

## Electronic Supplementary Information

for

### Effects of Temperature on Chaotropic Anion-Induced Shape Transitions of Star Molecular Bottlebrushes with Heterografted Poly(ethylene oxide) and Poly(*N,N*-dialkylaminoethyl methacrylate) Side Chains in Acidic Water

*Evan M. Lewoczko, Michael T. Kelly, Ethan W. Kent, and Bin Zhao\**

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States

\* Corresponding author. Email: bzhao@utk.edu

#### Experimental Section

**Materials.** Copper(I) chloride (CuCl, 97%, Alfa-Aesar) was stirred in glacial acetic acid overnight, collected by vacuum filtration, rinsed sequentially with absolute ethanol and diethyl ether, and dried under high vacuum. 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA, 97%, Alfa-Aesar) was vacuum distilled. 2-(*N,N*-Dimethylamino)ethyl methacrylate (DMAEMA, 98.5%, TCI) and 2-(*N,N*-diethylamino)ethyl methacrylate (DEAEMA, 98.5%, TCI) were purified by passing through a basic alumina column with a silica gel plug in the bottom to remove the inhibitor prior to use. The synthesis of the azide-functionalized three-arm star backbone polymer with a DP of 434 per arm (PHEMA-N<sub>3</sub>) can be found in the literature.<sup>1</sup> The degree of azide functionalization was 88.3%, determined from the <sup>1</sup>H NMR spectroscopy analysis. Size exclusion

chromatography (SEC) analysis using PSS GRAL columns with DMF containing 50 mM LiBr as the eluent showed that the  $M_{n,SEC}$  of PHEMA- $N_3$  was 224.5 kDa and the dispersity ( $\mathcal{D}$ ) was 1.16, with respect to polystyrene standards. Propargyl 2-bromoisobutyrate was synthesized according to a procedure from the literature<sup>2</sup> and the molecular structure was verified by NMR spectroscopy analysis. Alkyne-end-functionalized poly(ethylene oxide) was synthesized from poly(ethylene glycol) monomethyl ether (5 kDa, Sigma-Aldrich) and 4-pentynoic acid (95%, Acros Organics) according to a procedure in the literature.<sup>2</sup> SEC analysis using the PL-GPC 20 system showed that the  $M_{n,SEC}$  was 8.4 kDa and the  $\mathcal{D}$  was 1.04, with respect to polystyrene standards. Sodium ferrocyanide decahydrate ( $Na_4[Fe(CN)_6] \cdot 10H_2O$ , 99%, Acros Organics), potassium ferricyanide ( $K_3[Fe(CN)_6]$ , 98%, Acros Organics), sodium hexafluorophosphate ( $NaPF_6$ , 98.5%, Acros Organics), sodium perchlorate ( $NaClO_4$ , 98%, Alfa Aesar), sodium iodide (NaI, 99%, Alfa Aesar), and sodium sulfate ( $Na_2SO_4$ , 99%, Fisher Scientific) were used as received. Aqueous solutions of each salt with various concentrations were prepared by dissolving calculated amounts of the salt in Milli-Q and then filtered through 0.45  $\mu m$  hydrophilic PTFE filters. *N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC, 98%, Acros Organics), and 4-(dimethylamino)pyridine (DMAP, 99%, TCI America) were used as received. All other chemicals were purchased from commercial vendors and used as received.

**General Characterization.** The molecular weights and dispersities of alkyne end-functionalized tertiary amine-containing side chain polymers, PDMAEMA and PDEAEMA, were determined by SEC using a PL-GPC 50 Plus system, an integrated GPC/SEC system from Polymer Laboratories, Inc. This SEC instrument was equipped with a differential refractive index (RI) detector, one PSS GRAL guard column (10 micron particles, 50  $\times$  8 mm, Polymer Standards Service-USA, Inc.), and two PSS GRAL linear columns (10 micron particles, 300  $\times$  8 mm,

molecular weight range of 500 to 1 000 000 g/mol, Polymer Standards Service-USA, Inc.). The analysis was performed at 50 °C using *N,N*-dimethylformamide (DMF) containing 50 mM LiBr as the eluent at a flow rate of 1.0 mL/min. The system was calibrated with narrow dispersity linear polystyrene standards (Scientific Polymer Products, Inc.). The molecular weight and dispersity of the alkyne end-functionalized PEO was measured at room temperature using a PL-GPC 20 (Polymer Laboratories, Inc.) comprising a RI detector, one PLgel guard column (5 micron particles, 50 × 7.5 mm, Agilent Technologies, Inc.), and two PLgel mixed-C columns (each 5 micron particles, 300 × 7.5 mm, linear range of molecular weights from 200 to 2000000 g/mol, Agilent Technologies, Inc.). The eluent was tetrahydrofuran (THF) and the flow rate was 1.0 mL/min. This GPC system was also calibrated with narrow dispersity linear polystyrene standards (Scientific Polymer Products, Inc.). The SEC data were processed using the Cirrus SEC software (Polymer Laboratories, Inc.).

