (400 MHz, $CDCl_3$) : δ (ppm) 7.75-7.63 (m, 5H), 7.29 (t, 2H, *J* = 6.6 Hz), 7.11-7.06 (m, 6H), 6.98-6.88 (m, 8H), 6.74 (d, 2H, *J* = 7.6 Hz), 6.50 (d, 1H, *J* = 2.1 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2): δ(ppm) 151.0, 149.8, 148.9, 147.4, 147.2, 144.7, 134.6, 130.5, 129.1, 128.5, 127.9, 127.8, 124.3, 124.2, 124.0, 123.8, 123.4, 123.1, 121.4, 120.2, 119.6, 118.9, 116.7, 65.7. FAB-MS: calcd MW 1040.39, m/e = 1040.4 (M^+). Anal. Found (calcd) for $C_{78}H_{48}N_4$: C 89.37 (89.97), H 4.51 (4.65), N 5.65 (5.38).

2,3-Bis(2-bis(2-fluorophenyl)amine)-9,9'-spirobifluorene-7-yl)fumaronitrile



This fumaronitrile compound was prepared by a similar procedure to that of 2,3-bis(2-(diphenylamino)-9,9'-spirobifluorene-7-yl)fumaronitrile, except bis(2-fluorophenyl)amine used as the diarylamine and toluene as the solvent instead of xylenes: 2,3-bis(2-(diphenylamino)-9,9'-spirobifluorene-7-yl)fumaronitrile (0.80 g, 0.93 mmol), bis(2-fluorophenyl)amine (0.45 g, 2.2 mmol), cesium carbonate (0.72 g, 2.2 mmol), palladium acetate (0.012 g, 0.05 mmol), P(*t*Bu)$_3$ (0.046 mL, 0.19 mmol), and dry xylenes (10 mL) The product was obtained as a bright orange solid. Yield: 73% (0.75 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73-7.62 (m, 5H), 7.28 (t, 2H, J = 7.5 Hz), 7.07 (t, 2H, J = 7.6 Hz), 7.01-6.90 (m, 8H), 6.86 (s, 1H), 6.78 (d, 1H, J = 8.3 Hz), 6.73 (d, 2H, J = 7.6 Hz), 6.22 (s, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 157.7 (d, J_{CF} = 249.5 Hz), 151.2, 150.0, 148.5, 147.7, 146.1, 145.2, 141.8, 134.2, 133.7 (d, J_{CF} = 10.9 Hz), 130.5, 128.7, 128.1, 128.0, 126.4 (d, J_{CF} = 6.9 Hz), 124.8, 124.3, 124.1, 121.5, 120.3, 119.7, 119.3, 117.1(d, J_{CF} = 19.7 Hz), 115.0, 66.4. FAB-MS: calcd MW 1112.4, m/e = 1113.3 ([M+H]$^+$). Anal. Found (calcd) for $C_{78}H_{44}F_4N_4$: C 84.17 (84.16), H 3.92 (3.98), N 4.90 (5.03).



–Fig. S1. Top: Low energy photoelectron spectra of thin film samples of **PhSPFN** and **FPhSPFN**. Bottom: relative energy level (HOMO and LUMO) diagram of NPB, **PhSPFN**, **FPhSPFN**, BCP, and TPBI of non-dopant-based OLEDs.