# Shape Adaptable Water Soluble Conjugated Polymers

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## Supplementary Information

## Experimental Section

**General Details.** $^1$H and $^{13}$C NMR spectra were collected on Varian ASM-100 200 MHz spectrometers. 500 MHz NMR spectroscopy was performed using the NMR lab facilities at the Materials Research Labs, UCSB. The UV-Vis absorption spectra were recorded on a Shimadzu UV-2401 PC diode array spectrometer. Photoluminescence spectra were obtained on a Spex Fluorolog 2 spectrometer, using 90 degree angle detection for solution samples. Reagents were obtained from Aldrich Co. and were used as received.

Poly(9,9-bis(6'-bromohexyl)fluorene-co-alt-1,3 -phenylene) ($M_{100}P_0$).

2,7-Dibromo-9,9-bis(6'-bromohexyl)fluorene (325 mg, 0.5 mmol), 1,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan)phenylene (166 mg, 0.5 mmol), $Pd(PPh_3)_4$ (8 mg) and potassium carbonate (830 mg, 6 mmol) were placed in a 25 mL round bottom flask. A mixture of water (3 mL) and toluene (5 mL) was added to the flask. After degassing, the mixture was refluxed at 85 °C for 20 h, and then precipitated into methanol. The polymer was filtered, washed with methanol and acetone, and dried in vacuum for 24 h to afford $M_{100}P_0$ (251 mg, 88%) as a light yellow solid. $^1$H NMR (200 MHz, $CDCl_3$): δ 7.9-7.6 (m, 10H), 3.3-3.2 (t, 4H), 2.1 (m, 4H), 1.7-1.6 (m, 4H), 1.3-1.2 (m, 8H), 0.8 (m, 4H). $^{13}$C NMR (50 MHz, $CDCl_3$): δ 151.8, 142.7, 140.7, 140.6, 129.7, 126.8, 126.6, 126.4, 122.0, 120.7, 55.7, 40.8, 34.3, 33.1, 29.5, 28.3, 24.1. GPC (THF, polystyrene standard), $M_w$: 40,250 g/mol; $M_n$: 14,980 g/mol; PDI: 2.8.

Poly(9,9-bis(6'-bromohexyl)fluorene-co-alt-1,4-phenylene) ($M_0P_{100}$).

2,7-Dibromo-9,9-bis(6'-bromohexyl)fluorene (325 mg, 0.5 mmol), 1,4-phenyldiboronic acid (82.9 mg, 0.5 mmol), Pd(dppf)$Cl_2$ (7 mg) and potassium carbonate (830mg, 6 mmol) were placed in a 25 mL round bottom flask. A mixture of water (3 mL) and THF (6 mL) was added to the flask and the reaction vessel was degassed. The mixture was refluxed at 85 °C for 24 h, and then precipitated into methanol. The polymer was filtered and washed with methanol and acetone, and then dried under vacuum for 24 h to afford $M_0P_{100}$ (220 mg, 78%), as an off-white solid. $^1$H NMR (200 MHz, $CDCl_3$): δ 7.8 (m, 5H), 7.7-7.6 (m, 4H), 7.5 (m, 1H), 3.3 (t, 4H), 2.1 (m, 4H), 1.7 (m, 4H), 1.3-1.2 (m, 8H), 0.8 (m, 4H). $^{13}$C NMR (50 MHz, $CDCl_3$): δ 151.9, 140.9, 140.7, 140.2, 128.1, 126.6, 121.8, 120.8, 55.7, 40.9, 34.5, 33.2, 29.6, 28.3, 24.2. GPC (THF, polystyrene standard), $M_w$: 25,850 g/mol; $M_n$: 12,840 g/mol; PDI: 2.0.

Random copolymer $M_{25}P_{75}$.