The absolute weight-average molecular weights ( $M_w$ ) of the purified star molecular bottlebrushes, SMB-11 and SMB-22, were measured at 50 °C by a GPC-MALS system, equipped with one PSS GRAM guard column (10 micron particles, 8 × 50 mm, Polymer Standards Service-USA, Inc.), three PSS GRAM linear columns (10 micron particles, 8 × 300 mm; 100, 1000, and 3000 Å, Polymer Standards Service-USA, Inc.), an Agilent model 1260 Infinity pump, a Rheodyne model 7725 manual injector with a 200 µL loop, and a Varian 390 LC detector system composed of a RI detector and a two-angle light scattering detector (15° and 90°). The mobile phase was DMF with 0.10 M LiBr. <sup>1</sup>H NMR spectra were obtained from either a Varian VNMRS 500 NMR or a Varian VNMRS 600 NMR spectrometer.

**Synthesis of Alkyne End-Functionalized Poly(2-(*N,N*-dimethylamino)ethyl methacrylate) (PDMAEMA) by Atom Transfer Radical Polymerization (ATRP).** Propargyl

2-bromoisobutyrate (48.8 mg,  $2.38 \times 10^{-4}$  mol), DMAEMA (3.016 g,  $1.918 \times 10^{-2}$  mol), HMTETA (65.1 mg,  $2.83 \times 10^{-4}$  mol), and anisole (5.233 g) were added to a 25 mL two-necked round-bottom flask equipped with a magnetic stir bar, a rubber septum, and a gas-flow adapter. After the mixture was degassed by one round of freeze-pump-thaw, CuCl (23.8 mg,  $2.40 \times 10^{-4}$  mol) was added under a slightly positive pressure of nitrogen. The flask was then sealed with a rubber septum, and three more freeze-pump-thaw cycles were performed. The degassed flask was placed in a preheated oil bath with a temperature of 50 °C under nitrogen gas, and the mixture was stirred by a magnetic stirrer. After 3.5 h, the polymerization was stopped by quickly cooling and exposing to air. An aliquot was taken for  $^1\text{H}$  NMR spectroscopy analysis for the determination of the final monomer conversion, and the polymerization mixture was diluted with methylene chloride and passed through a basic alumina (top)/silica gel (bottom) plug to remove the copper catalyst using methylene chloride as the eluent. The polymer solution was concentrated using a rotary evaporator, followed by precipitation into cold hexanes ( $\sim 0$  °C, cooled in an ice/water bath) three times. The purified product was dried under high vacuum, yielding a white rubbery polymer (yield: 0.931 g, 30.9 %). The monomer conversion was determined to be 70.0% by comparing the integrals of the peaks at 4.30-4.13 ppm ( $-\text{COOCH}_2-$  of the monomer) and at 4.13-4.01 ppm ( $-\text{COOCH}_2$  of the polymer) in the  $^1\text{H}$  NMR spectrum of the final polymerization mixture. The DP of the polymer was calculated to be 56 using the monomer conversion and the initial monomer-to-initiator ratio. SEC analysis using the DMF SEC system with GRAL columns gave a  $M_{n,\text{SEC}}$  value of 8.6 kDa and a  $D$  of 1.25, relative to polystyrene standards.

**Synthesis of Alkyne End-Functionalized Poly(2-(*N,N*-diethylamino)ethyl methacrylate) (PDEAEMA) by ATRP.** Propargyl 2-bromoisobutyrate (41.8 mg,  $2.04 \times 10^{-4}$  mol), DEAEMA (3.007 g,  $1.623 \times 10^{-2}$  mol), HMTETA (51.8 mg,  $2.25 \times 10^{-4}$  mol), CuCl (20.2 mg,  $2.04 \times 10^{-4}$

mol), and anisole (4.506 g) were added to a 25 mL round-bottom flask equipped with a stir bar, a rubber septum, and a gas flow adapter. The polymerization mixture was degassed by three freeze-pump-thaw cycles, placed in an oil bath with a preset temperature of 50 °C under nitrogen, and stirred. After 4 h, the polymerization was stopped by removing the flask from the oil bath, cooling it to room temperature, and opening it to air. An aliquot was taken for <sup>1</sup>H NMR spectroscopy analysis to determine the monomer conversion, and the reaction mixture was quickly diluted with CH<sub>2</sub>Cl<sub>2</sub> and passed through a basic alumina (top)/silica gel (bottom) column to remove the catalyst. The polymer was purified by precipitation of the concentrated mixture into cold hexanes (-78 °C, cooled with an acetone/dry ice bath) five times. The polymer was dried under high vacuum, yielding a white tacky polymer (1.828 g, 60.8 %). From the integrals of the peaks at 4.29-4.15 ppm (-COOCH<sub>2</sub>- of the monomer) and at 4.15-3.91 ppm (-COOCH<sub>2</sub>- of the polymer) in the <sup>1</sup>H NMR spectrum of the final reaction mixture, the monomer conversion was found to be 66.0 %. The DP of the polymer was calculated to be 53 using this conversion and the initial monomer-to-initiator ratio. SEC analysis using the DMF SEC system with GRAL columns showed that the M<sub>n,SEC</sub> was 9.4 kDa and the *D* was 1.19, relative to polystyrene standards.

