Supporting materials for

Synthesis and self-assembly behaviour of poly(fluorenyl styrene)-*block*-poly(2-vinyl pyridine) block copolymers and their blends with single wall carbon nanotubes (SWCNTs)

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Experimental section

2-Bromo-9,9-dihexylfluorene (2). 1-Bromohexane (50.3 mL, 357 mmol) was added to a mixture of 2-bromofluorene (25.0 g, 102 mmol) and $(C_4H_9)_4NBr$ (3.30 g, 10.2 mmol) dissolved in DMSO (250 mL) and 50 % (*w/w*) aqueous NaOH (35 mL). The reaction mixture was stirred at 70 °C for overnight and then poured into a large excess of ethyl acetate. After filtration to remove precipitated NaOH, the organic layer was washed with dilute 2*N* HCl, brine, and then dried over anhydrous $MgSO_4$. After filtration, followed by removal of the solvents by evaporation, the residual product was purified by chromatography on silica gel with hexane as eluent to yield the title compound (36.0 g, 85.2%) as a light yellow liquid. ^{1}H NMR ($CDCl_3$, ppm): 7.64 (m, 1H), 7.54 (d, 1H), 7.43 (m, 2H), 7.30 (d, 3H), 1.94 (m, 4H), 1.12 (m, 12H), 0.77 (m, 6H), 0.60 (m, 4H).

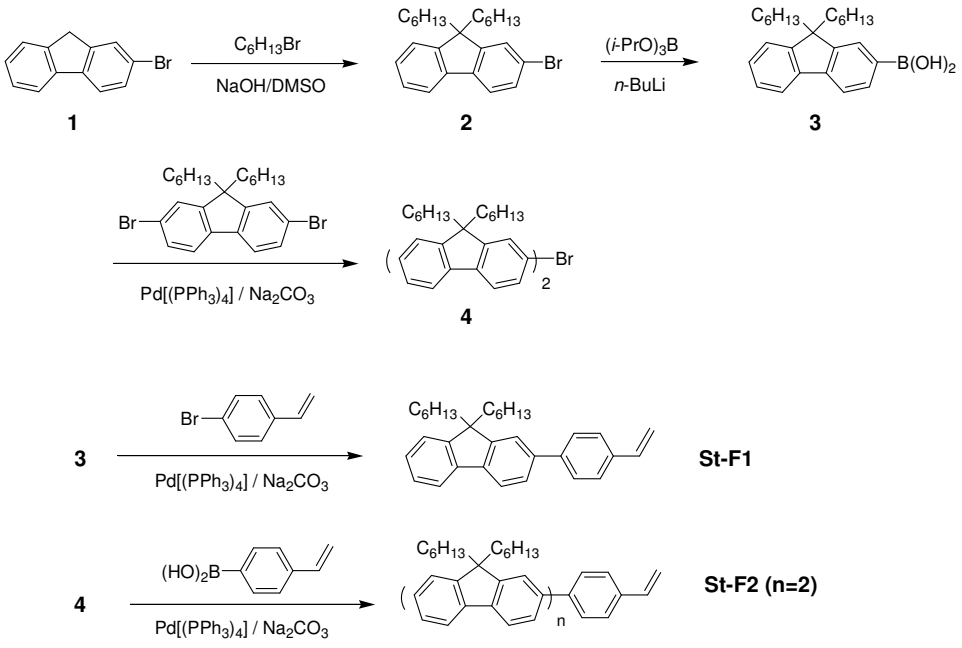
9,9-Dihexylfluorenyl-2-boronic acid (3). To an absolute THF solution (250 mL) of 2-bromo-9,9-dihexylfluorene (37.0 g, 89.5 mmol) was slowly added BuLi (2.5 *M* in hexane, 50.1 mL, 125 mmol) at -78 °C. The reaction mixture was stirred for an additional 1 h at -78 °C and then, tri(isopropyl) borate (82.6 mL, 358 mmol) was added to the mixture. The reaction mixture was gradually warmed to room temperature and stirred for overnight, followed by quenching with dilute 2*N* HCl. The organic layer was washed with water and dried over anhydrous $MgSO_4$. After filtration, followed by removal of the solvents by evaporation, the residual product was purified by column chromatography on silica gel with hexane to afford the title compound as a white solid (26.5 g, 78 %). ^{1}H NMR (CD_2Cl_2, ppm): 8.34 (d, 1H), 8.21 (s, 1H), 7.92 (d, 1H), 7.85-7.82 (m, 1H), 7.76-7.72 (m, 2H), 7.44-7.31 (m, 3H), 2.14-1.97 (m, 4H), 1.26-1.02 (m, 12H), 0.77-0.55 (m, 10H).

