

Supporting Information

Living Anionic Polymerization of Styrene Derivatives *p*-Substituted with π -Conjugated Oligo(fluorene) Moieties

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Experiment 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. 1H 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 %). 1H 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).

9,9,9',9'-Tetra-*n*-hexyl-2,2'-bifluorenyl-7-boronic acid (4). The procedure for 9,9-di-*n*-hexylfluorenyl-2-boronic acid was followed to prepare 9,9,9',9'-tetra-*n*-hexyl-2,2'-bifluorenyl-7-boronic acid as a white solid (12.0 g, 87 %) using 7-bromo-9,9,9',9'-tetra-*n*-hexyl-2,2'-bifluorene (14.3 g, 19.16

mmol). ¹H NMR (CDCl₃, ppm): 8.34 (d, 1H), 8.27 (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 (5). 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(PPh₃)₄ (304 mg, 0.26 mmol), Na₂CO₃ (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 MgSO₄. 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%). ¹H NMR (CD₂Cl₂, 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).

7-Bromo-9,9,9',9',9'',9''-hexa-*n*-hexyl-2,7';2',7''-terfluorene (6). The procedure for 7-bromo-9,9,9',9'-tetra-*n*-hexyl-2,2'-bifluorene was followed to prepare 7-bromo-9,9,9',9',9'',9''-hexa-*n*-hexyl-2,7';2',7''-terfluorene as white solids (8.6 g, 47 %) using 9,9,9',9'-tetra-*n*-hexyl-2,2'-bifluorenyl-7-boronic acid (12.0 g, 16.8 mmol). ¹H NMR (CD₂Cl₂, ppm): 7.85-7.78 (m, 5H), 7.70-7.62 (m, 9H), 7.57-7.53 (m, 2H), 7.44-7.39 (m, 3H), 2.12-2.06 (m, 12H), 1.14-1.08 (m, 36H), 0.79-0.69 (m, 30H).

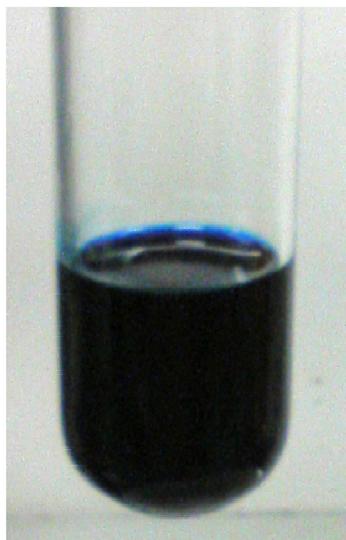


Figure S1. Characteristic color observed in the anionic polymerization of **St-FI** in THF at $-78\text{ }^{\circ}\text{C}$.