**Synthesis of SMB-11 and SMB-22.** The following shows the detailed procedure for the synthesis and purification of SMB-11. PHEMA-N<sub>3</sub> (6.00 mg, 2.49 × 10<sup>-5</sup> mol azide moieties assuming quantitative functionalization, delivered by the addition of 0.853 g of a 7.03 mg/g stock solution in THF), alkyne end-functionalized PEO (76.7 mg, 1.50 × 10<sup>-5</sup> mol), alkyne end-functionalized PDMAEMA (109.0 mg, 1.21 × 10<sup>-5</sup> mol), copper(I) chloride (2.5 mg, 2.5 × 10<sup>-5</sup> mol), and dry THF (7 mL) were added to a 20 mL scintillation vial equipped with a magnetic stir bar and sealed by a rubber septum with needles for purging. After flushing the headspace with nitrogen gas, PMDETA (5.8 μL, 2.8 × 10<sup>-5</sup> mol) was injected by microsyringe. The headspace was

purged for an additional 15 min; the needles were removed, and the reaction mixture was stirred at room temperature. After 6 h, propargyl benzyl ether (10  $\mu$ L) was injected by microsyringe to react with unreacted azide groups. After 2 h, a second round of capping of unreacted azide groups with propargyl benzyl ether was performed as detailed below. The reaction mixture was diluted with THF, passed through a basic alumina (top)/silica gel (bottom) plug to remove the copper catalyst, and concentrated to about 7 mL. Additional copper(I) chloride (3.0 mg,  $3.0 \times 10^{-5}$  mol) and PMDETA (6.0  $\mu$ L,  $2.9 \times 10^{-5}$  mol) were added. The headspace was purged with nitrogen gas for 5 min, and propargyl benzyl ether (10  $\mu$ L) was added and stirred overnight. The reaction mixture was passed through a basic alumina (top)/silica gel (bottom) column to remove the copper catalyst using methylene chloride as the eluent. The solution was slowly concentrated by rotary evaporation in a warm water bath ( $\sim 35$   $^{\circ}$ C) to avoid the formation of de-solvated polymer on the wall of the flask. The concentrated polymer solution was diluted with 200 proof ethanol (30 mL) and carefully concentrated again to  $\sim 8$  mL. This process was repeated three times to remove as much THF and methylene chloride as possible. The concentrated solution in ethanol was then diluted with an equal volume of Milli-Q water. The obtained molecular bottlebrush polymer was purified by seven rounds of centrifugal filtration at 5000 rpm using a 50 kDa MWCO ultracentrifugal filter (Millipore<sup>TM</sup> Amicon<sup>TM</sup>) to remove unreacted side chains. The complete removal of the remaining side chain polymers was confirmed by SEC analysis using a PL-GPC 50 Plus system comprising GRAL columns with DMF containing 50 mM LiBr as the mobile phase. The polymer solution was slowly concentrated and freeze dried (LABCONCO 76705 Series Freeze Dryer), which yielded SMB-11 as a white powder (yield: 69.7 mg, 39.7 %). The absolute  $M_w$  from GPC-MALS analysis was  $9.49 \times 10^6$  g/mol. A similar procedure was used to prepare SMB-22. The molar ratios of azide groups in PHEMA- $N_3$  to alkyne-end-functionalized PEO and

PDEAEMA were 1 : 0.60 : 0.60. After freeze-drying, the yield was 23.0 %. The absolute  $M_w$  from GPC-MALS was  $9.77 \times 10^6$  g/mol.

**Dynamic Light Scattering (DLS) Study of SMB-11 and -22 in Acidic Water.** DLS measurements of SMB-11 and -22 in acidic water under various conditions were taken using a Malvern Zetasizer Nano ZS instrument with a He-Ne 644 nm laser and a temperature controller at a scattering angle of  $173^\circ$ . A stock solution of each brush polymer in pH 4.50 water with a certain concentration (for SMB-11: 3.00 mg/g; for SMB-22: 3.67 mg/g) was prepared first and then diluted to a concentration of 0.2 mg/g using pH 4.50 water for DLS experiments. The pH values of the acidic water and the brush polymer solution were monitored by an Accumet AB-15 pH meter or a Denver Instrument UltraBasic pH meter (calibrated using standard buffer solutions with pH 4.01, 7.00, and 10.01 at room temperature) and were adjusted to 4.50, if needed, using 0.1 M HCl or 0.1 M NaOH aqueous solution. The 0.2 mg/g solution of each brush polymer with a pH value of 4.50 was slowly filtered through a  $0.45 \mu\text{m}$  hydrophilic PTFE filter. To investigate the effects of salts on the conformations of SMB-11 and -22 in a pH 4.50 solution, aqueous stock solutions of six salts ( $\text{Na}_4[\text{Fe}(\text{CN})_6]$ ,  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ,  $\text{NaPF}_6$ ,  $\text{NaClO}_4$ ,  $\text{NaI}$ , and  $\text{Na}_2\text{SO}_4$ ) with concentrations of 0.010, 0.10, and 1.0 M were made using Milli-Q water, filtered through  $0.45 \mu\text{m}$  hydrophilic PTFE filters, and added in a small aliquot each time ( $< 10 \mu\text{L}$ ) into a 1.0 mL solution of 0.2 mg/g SMB-11 or SMB-22 to obtain an appropriate salt concentration using a pipette (Gilson, Pipetman Classic P20). The DLS measurements were performed at  $25^\circ\text{C}$  first to study the effects of salt concentration on the hydrodynamic size of the brush polymer. The temperature effects of the salts were examined at selected salt concentrations in a typical temperature range of 5 to  $70^\circ\text{C}$ . The DLS samples were heated or cooled in the cell holder of the instrument, and at each selected temperature the samples were equilibrated for 2 min before the measurements were taken.