7-Bromo-9,9,9',9'-tetrahexyl-2,2'-bifluorene (4). A mixture of 9,9-dihexylfluorenyl-2-boronic acid (5.00 g, 13.2 mmol), 9,9-dihexyl-2,7-dibromofluorene (11.4 g, 22.4 mmol), $Pd(PPh_3)_4$ (304 mg, 0.26 mmol), Na_2CO_3 (2.0 *M* aqueous solution, 25.0 mL), and toluene (30 mL) was stirred at 90 °C for 1 day. After cooling to room temperature, the reaction mixture was poured into a large excess of petroleum ether. The organic layer separated was washed with brine and dried over anhydrous $MgSO_4$. After filtration and evaporation of the solvents, the crude product was purified by column chromatography on silica gel with hexane to afford the title compound as a white solid (5.0 g, 50%). ^{1}H NMR (CD_2Cl_2, ppm): 7.80-7.76 (m, 3H), 7.67-7.61 (m, 5H), 7.53-7.49 (m, 2H), 7.38-7.33 (m, 3H), 2.10-2.03 (m, 8H), 1.27-1.04 (m, 24H), 0.78-0.65 (m, 20H).

9,9-Dihexyl-2-(4-vinylphenyl)-9H-fluorene (St-F1). A mixture of 9,9-dihexylfluorenyl-2-boronic acid (18.0 g, 47.6 mmol), 4-bromostyrene (10.4 g, 57.1 mmol), $Pd(PPh_3)_4$ (1.06 g, 0.95 mmol), Na_2CO_3 (2.0 M aqueous solution, 30.0 mL), and THF (150 mL) was stirred at 90 °C for 2 days. After the reaction mixture was cooled to room temperature, it was poured into a large excess of petroleum ether. The organic portion separated was washed with brine and dried over anhydrous $MgSO_4$. After filtration, followed by removal of the solvents by evaporation, the crude product was purified by column chromatography on silica gel with hexane to afford **St-F1** as an oily product (5.2 g, 25 %). 300 MHz ^{1}H NMR ($CDCl_3$, ppm): 7.76-7.71 (m, 2H, Ar), 7.65 (d, 2H, Ar), 7.59-7.51 (m, 4H, Ar), 7.36-7.26 (m, 3H, Ar), 6.79-6.75 (m, 1H, CH=), 5.83 and 5.30 (2d, 2H, CH_2=), 2.01-1.99 (m, 4H, $C(C\underline{H}_2C_5H_{11})_2$), 1.13-1.04 and 0.77-0.64 (m,

22H, C($CH_2C_5\underline{H}_{11}$)$_2$). 75 MHz ^{13}C NMR ($CDCl_3$, ppm) 151.38, 150.95, 141.08, 140.72, 140.50, 139.50 (Ar), 136.45 (CH=), 127.21, 127.02, 126.77, 126.63, 125.77, 122.84, 121.22, 119.92, 119.73 (Ar), 113.7 (CH_2=), 55.12 ($\underline{C}(C_6H_{13})_2$), 40.41, 31.45, 29.70, 23.75, 22.55 (CH_2), 13.97 (CH_3). Anal. Cal for $C_{33}H_{40}$: C, 90.77; H, 9.23. Found: C, 90.89%; H, 9.11%.

9,9-Dihexyl-2-(9,9-dihexyl-2-(4-vinylphenyl)-9H-fluoren-7-yl)-9H-fluorene(St-F2). A mixture of 7-bromo-9,9,9',9'-tetrahexyl-2,2'-bifluorene (10.0 g, 13.4 mmol), 4-vinylphenylboronic acid (3.00 g, 20.1 mmol), $Pd(PPh_3)_4$ (300 mg, 0.26 mmol), Na_2CO_3 (2.0 M aqueous solution, 6.7 mL), and THF (100 mL) was stirred at 80 °C for 2 days. After the reaction mixture was cooled to room temperature, it was poured into a large excess of petroleum ether. The organic layer separated was washed with brine and dried over anhydrous $MgSO_4$. After filtration, followed by removal of the solvents by evaporation, the crude product was purified by column chromatography on silica gel with hexane to afford **St-F2** as a semi-solid (4.5 g, 43 %). 300 MHz ^{1}H NMR ($CDCl_3$, ppm): 7.80-7.73 (m, 4H, Ar), 7.67-7.52 (m, 10H, Ar), 7.36-7.26 (m, 3H, Ar), 6.80-6.76 (m, 1H, CH=), 5.84 and 5.30 (2d, 2H, CH_2=), 2.07-2.02 (m, 8H, C($C\underline{H}_2C_5H_{11}$)$_2$), 1.14-1.08 and 0.78-0.71 (m, 44H, C($CH_2C_5\underline{H}_{11}$)$_2$). 75 MHz ^{13}C NMR ($CDCl_3$, ppm) 151.75, 151.46, 151.00, 141.08, 140.79, 140.61, 140.49, 140.34, 140.21, 139.91, 139.51 (Ar), 136.47 (CH=), 127.23, 126.98, 126.79, 126.66, 126.16, 126.04, 125.88, 122.91, 121.46, 121.41, 121.33, 120.00, 119.88, 119.71 (Ar), 113.76 (CH_2=), 55.29, 55.16 ($\underline{C}(C_6H_{13})_2$), 40.39, 31.46, 29.68, 23.78, 22.55 (CH_2), 13.99 (CH_3). Anal. Cal for $C_{58}H_{72}$: C, 90.57; H, 9.43. Found: C, 90.73%; H, 9.31%.