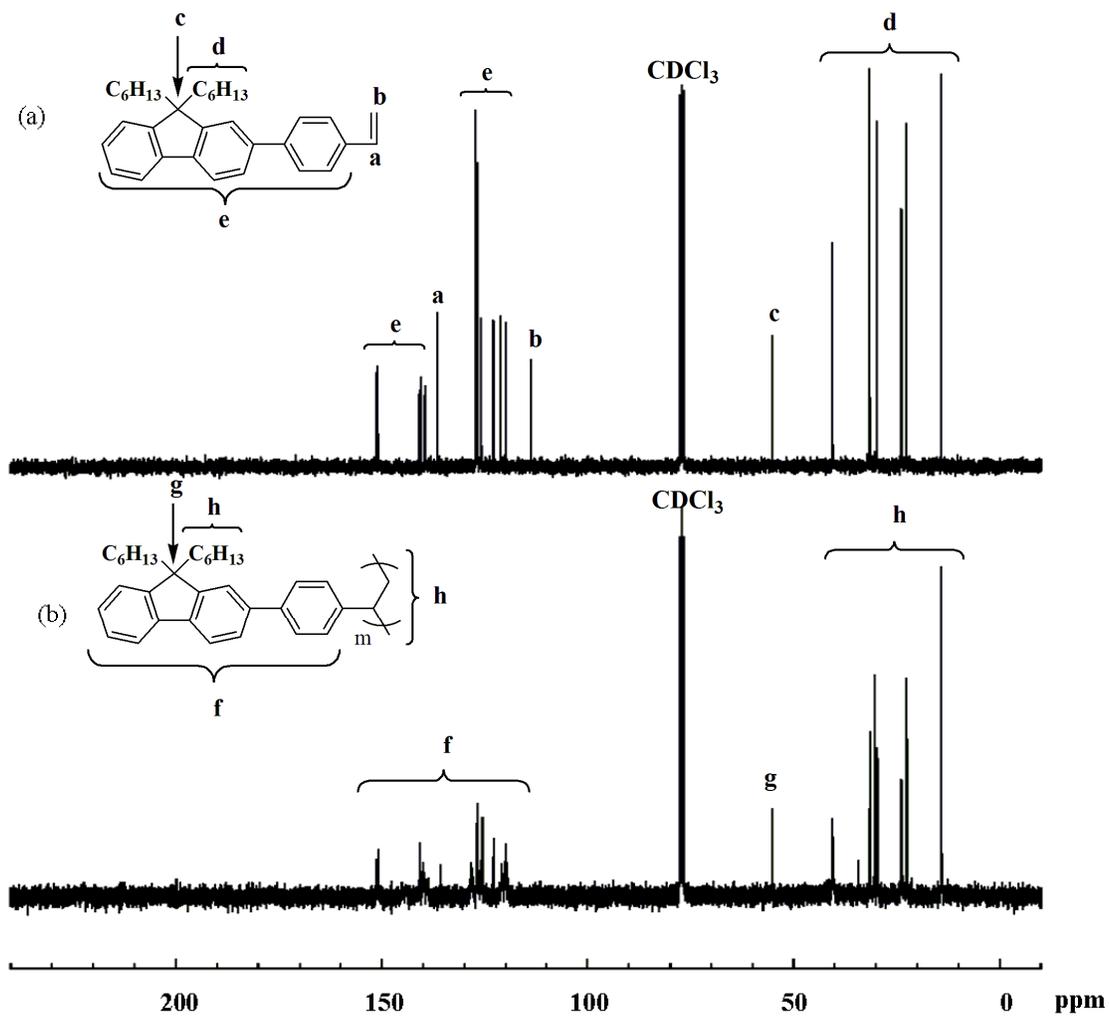


Figure S2. ^{13}C NMR spectra of (a) St-FI and (b) poly(St-FI) in CDCl_3 .

