

Supporting Information

## Fluorene Copolymers with High Efficiency Deep-Blue Electroluminescence

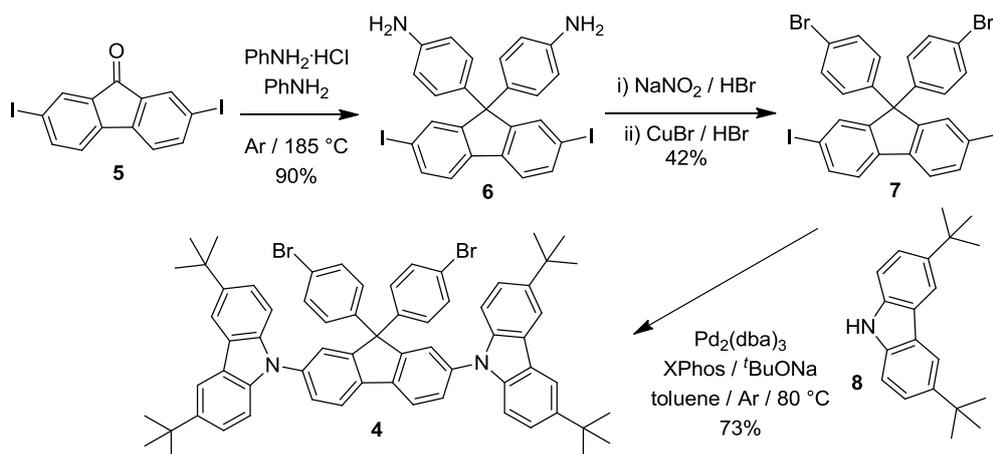
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### Synthesis

**Materials and Characterisation:** Materials obtained from commercial suppliers were used without further purification. Solvents were dried and degassed following standard procedures. <sup>1</sup>H NMR and <sup>13</sup>C 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 **5**<sup>1</sup> and **8**<sup>2</sup> were obtained according to previously reported procedures.



Scheme S1. Synthesis of Monomer **4**.

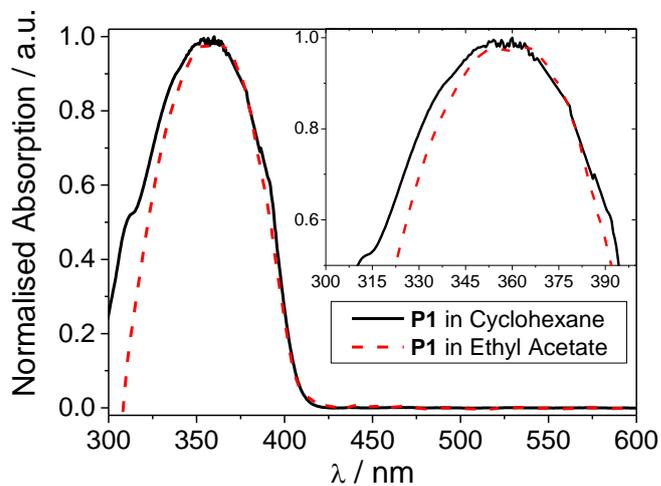
**9,9-Di(4-aminophenyl)-2,7-diiodofluorene (6):** A suspension of 2,7-diiodofluorenone (**1**) (6.4 g, 14.81 mmol) and aniline hydrochloride (2.0 g, 14.81 mmol) in aniline (7 mL) was heated at 185 °C for 4 h under argon. Upon cooling, the resulting precipitate was filtered and

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. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): 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). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): 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]<sup>+</sup>). HRMS (ASAP): *m/z* = calculated for C<sub>25</sub>H<sub>18</sub>N<sub>2</sub>I<sub>2</sub> [M]<sup>+</sup> 599.9560, Found: 599.9570.

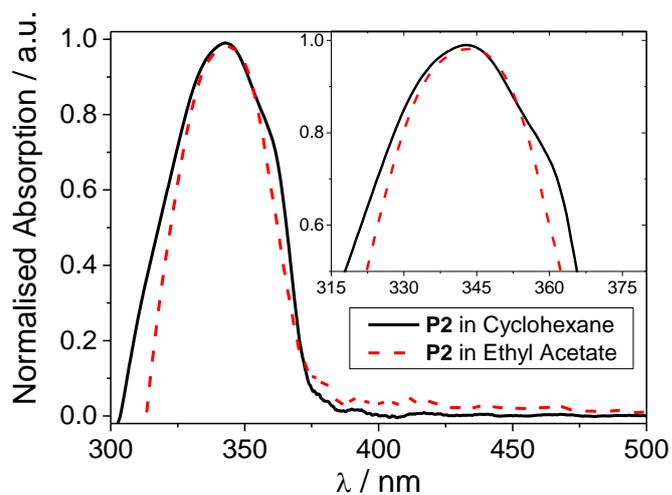
**9,9-Di(4-bromophenyl)-2,7-diiodofluorene (7):** 9,9-Di(4-aminophenyl)-2,7-diiodofluorene (**6**) (2.00 g, 5.74 mmol) was dissolved in a HBr (48 %)/water/DMSO 4:1:4 v/v mixture (30 mL) at 0 °C. A solution of NaNO<sub>2</sub> (792 mg, 11.48 mmol) in water (20 mL) was then slowly added at 0 °C and stirred 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 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 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). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): 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]<sup>+</sup>). HRMS (ASAP): *m/z* = calculated for C<sub>25</sub>H<sub>14</sub>Br<sub>2</sub><sup>127</sup>I<sub>2</sub> [M]<sup>+</sup> 725.7552, Found: 725.7575.