Scheme S1. Synthesis of Monomer: Vinyl-oligo(fluorene)s with Different Chain Lengths.

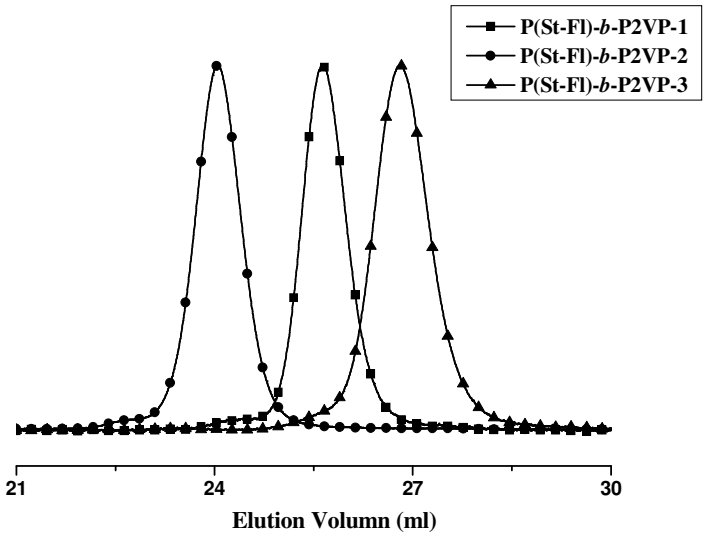


Figure S1. SEC Curves of Poly(**St-Fl**)-*block*-P2VP.

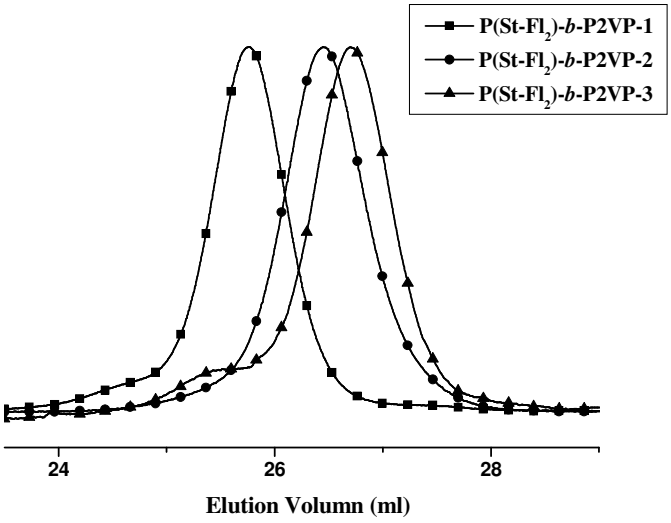


Figure S2. SEC Curves of Poly(**St-Fl$_2$**)-*block*-P2VP.

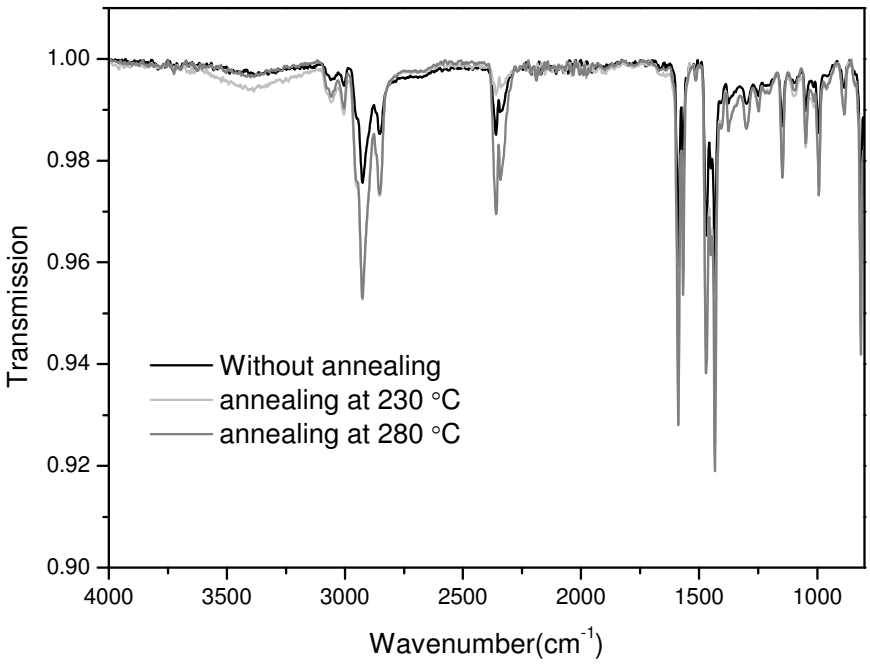


Figure S3. FTIR of P(St-Fl_2)-*b*-P2VP-1 with different annealing history.