

## Supporting Information to PEHCP-Manuscript to Macromolecules

**Synthesis of 4,4'-dinitro-2-azidobiphenyl (II).** To a solution of 10.0g (38.6mmol) of 4,4'-dinitro-2-biphenylamine in a mixture of 200ml of acetic acid and 40ml of sulfuric acid at 0 °C was added dropwise 5.32g (77.1mmol) of sodium nitrite. The mixture was stirred at 5-10 °C for 2h before approximately 5.00g of urea (to destroy the excess of nitrous acid), 500ml of ice water and 5.00g of activated carbon were added. The mixture was stirred again for 20 minutes and filtrated rapidly through a Buchner funnel into a flask immersed in an ice bath. A solution of 5.07g (78.0mmol) of sodium azide in 100ml of water was added dropwise to the clear yellow filtrate. The resulting solution was stirred at 0 °C for 1h and at room temperature for 24h. The mixture was quenched with 500 ml of a solution of NaHCO<sub>3</sub> in water and extracted three times with ethyl acetate. The organic layer was dried over magnesium sulfate and the solvent was removed under vacuum. Recrystallization from ethanol afforded 8.81g of the title product as a yellow solid. (Yield: 80.1%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 8.33 (d, 2H), 8.16 (d, 1H), 8.10 (dd, 1H), 7.64(d, 2H), 7.53(d, 1H). <sup>13</sup>C NMR (300 MHz, Acetone-d<sub>6</sub>): δ (ppm) 150.30, 149.49, 144.42, 140.94, 138.57, 133.79, 132.40, 124.89, 121.30, 116.04.

**Synthesis of 2,7-dinitrocarbazole (III).** To 600ml of boiling kerosene (first washed with concentrated sulfuric acid) was added very slowly 6.00g (21.0mmol) of 4,4'-dinitro-2-azidobiphenyl. The resulting solution was maintained at reflux for 1h. After cooling, the solution was kept at 0 °C for 24h. The precipitate was filtered through a Buchner funnel and the solid was washed with petroleum ether. Final purification was obtained by recrystallization from ethanol to afford 4.66g of the title product. (Yield: 86%). <sup>1</sup>H NMR

(300 MHz, D<sub>6</sub>-Acetone):  $\delta$  (ppm) 11.35 (s, 1H), 8.53 (dd, 4H), 8.16 (dd, 2H). <sup>13</sup>C NMR (300 MHz, Acetone-d<sub>6</sub>):  $\delta$  (ppm) 148.81, 142.63, 127.93, 123.65, 116.32, 109.28.

**Synthesis of 2,7-diaminocarbazole (IV).** To a solution of 2,7-dinitrocarbazole (6.00g, 23.3mmol) in a mixture of acetic acid (200ml) and hydrochloric acid 8N (70ml) was added 44.3g (0.23mol) of tin (II) chloride. The mixture was refluxed for 24h under nitrogen. After cooling, the precipitate was separated from the solvent by filtration and washed several times with cold acetic acid. The resulting diammonium salt was dissolved in water followed by addition of an aqueous solution of sodium hydroxide until the PH reached a value of 10. The precipitate was collected by filtration and dried under reduced pressure. Recrystallization in ethanol afforded 3.08g of the title product as a shiny gray solid. (Yield: 67%). <sup>1</sup>H NMR (300 MHz, D<sub>6</sub>-Acetone):  $\delta$  (ppm) 9.42 (s, 1H), 7.53 (d, 2H), 6.63 (dd, 2H), 6.47 (dd, 2H), 4.43(s, 4H). <sup>13</sup>C NMR (300 MHz, Acetone-d<sub>6</sub>):  $\delta$  (ppm) 147.22, 143.19, 120.39, 117.22, 109.34, 97.05.

**Synthesis of 2,7-diiodocarbazole (V).** To a solution of 1.50g (7.61mmol) of 2,7-diaminocarbazole in 100ml of 3M HCl solution at 0 °C was added very slowly 1.10g (15.9mmol) of sodium nitrite in 5ml of water. The mixture was stirred at 0 °C for 2h and then added to 100ml of a solution of potassium iodide. The precipitate was collected by filtration and washed with aqueous solution of NaHCO<sub>3</sub>. The solid was dried under vacuum for 24h and use directly in the next reaction without further purification.

**Synthesis of N-(2-ethylhexyl)-2,7-diiodocarbazole (VI).** This compound was synthesized by a modification method of reference.<sup>16</sup> A typical procedure is as following: a mixture of 2,7-diiodocarbazole (6g, 14.3 mmol) and benzytrimethylammonium chloride (0.35 g, 1.4 mmol) in 30 ml of DMSO and 10 ml of aqueous NaOH (50 %, w/w) was

stirred under N<sub>2</sub> at 80 °C . 2-ethylhexyl bromide(7.0g, 36.3 mmol) was added to the mixture, the resulting mixture was stirred at the same temperature for 3 h before 20 ml of water was added. Then the solution was extracted three times with diethyl ether (80 ml). The combined organic layers were washed with saturated brine and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure. The crude product was further purified by column chromatography(silica gel, hexane as eluent) followed by recrystallization in ethanol to afford 1.57g of the title product as a white solid. (Global yield for the last two steps: 38.5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.78 (d, 2H), 7.71 (d, 2H), 7.52 (dd, 2H), 4.05 (dd, 2H), 2.01(m, 1H), 1.34(m, 8H) 0.90(m, 6H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 141.6, 128.1, 121.6, 118.2, 90.7, 47.4, 39.0, 30.6, 28.4, 24.2, 22.9, 13.9, 10.8.

**Synthesis of 2,7-bis(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan - 2-yl) – N - (2 – ethylhexyl)carbazole (VII).** A typical synthetic procedure for the synthesis of the carbazole derivative monomer: to a solution of N-(2-ethylhexyl)-2,7-diiodocarbazole (10.6 g, 20 mmol) in anhydrous THF (150 ml) under N<sub>2</sub> at –78 °C , was added 37.5 ml (60mmol) of n-BuLi(1.6 M in hexane) by syringe. The mixture was stirred at -78 °C and warmed to 0 °C for 30 mins, and cooled again at –78 °C, then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12.24 ml, 60mmol) was rapidly injected into the solution by syringe, the resulting mixture was stirred at –78 °C for 1 h and left to stir overnight at room temperature. The resulting mixture was poured into water and extracted with ether. The ether extracts were washed with saturated brine and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure, the crude solid product was further purified by column chromatography(silica gel, hexane:dichloromethane=2:1 as eluent) followed by recrystallization in ethanol to afford 4.5g of the title product as a

white solid. (Yield 42.4%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.11 (d, 2H), 7.88 (s, 2H), 7.66 (d, 2H), 4.26 (m, 2H), 2.12 (m, 1H), 1.39(m, 32H), 0.90(m, 6H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 140.82, 124.91, 124.62, 119.82, 115.53, 83.64, 47.04, 39.10, 30.56, 28.40, 24.85, 24.31, 22.94, 14.01, 10.88.