Each data point in the DLS size plots is the average of three measurements and each measurement is the average of 10 runs. All data points in the DLS plots are single size distributions without any large aggregates, unless explicitly stated. Representative hydrodynamic size distributions are presented as examples.

#### **Atomic Force Microscopy (AFM) Study of SMB-11 and -22 Under Various Conditions.**

AFM of SMB-11 and -22 was performed at ambient conditions using a Digital Instruments Multimode IIIa scanning probe microscope in the tapping mode. The probes were reflective Al-coated Si probes (Budget Sensors or Ted Pella, Inc., resonant frequency: 300 kHz, force constant:  $40 \text{ Nm}^{-1}$ ). Glass disks (Ted Pella, Inc.) were used for the preparation of AFM samples. These substrates were thoroughly cleaned with a “Piranha” solution (97.2% sulfuric acid/30%  $\text{H}_2\text{O}_2$ , 70/30, v/v), rinsed with Milli-Q water extensively, and stored in isopropanol (Honeywell, 99.9%, HPLC grade). For AFM study, aqueous solutions of SMB-11 and -22 with a concentration of 0.050 mg/g and a pH of 4.50 in the absence or presence of a salt were prepared from the 0.2 mg/g DLS samples by diluting with pH 4.50 water. To prepare AFM samples at room temperature ( $\sim 20 \text{ }^\circ\text{C}$ ), two drops of a brush solution were added onto a glass disk under ambient conditions. After 2 s, the solution was removed from the glass substrate using a glass pipet and any residual solution was wicked away using a Kimwipe tissue (for solutions with a salt) or blown away from the glass disk with a gentle stream of a filtered nitrogen gas (for solutions without any salt). To prepare AFM samples at  $70 \text{ }^\circ\text{C}$  from pH 4.50 aqueous solutions of brush polymers with a polymer concentration of 0.050 mg/g in the presence of a salt (diluted from the 0.20 mg/g DLS samples using pH 4.50 water), the polymer solutions, glass disks, and glass pipets were placed in a  $70 \text{ }^\circ\text{C}$  oven and equilibrated for 15 min. The drop casting was performed inside the oven to maintain the temperature. For the preparation of AFM samples at  $0 \text{ }^\circ\text{C}$ , the brush polymer solutions were



equilibrated in an ice/water bath, while glass disks and pipets were placed in a fridge with a temperature of  $\sim 4$  °C. After 30 min, the glass disks and pipets were removed from the fridge, and the AFM samples were prepared quickly under the ambient conditions.

**Calculation of Grafting Densities of SMB-11 and -22.** The side chain composition of purified SMB-11 was determined by  $^1\text{H}$  NMR spectroscopy analysis using the integrals of the peaks at 4.15 – 3.96 (-COOCH<sub>2</sub>- of PDMAEMA) and at 3.38 ppm (-OCH<sub>3</sub> of PEO). Taking the DP of PDMAEMA (DP = 56) into the account, the number ratio (molar ratio) of PDEAEMA and PEO side chains in SMB-11 was determined to be 43.7% : 56.3%. For SMB-22, the integrals of the peaks at 4.16 – 3.87 ppm (-COOCH<sub>2</sub>- of PDEAEMA) and at 3.38 ppm (-OCH<sub>3</sub> of PEO) were used along with the DP of PDEAEMA (DP = 53). The molar ratio of PDEAEMA and PEO side chains in SMB-22 was determined to be 41.8% : 58.2%.