2,7-Dibromo-9,9-bis(6'-bromohexyl)fluorene (325 mg, 0.5 mmol), 1,4-phenyldiboronic acid (62.2 mg, 0.375 mmol), 1,3-phenyldiboronic acid (20.7 mg, 0.125 mmol), Pd(dppf)$Cl_2$ (7 mg) and potassium carbonate (830mg, 6 mmol) were placed in a 25 mL round bottom flask. A mixture of water (3 mL) and THF (6 mL) was added to the flask and the reaction vessel was degassed. The mixture was refluxed at 85 °C for 24 h, and then precipitated into methanol. The polymer was filtered and washed with methanol and acetone, and then dried under vacuum for 24 h to afford $M_{25}P_{75}$ (248 mg, 88%) as an off-white solid. $^1$H NMR (200 MHz, $CDCl_3$): δ 7.9-7.6 (m, 10H), 3.3-3.2 (t, 4H), 2.1 (m, 4H), 1.7-1.6 (m, 4H), 1.3-1.2 (m, 8H), 0.8 (m, 4H). GPC (THF, polystyrene standard), $M_w$: 29,000 g/mol; $M_n$: 14,720 g/mol; PDI: 1.9.

Random copolymer $M_{50}P_{50}$.

2,7-Dibromo-9,9-bis(6'-bromohexyl)fluorene (325 mg, 0.5 mmol), 1,4-phenyldiboronic acid (41.5 mg, 0.25 mmol), 1,3-phenyldiboronic acid (41.5 mg, 0.25 mmol), Pd(dppf)$Cl_2$ (7 mg) and potassium carbonate (830mg, 6 mmol) were placed in a 25 mL round bottom flask. A mixture of water (3 mL) and THF (6 mL) was added to the flask and the reaction vessel was degassed. The mixture was refluxed at 85 °C for 24 h, and then precipitated into methanol. The polymer was filtered and washed with methanol and acetone, and then dried in vacuum for 24 h to afford $M_{50}P_{50}$ (220 mg, 78%) as an off-white solid. $^1$H NMR (200 MHz, $CDCl_3$): δ 7.9-7.6 (m, 10H), 3.3-3.2 (t, 4H), 2.1 (m, 4H), 1.7-1.6 (m, 4H), 1.3-1.2 (m, 8H), 0.8 (m, 4H). GPC (THF, polystyrene standard), $M_w$: 17,340 g/mol; $M_n$: 10,080 g/mol; PDI: 1.7.

Random copolymer $M_{75}P_{25}$.

2,7-Dibromo-9,9-bis(6'-bromohexyl)fluorene (325 mg, 0.5 mmol), 1,4-phenyldiboronic acid (20.7 mg, 0.125 mmol), 1,3-phenyldiboronic acid (62.2 mg, 0.375 mmol), Pd(dppf)$Cl_2$ (7 mg) and potassium carbonate (830mg, 6 mmol) were placed in a 25 mL round bottom flask. A mixture of water (3 mL) and THF (6 mL) was added to the flask. After degassing, the mixture was refluxed at 85 °C for 24 h, and then precipitated into methanol. The polymer was filtered and washed with methanol and acetone, and then dried under vacuum for 24 h to afford $M_{75}P_{25}$ (130 mg, 46%) as an off-white solid. $^1$H NMR (200 MHz, $CDCl_3$): δ 7.9-7.6 (m, 10H), 3.3-3.2 (t, 4H), 2.1 (m, 4H), 1.7-1.6 (m, 4H), 1.3-1.2 (m, 8H), 0.8 (m, 4H). GPC (THF, polystyrene standard), $M_w$: 13,000 g/mol; $M_n$: 10,000 g/mol; PDI: 1.3.

Random copolymer $M_{90}P_{10}$.

2,7-Dibromo-9,9-bis(6'-bromohexyl)fluorene (325 mg, 0.5 mmol), 1,4-phenyldiboronic acid (8 mg, 0.05 mmol), 1,3-phenyldiboronic acid (75 mg, 0.45 mmol), $Pd(dppf)Cl_2$ (7 mg) and potassium carbonate (830mg, 6 mmol) were placed in a 25 mL round bottom flask. A mixture of water (3 mL) and THF (6 mL) was added to the flask. After degassing, the mixture was refluxed at 85 °C for 24 h, and then precipitated into methanol. The polymer was filtered and washed with methanol and acetone and then dried in vacuum for 24 h to afford $M_{90}P_{10}$ (110 mg, 39%) as an off-white solid. $^1$H NMR (200 MHz, $CDCl_3$): δ 7.9-7.6 (m, 10H), 3.3-3.2 (t, 4H), 2.1 (m, 4H), 1.7-1.6 (m, 4H), 1.3-1.2 (m, 8H), 0.8 (m, 4H). GPC (THF, polystyrene standard), $M_w$: 8,400 g/mol; $M_n$: 5,800 g/mol; PDI: 1.4.