**9,9'-(9,9-di(4-bromophenyl)-9H-fluorene-2,7-diyl)bis-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), Pd<sub>2</sub>(dba)<sub>3</sub> (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 <sup>t</sup>BuONa (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 Na<sub>2</sub>SO<sub>4</sub>, 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. <sup>1</sup>H-NMR (400 MHz, acetone-d<sub>6</sub>): δ = 8.29 (dd, *J*<sub>1</sub> = 2.1 Hz, *J*<sub>2</sub> = 0.7 Hz, 4H), 8.26 (d, *J*<sub>3</sub> = 8.1 Hz, 2H), 7.78 (d, *J*<sub>4</sub> = 2.0 Hz, 2H), 7.73 (dd, *J*<sub>3</sub> = 8.1 Hz, *J*<sub>4</sub> = 2.0 Hz, 2H), 7.54-7.52 (m, 4H), 7.47 (dd, *J*<sub>5</sub> = 8.7 Hz, *J*<sub>1</sub> = 2.1 Hz, 4H), 7.41-7.39 (m, 4H), 7.30 (dd, *J*<sub>5</sub> = 8.7 Hz, *J*<sub>2</sub> = 0.7 Hz, 4H), 1.43 (s, 36H). <sup>13</sup>C-NMR (100 MHz, acetone-d<sub>6</sub>): δ = 153.1, 145.2, 143.9, 139.8, 139.0,

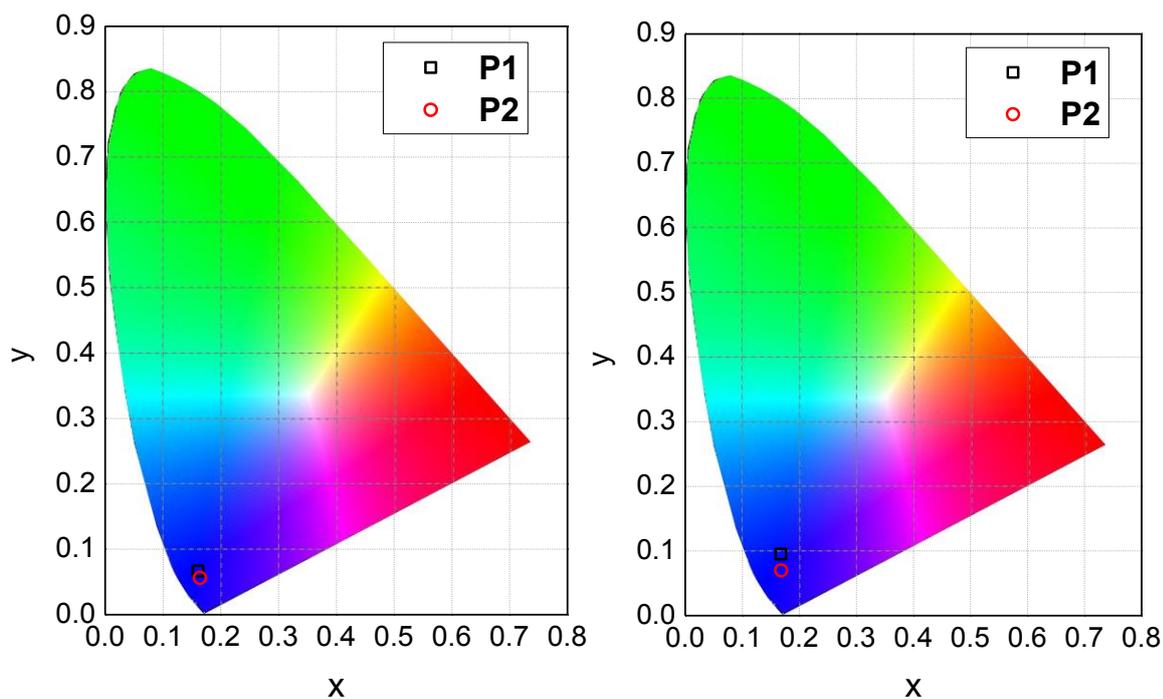
138.8, 132.7, 131.0, 127.5, 125.0, 124.6, 124.5, 123.1, 121.8, 117.4, 110.0, 65.9, 35.3, 32.3.  
MS (ASAP):  $m/z = 1031.3$  ( $[M]^+$ ). HRMS (ASAP):  $m/z =$  calculated for  $C_{65}H_{62}Br_2N_2$   $[M]^+$   
1028.3280, Found: 1028.3309.



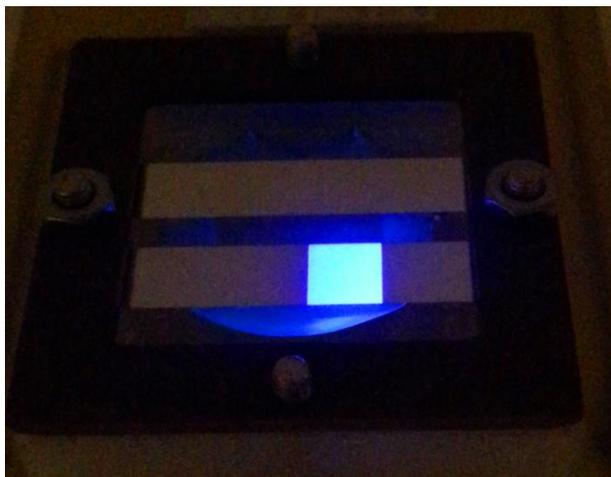
**Fig. S1.** Absorption spectra of polymer **P1**.



**Fig. S2.** Absorption spectra of polymer **P2**.



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



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

### References for the Supporting Information

1. F. Dewhurst and P. K. J. Shah, *J. Chem. Soc. C*, 1969, **11**, 1503–1504.
2. S. S. Palayangoda, X. Cai, R. M. Adhikari and D. C. Neckers, *Org. Lett.*, 2008, **10**, 281–284.