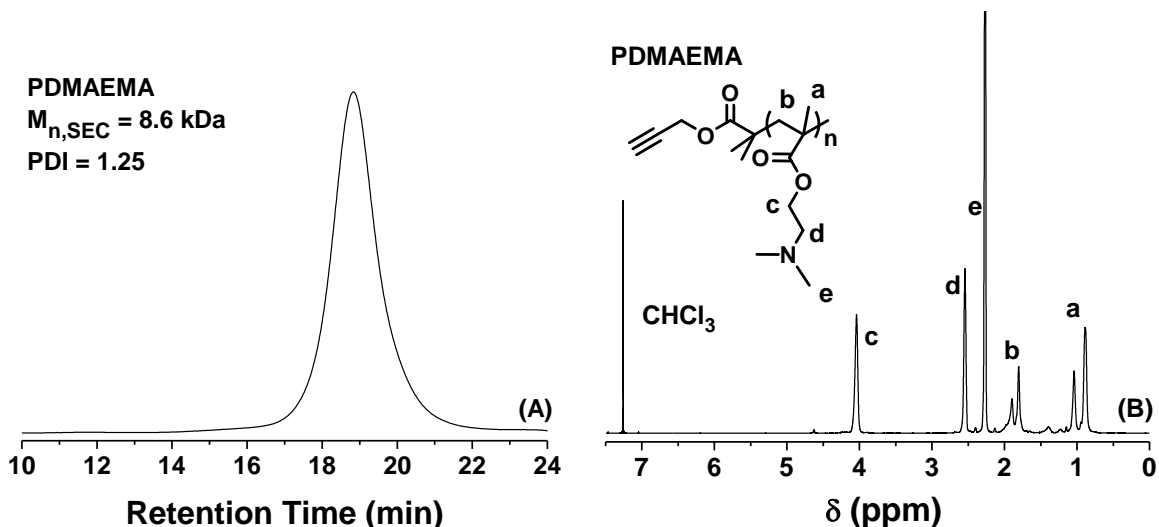
The grafting density of SMB-11 was calculated to be 86.7% by using the SEC peak area fractions of the star brush polymer and the remaining unreacted side chains in the final reaction mixture, the feed masses, and the side chain composition of purified SMB-11 as detailed below. The peak area percentages of the brush polymer and the unreacted side chains from the SEC analysis of the final reaction mixture were 79.9% and 20.1%, respectively, which are related to the mass percentages of the brushes and the side chain polymers. The  $M_n$  value of PDMAEMA calculated from the DP, including end groups, was 9010 g/mol, while the  $M_n$  for PEO with end groups was 5100 g/mol. Thus, based on the side chain molar composition of SMB-11 from  $^1\text{H}$  NMR spectroscopy analysis (43.7% for PDMAEMA and 56.3% for PEO), the mass percentages of PDMAEMA and PEO were calculated to be 57.8% and 42.2%, respectively. To determine the total mass of the reacted side chain polymers, the sum of the feed masses of backbone and side chain polymers was multiplied by the SEC area fraction of the brush polymer (79.9%), from which

the mass of the backbone polymer was subtracted. This gave the total mass of 147.2 mg for the reacted side chain polymers. Therefore, the masses of reacted PDMAEMA and PEO were 85.1 mg and 62.1 mg, respectively. Using the aforementioned  $M_n$  values of PDMAEMA and PEO, the total number of moles of the reacted side chain polymers was  $2.16 \times 10^{-5}$  mol. The number of moles of the azide groups on PHEMA- $N_3$  in the feed was  $2.49 \times 10^{-5}$  mol, assuming that the azide functionalization of PHEMA- $N_3$  was 100%. The grafting density of SMB-11 was calculated by dividing the number of moles of reacted side chain polymers by the number of moles of azide groups, which gave 86.7%. Using the same method, the grafting density of SMB-22 was calculated to be 83.9%.

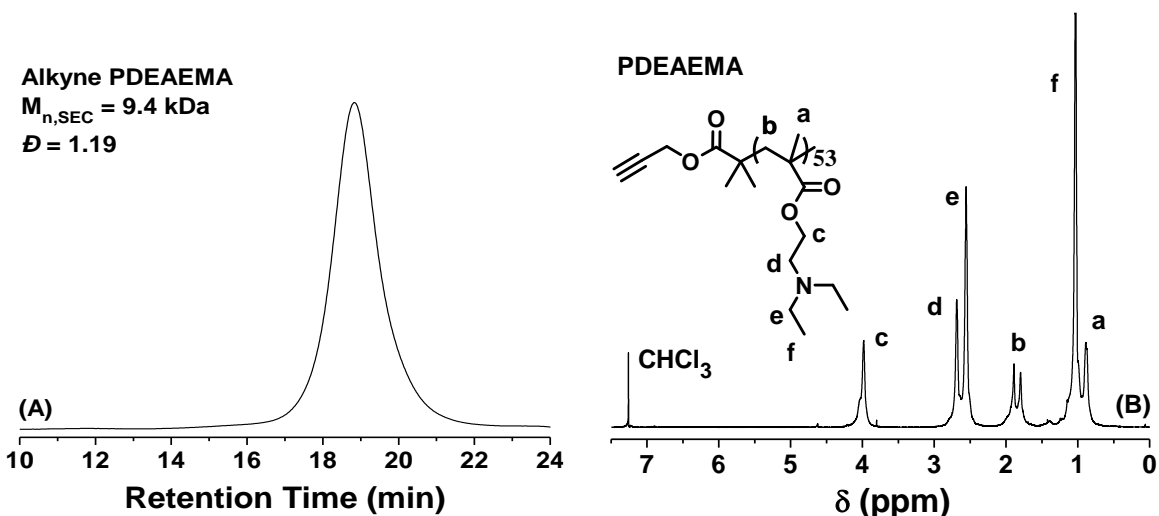
**Calculation of Weight-Average Molecular Weights of SMB-11 and -22.** The calculated weight average molecular weight of SMB-11 was found to be  $9.31 \times 10^6$  g/mol. The value was obtained by adding together the weight-average molecular weights of the backbone and all the grafted PDMAEMA and PEO side chains. The weight-average molecular weight of the backbone was calculated to be  $3.65 \times 10^5$  g/mol by multiplying the  $M_n$ , calculated using the total DP of the backbone and including the molar mass of the trifunctional initiator, by the dispersity of azide backbone polymer PHEMA- $N_3$  ( $D = 1.16$ ). The calculated weight-average molecular weight of PDMAEMA from the DP and  $D$  was  $1.13 \times 10^4$  g/mol ( $M_n \times 1.25$ ), and the calculated weight average molecular weight of PEO was  $5.3 \times 10^3$  g/mol). The grafting density of SMB-11 was 86.7%, and the brushes were composed of 43.7% for PDMAEMA and 56.3% for PEO as detailed earlier. Therefore, there were 569 PDMAEMA chains and 733 PEO chains grafted in each SMB-11 brush molecule, and the calculated weight average molecular weight of SMB-11 was  $9.31 \times 10^6$  g/mol. Using the same method, the calculated average molecular weight of SMB-22 was  $9.17 \times 10^6$  g/mol.