Poly(9,9-bis(6'-N,N,N,-trimethylammonium)hexyl)fluorene-co-alt-1,3-phenylene) bromide ($M_{100}P_0^+$).

Condensed trimethylamine (2 mL) was added dropwise to a solution of the neutral polymer $M_{100}P_0$ (60 mg) in THF (10 mL) at -78 °C. The mixture was allowed to warm up to room temperature. The precipitate was re-dissolved by the addition of water (10 mL). After the mixture was cooled down to -78 °C, extra trimethylamine (2 mL) was added and the mixture was stirred for 24 h at room temperature. After removing most of the solvent, acetone was added to precipitate $M_{100}P_0^+$ (63 mg, 78%) as a light yellow powder. $^1$H NMR (500 MHz, $CD_3OD$): δ 8.1-7.7 (m, 10H), 3.3-3.2 (t, 4H), 3.1 (s, 18H), 2.3 (br, 4H), 1.6 (br, 4H), 1.3 (br, 8H), 0.8 (br, 4H). $^{13}$C NMR (125 MHz, $CD_3OD$): δ 151.9, 142.4, 140.9, 140.6, 129.77, 126.5, 126.1, 125.6, 121.6, 120.5, 66.7, 55.7, 52.5, 40.1, 29.2, 25.8, 23.8, 22.6.

Poly(9,9-bis(6'-N,N,N,-trimethylammonium)hexyl)fluorene-co-alt-1,4 - phenylene) bromide ($M_0P_{100}^+$).

Condensed trimethylamine (2 mL) was added dropwise to a solution of the neutral polymer $M_0P_{100}$ (60 mg) in THF (10 mL) at -78 °C. The mixture was allowed to warm up to room temperature. The precipitate was re-dissolved by the addition of water (10 mL). After the mixture was cooled down to -78 °C, extra trimethylamine (2 mL) was added and the mixture was stirred for 24 h at room temperature. After removing most of the solvent, acetone was added to precipitate $M_0P_{100}^+$ (72 mg, 89%) as an off-white powder. $^1$H NMR (500 MHz, $CD_3OD$): δ 8.0-7.8 (m, 10H), 3.3-3.2 (t, 4H), 3.1 (s, 18H), 2.3 (br, 4H), 1.6 (br, 4H), 1.3 (br, 8H), 0.8 (br, 4H). $^{13}$C NMR (125 MHz, $CD_3OD$): δ 151.8, 140.9, 140.4, 140.0, 127.6, 126.1, 121.2, 120.5, 66.7, 55.7, 52.5, 40.2, 29.2, 25.8, 23.7, 22.5.

Cationic water-soluble polymer $M_{25}P_{75}^+$.

Condensed trimethylamine (2 mL) was added dropwise to a solution of the neutral polymer $M_{25}P_{75}$ (60 mg) in THF (10 mL) at -78 °C. The mixture was allowed to warm up to room temperature. The precipitate was re-dissolved by the addition of water (10 mL). After the mixture was cooled down to -78 °C, extra trimethylamine (2 mL) was added and the mixture was stirred for 24 h at room temperature. After removing most of the solvent, acetone was added to precipitate $M_{25}P_{75}^{+}$ (72 mg, 89%) as an off-white powder. $^{1}$H NMR (500 MHz, $CD_3OD$): δ 8.0-7.5 (m, 10H), 3.3 (br, 4H), 3.1 (s, 18H), 2.3 (br, 4H), 1.6 (br, 4H), 1.2 (br, 8H), 0.9 (br, 4H).

Cationic water-soluble polymer $M_{50}P_{50}^{+}$.