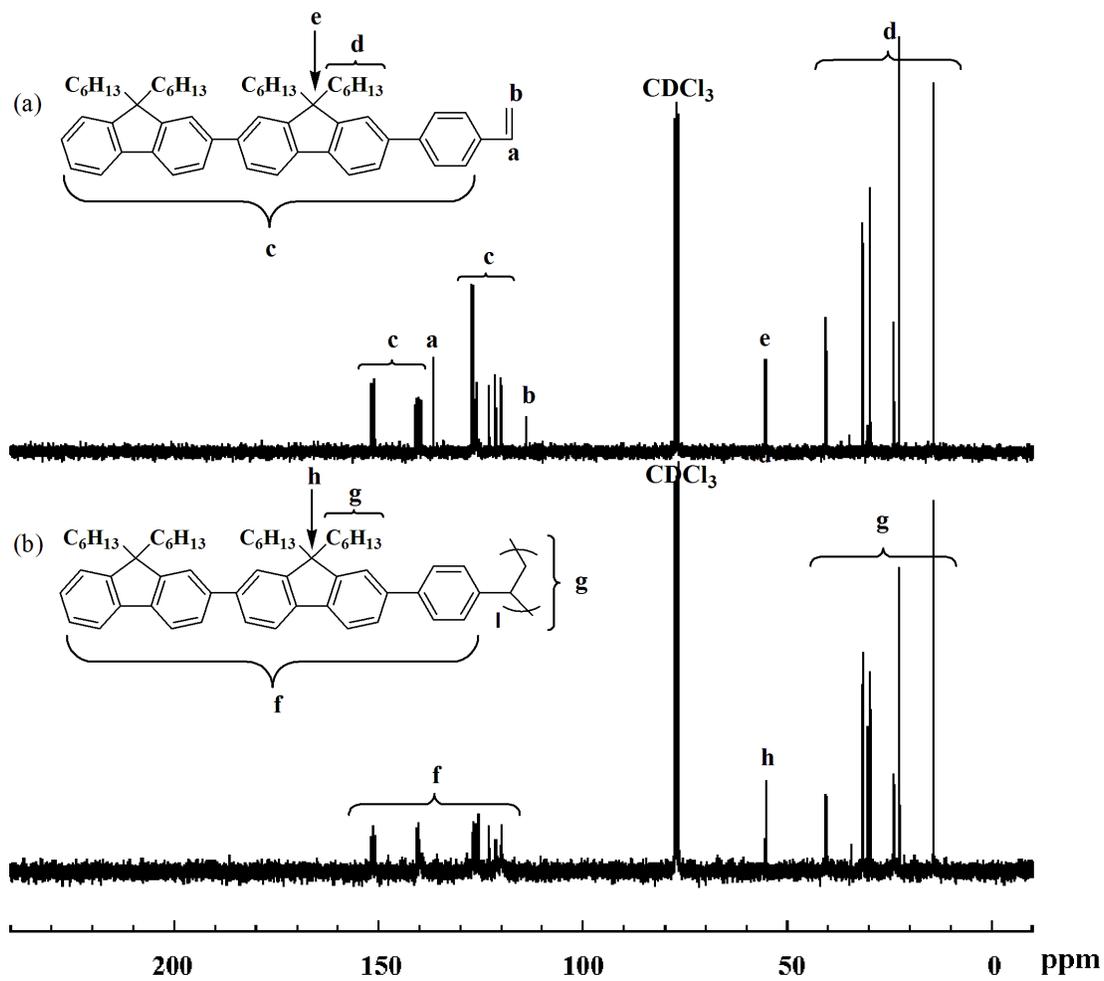


Figure S3. ^{13}C NMR spectra of (a) St-Fl₂ and (b) poly(St-Fl₂) in CDCl_3 .