## References:

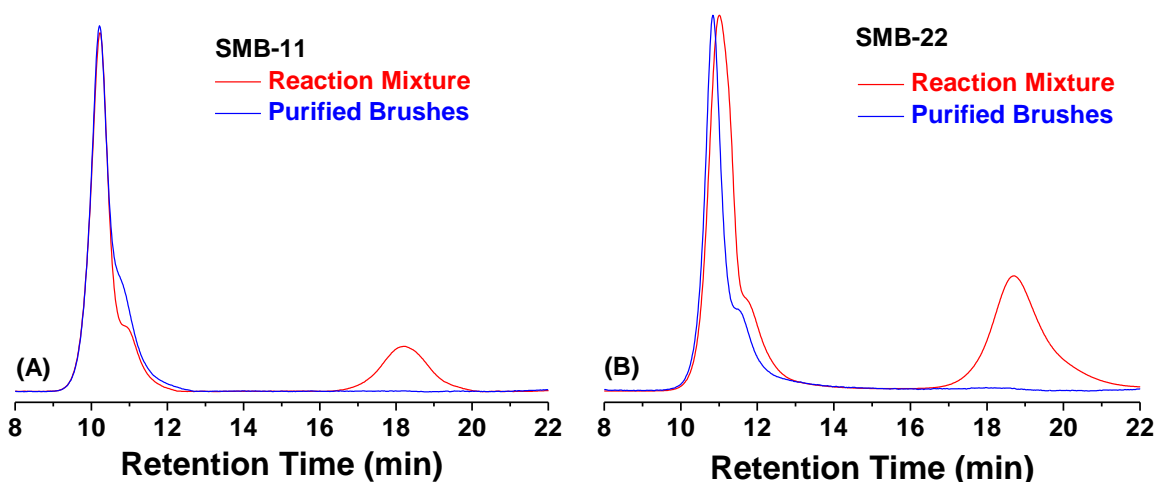
1. Kent, E. W.; Zhao, B. Stimuli-Induced Star-Globule Shape Transitions of Dually Responsive Binary Heterografted Three-Arm Star Molecular Brushes in Aqueous Solution. *Macromolecules*, **2019**, *52*, 6714-6724.
2. Henn, D. M.; Fu, W. X.; Mei, S.; Li, C. Y.; Zhao, B. Temperature-Induced Shape Changing of Thermosensitive Binary Heterografted Linear Molecular Brushes between Extended Wormlike and Stable Globular Conformations. *Macromolecules*, **2017**, *50*, 1645-1656.