Condensed trimethylamine (2 mL) was added dropwise to a solution of the neutral polymer $M_{50}P_{50}$ (60 mg) in THF (10 mL) at -78 °C. The mixture was allowed to warm up to room temperature. The precipitate was re-dissolved by the addition of water (10 mL). After the mixture was cooled down to -78 °C, extra trimethylamine (2 mL) was added and the mixture was stirred for 24 h at room temperature. After removing most of the solvent, acetone was added to precipitate $M_{50}P_{50}^{+}$ (68 mg, 84%) as an off-white powder. $^{1}$H NMR (500 MHz, $CD_3OD$): δ 8.1-7.7 (m, 10H), 3.3 (br, 4H), 3.1 (s, 18H), 2.3 (br, 4H), 1.6 (br, 4H), 1.3 (br, 8H), 0.8 (br, 4H).

Cationic water-soluble polymer $M_{75}P_{25}^{+}$.

Condensed trimethylamine (2 mL) was added dropwise to a solution of the neutral polymer $M_{75}P_{25}$ (60 mg) in THF (10 mL) at -78 °C. The mixture was allowed to warm up to room temperature. The precipitate was re-dissolved by the addition of water (10 mL). After it was cooled down to -78 °C, extra trimethylamine (2 mL) was added and the mixture was stirred for 24 h at room temperature. After removing most of the solvent, acetone was added to precipitate $M_{75}P_{25}^{+}$ (70 mg, 87%) as an off-white powder. $^{1}$H NMR (500 MHz, $CD_3OD$): δ 8.0-7.7 (m, 10H), 3.3 (br, 4H), 3.1 (s, 18H), 2.3 (br, 4H), 1.6 (br, 4H), 1.3 (br, 8H), 0.8 (br, 4H).

Cationic water-soluble polymer $M_{90}P_{10}^{+}$.

Condensed trimethylamine (2 mL) was added dropwise to a solution of the neutral polymer $M_{90}P_{10}$ (60 mg) in THF (10 mL) at -78 °C. The mixture was allowed to warm up to room temperature. The precipitate was re-dissolved by the addition of water (10 mL). After the mixture was cooled down to -78 °C, extra trimethylamine (2 mL) was added and the mixture was stirred for 24 h at room temperature. After removal most of the solvent, acetone was added to precipitate $M_{90}P_{10}^{+}$ (61 mg, 75%) as an off-white powder. $^1$H NMR (500 MHz, $CD_3OD$): δ 8.0-7.7 (m, 10H), 3.3 (br, 4H), 3.1 (s, 18H), 2.3 (br, 4H), 1.6 (br, 4H), 1.3 (br, 8H), 0.8 (br, 4H).

General procedure for FRET experiments.

The oligonucleotide used in the single stranded DNA study is 5'-Fl-ATC TTG ACT ATG TGG GTG CT and its complementary strand 5'-AGC ACC CAC ATA GTC AAG AT. The samples were prepared by initially determining DNA strand concentrations based on 260 nm absorbance measurements done on 150 μL samples in a 500 μL quartz couvette using a Shimadzu UV-vis spectrometer. Once the concentration of both strands was established, a 1:1 mixture of complementary single strands was mixed for annealing. The mixtures were annealed at (2 ºC below its melting point 59.5 ºC) 57.5 ºC for 25 min, and then cooled to room temperature slowly, and in an identical fashion for the non-complementary strands. The absorbance of the hybridized strands was measured to determine concentration before use in quenching and FRET experiments. The extent of hybridization was verified by variable temperature absorbance spectroscopy. Fluorescence intensities were determined from the integrated areas under emission spectra of both the donor and the acceptor fluorescein. The differences in energy transfer were compared by measuring the fluorescence intensity of the acceptor in the presence of the same concentration of the donor.

Measurements were carried out in buffer (50 mmol phosphate buffer pH = 8.0), at a fixed ds-DNA-C* concentration ([ds-DNA-C*] = 2.0 E-8 M), by adding the polymer with concentration varying from 1.0 E-7 M to 1.0 E-6 M. The excitation wavelength for both polymers was chosen at 363 nm, where the optical density for both polymers is nearly identical.