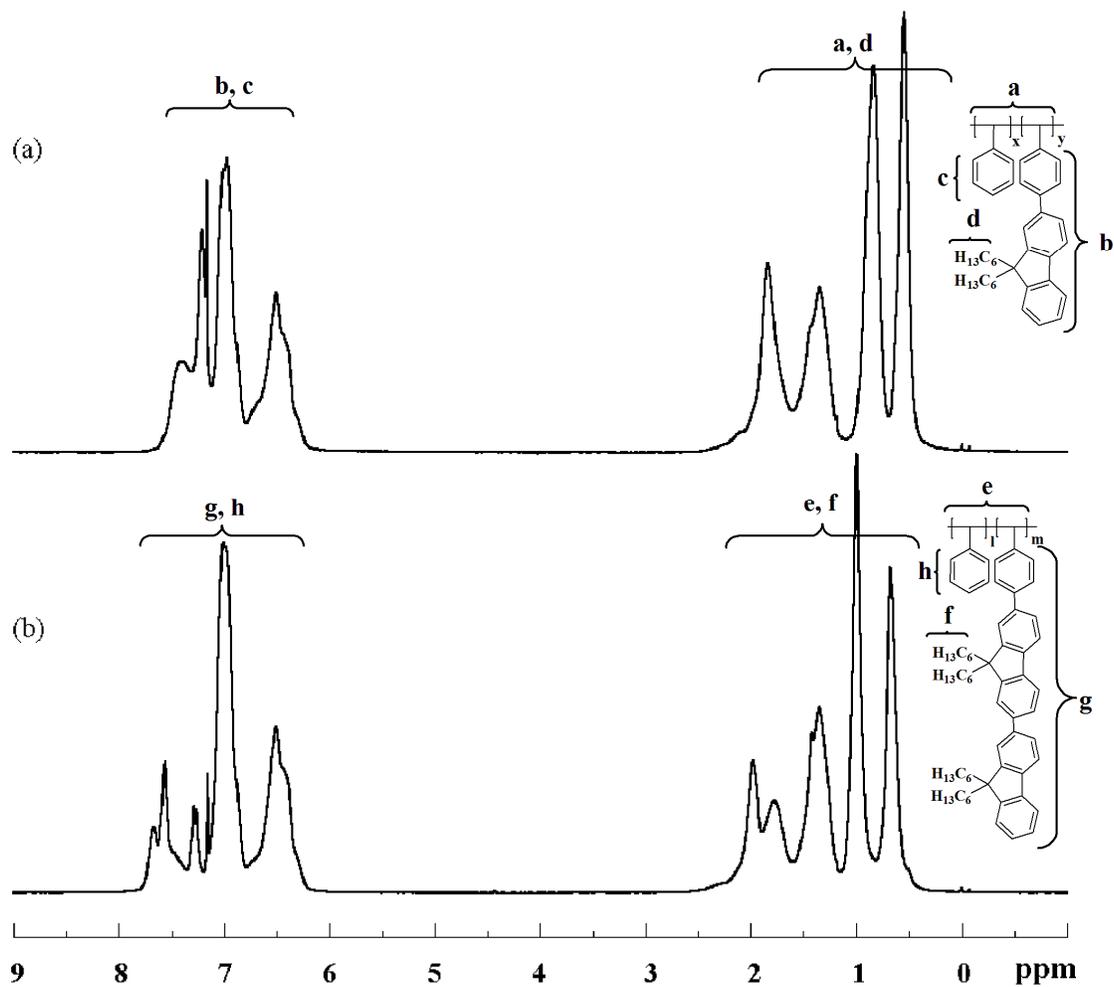


Figure S4. ^1H NMR spectra of (a) poly(St-FI)-*block*-polystyrene and (b) poly(St-FI₂)-*block*-polystyrene in CDCl_3 .

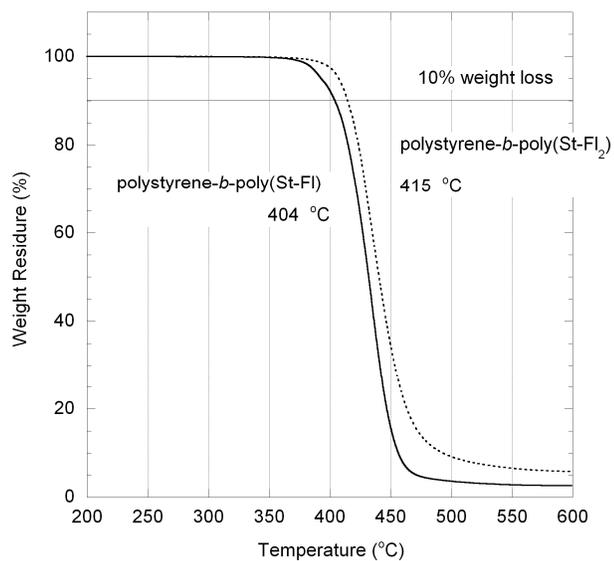


Figure S5. TG curves of the block copolymers, poly(St-FI)-*block*-polystyrene and poly(St-FI₂)-*block*-polystyrene.