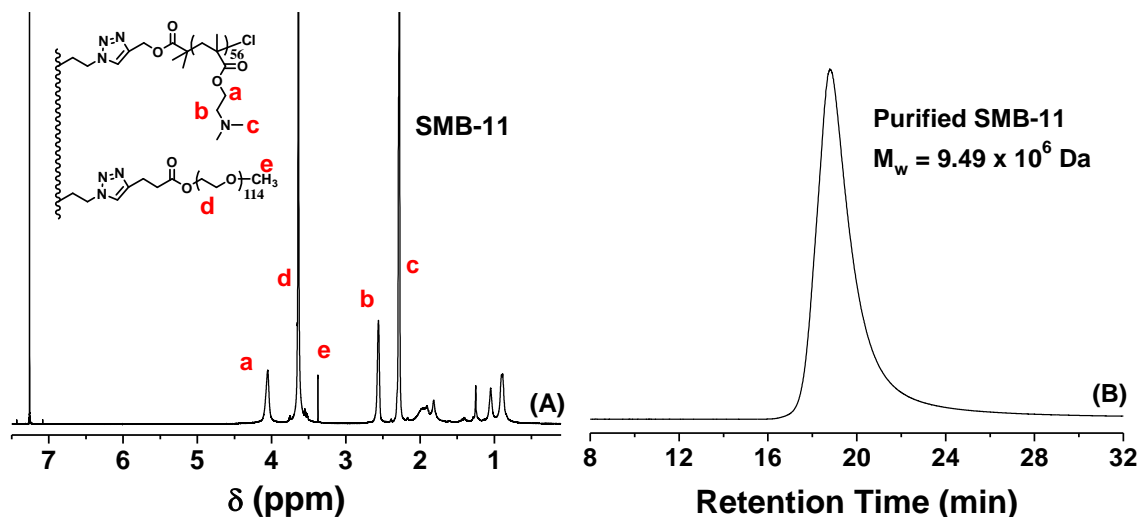
**Figure S1.** (A) Size exclusion chromatography (SEC) trace and (B) <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> of alkyne-end-functionalized poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA) with a degree of polymerization of 56. The SEC chromatogram was obtained from a SEC system equipped with GRAL columns using DMF with 50 mM LiBr as eluent.



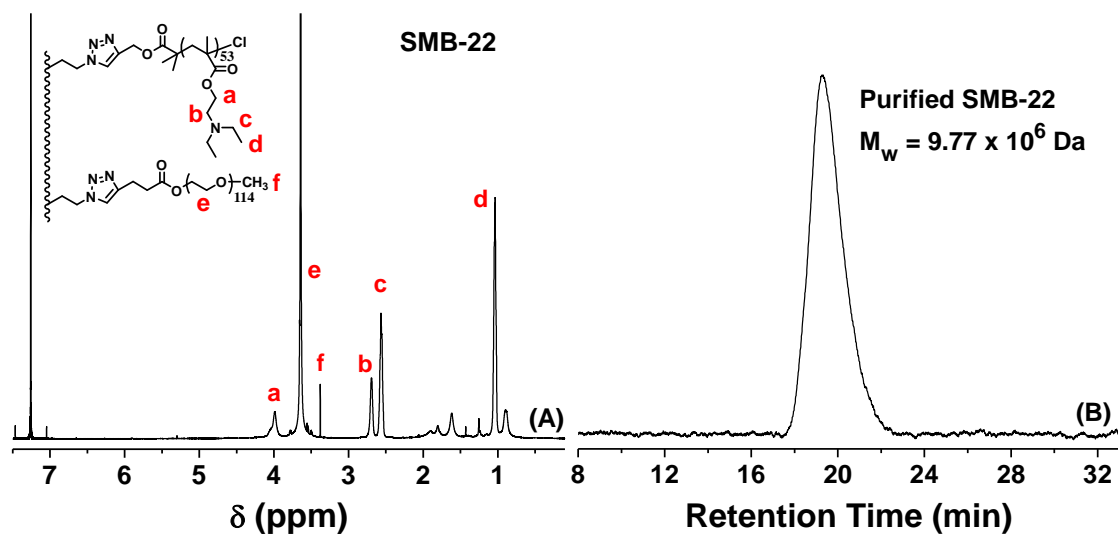
**Figure S2.** Size exclusion chromatograph (SEC) trace (A) and <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> (B) of alkyne-end-functionalized PDEAEMA with a degree of polymerization (DP) of 53. The SEC chromatogram was obtained from a SEC system equipped with GRAL columns using DMF with 50 mM LiBr as eluent.



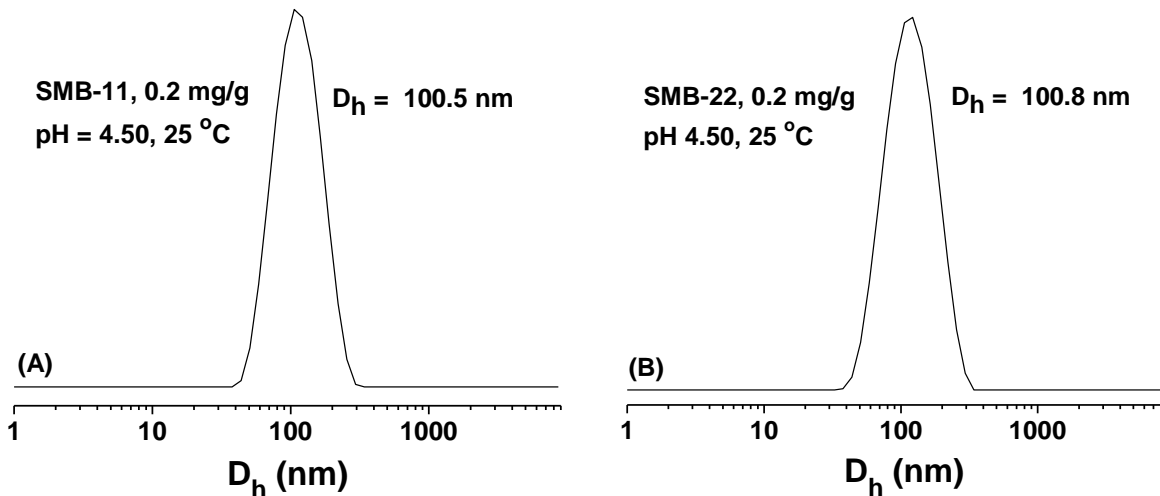
**Figure S3.** Size exclusion chromatography (SEC) curves of the reaction mixture at the end of the reaction for the synthesis of SMB-11 (red) and purified SMB-11 (blue) (A), and for the synthesis of SMB-22 (red) and purified SMB-22 (blue) (B), obtained using a SEC system equipped with GRAL columns and *N,N*-dimethylformamide containing 50 mM LiBr as the eluent.



