Supporting Information

Fluorene Copolymers with High Efficiency Deep-Blue Electroluminescence

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Synthesis

Materials and Characterisation: Materials obtained from commercial suppliers were used without further purification. Solvents were dried and degassed following standard procedures. 1H NMR and 13C NMR spectra were recorded on a Bruker Avance 400 spectrometer. Both ASAP-TOF and HR mass spectra were obtained either on a Xevo QToF mass spectrometer (Waters Ltd, UK) equipped with an Agilent 7890 GC (Agilent Technologies UK Ltd, UK) or a LCT Premier XE mass spectrometer and an Acquity UPLC (Waters Ltd, UK). Compounds 51 and 82 were obtained according to previously reported procedures.

Scheme S1. Synthesis of Monomer 4.

9,9-Di(4-aminophenyl)-2,7-diiodofluorene (6): A suspension of 2,7-diiodofluorenone (1) (6.4 g, 14.81 mmol) and aniline hydrochloride (2.0 g, 14.81 mmol) in aniline (7 mL) was heated at 185 °C for 4 h under argon. Upon cooling, the resulting precipitate was filtered and
washed with a large quantity of methanol. This solid was further purified by column chromatography (silica gel, hexane/AcOEt 1:1 v/v) to give compound 6 as a white solid (90%). M.p.: 261-263 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 7.70 (s, 4H), 7.59 (s, 2H), 6.73-6.71 (m, 4H), 6.46-6.43 (m, 4H), 5.03 (s, 4H). ¹³C NMR (100 MHz, DMSO-d₆): δ = 154.3, 147.4, 138.0, 135.9, 134.2, 131.2, 128.1, 122.7, 113.7, 93.9, 63.8. MS (ASAP): m/z = 600.0 ([M]+). HRMS (ASAP): m/z = calculated for C₂₅H₁₈N₂I₂ [M]+ 599.9560, Found: 599.9570.

9,9'-Di(4-bromophenyl)-2,7-diiodofluorene (7): 9,9'-Di(4-aminophenyl)-2,7-diiodofluorene (6) (2.00 g, 5.74 mmol) was dissolved in a HBr (48 %)/water/DMSO 4:1:4 v/v mixture (30 mL) at 0 °C. A solution of NaN₂ (792 mg, 11.48 mmol) in water (20 mL) was then slowly added at 0 °C and stirred for 1 h at that temperature. The resulting yellow diazonium salts were filtered off and added to a solution of CuBr (1.64 g, 11.48 mmol) in HBr (48%) (20 mL) at 0 °C and stirred for 1 h at the same temperature. The mixture was then refluxed until no gas generation was observed. The resulting suspension was filtered and the precipitate was washed with water, then dried at 70 °C and chromatographed (silica gel, hexane/DCM 9:1 v/v), yielding 7 as a white solid (1.23 g, 42%). M.p.: 198-201 ºC. ¹H NMR (400 MHz, CDCl₃): δ = 7.72 (d, J = 7.7 Hz, 2H), 7.62 (s, 2H), 7.49 (d, J = 7.7 Hz, 2H), 7.41-7.38 (m, 4H), 7.01-6.99 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ = 152.2, 143.3, 139.0, 137.6, 135.2, 132.2, 129.9, 122.5, 121.9, 94.0, 64.9. MS (ASAP): m/z = 725.8 ([M]+). HRMS (ASAP): m/z = calculated for C₂₅H₁₄Br₂I₂ [M]+ 725.7552, Found: 725.7575.

9,9'-Di(4-bromophenyl)-9H-fluorene-2,7-diylbis-9H-3,6-di-tert-butylcarbazole (4): 9,9'-Di(4-bromophenyl)-2,7-diiodofluorene (7) (500 mg, 0.661 mmol), 3,6-di-tert-butylcarbazole (8) (369 mg, 1.322 mmol), Pd₂(dba)₃ (12 mg, 0.013 mmol) and XPhos (32 mg, 0.066 mmol) were dissolved in dry toluene (15 mL) and degassed for 30 min, then tBuONa (180 mg, 1.850 mmol) was added and reaction mixture degassed for a further 15 min. The mixture was stirred overnight at 80 °C. Upon cooling, the mixture was diluted with toluene (50 mL) and washed with water. The organic layer was dried over Na₂SO₄, filtered and solvent removed at low pressure. The residue was chromatographed (silica gel, hexane/DCM 3:1 v/v) to give (4) as a pale yellow solid (497 mg, 73%). M.p.: 149-151 °C. ¹H-NMR (400 MHz, acetone-d₆): δ = 8.29 (dd, J₁ = 2.1 Hz, J₂ = 0.7 Hz, 4H), 8.26 (d, J₁ = 8.1 Hz, 2H), 7.78 (d, J₁ = 2.0 Hz, 2H), 7.73 (dd, J₁ = 8.1 Hz, J₂ = 2.0 Hz, 2H), 7.54-7.52 (m, 4H), 7.47 (dd, J₁ = 8.7, J₂ = 2.1 Hz, 4H), 7.41-7.39 (m, 4H), 7.30 (dd, J₁ = 8.7 Hz, J₂ = 0.7 Hz, 4H), 1.43 (s, 36H). ¹³C-NMR (100 MHz, acetone-d₆): δ = 153.1, 145.2, 143.9, 139.8, 139.0,
138.8, 132.7, 131.0, 127.5, 125.0, 124.6, 124.5, 123.1, 121.8, 117.4, 110.0, 65.9, 35.3, 32.3.

MS (ASAP): \( m/z = 1031.3 \) ([M]\(^+\)). HRMS (ASAP): \( m/z = \) calculated for C\(_{65}H_{62}Br_2N_2 \) [M]\(^+\) 1028.3280, Found: 1028.3309.

**Fig. S1.** Absorption spectra of polymer P1.

**Fig. S2.** Absorption spectra of polymer P2.
**Fig. S3.** CIE diagrams for P1 and P2 devices at the turn-on voltage (10 cd m$^{-2}$) (left) and at the maximum brightness (right). The device structure is stated in Table 2, footnote a.

![CIE Diagrams](image)

**Fig. S4.** A photograph of a P1 PLED. The device structure is stated in Table 2, footnote a.

**References for the Supporting Information**