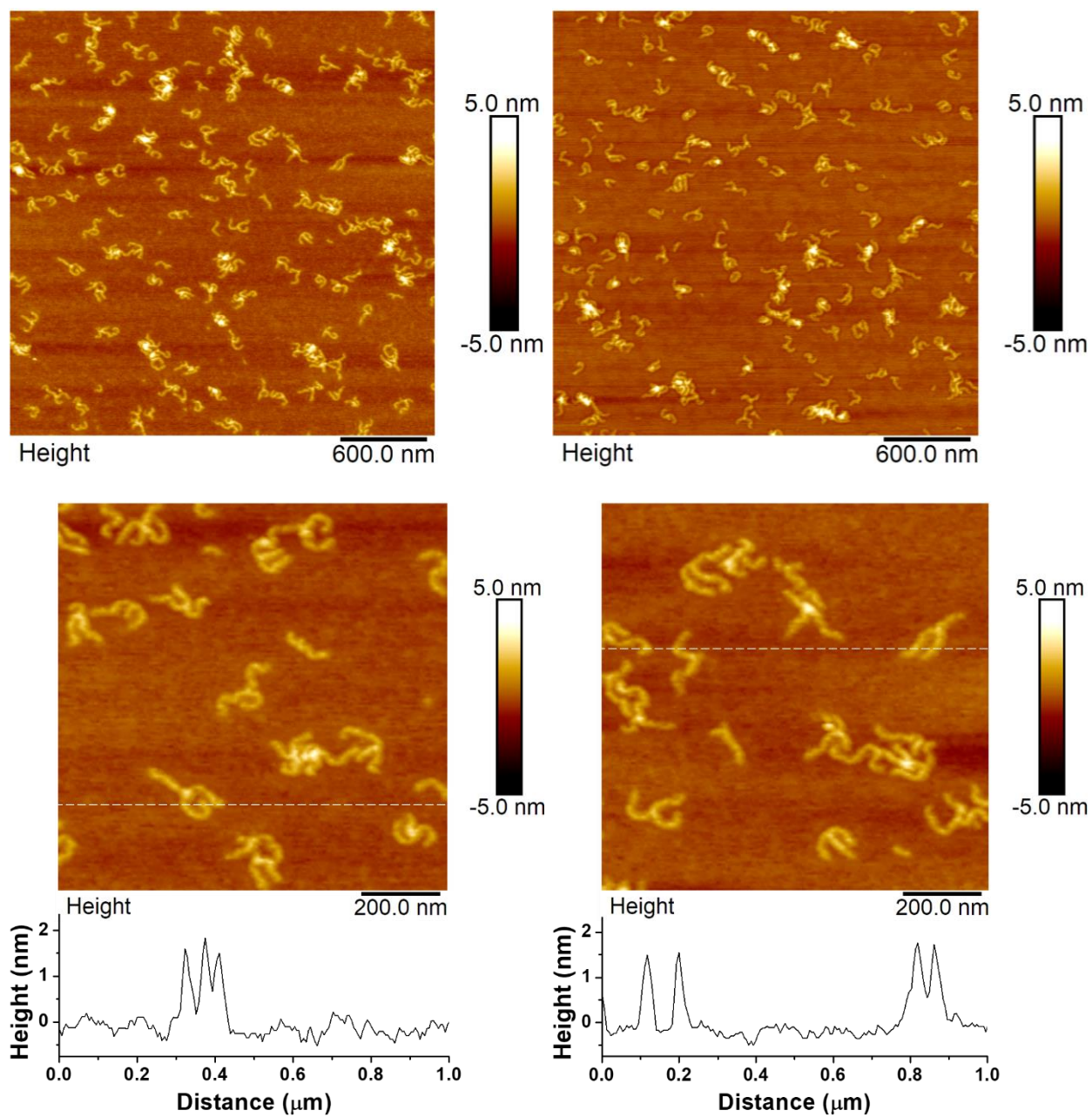
**Figure S4.** (A)  $^1\text{H}$  NMR spectrum of purified SMB-11 in  $\text{CDCl}_3$ . (B) SEC trace of purified SMB-11 from a GPC-MALS system using DMF with 0.10 M LiBr as the eluent.



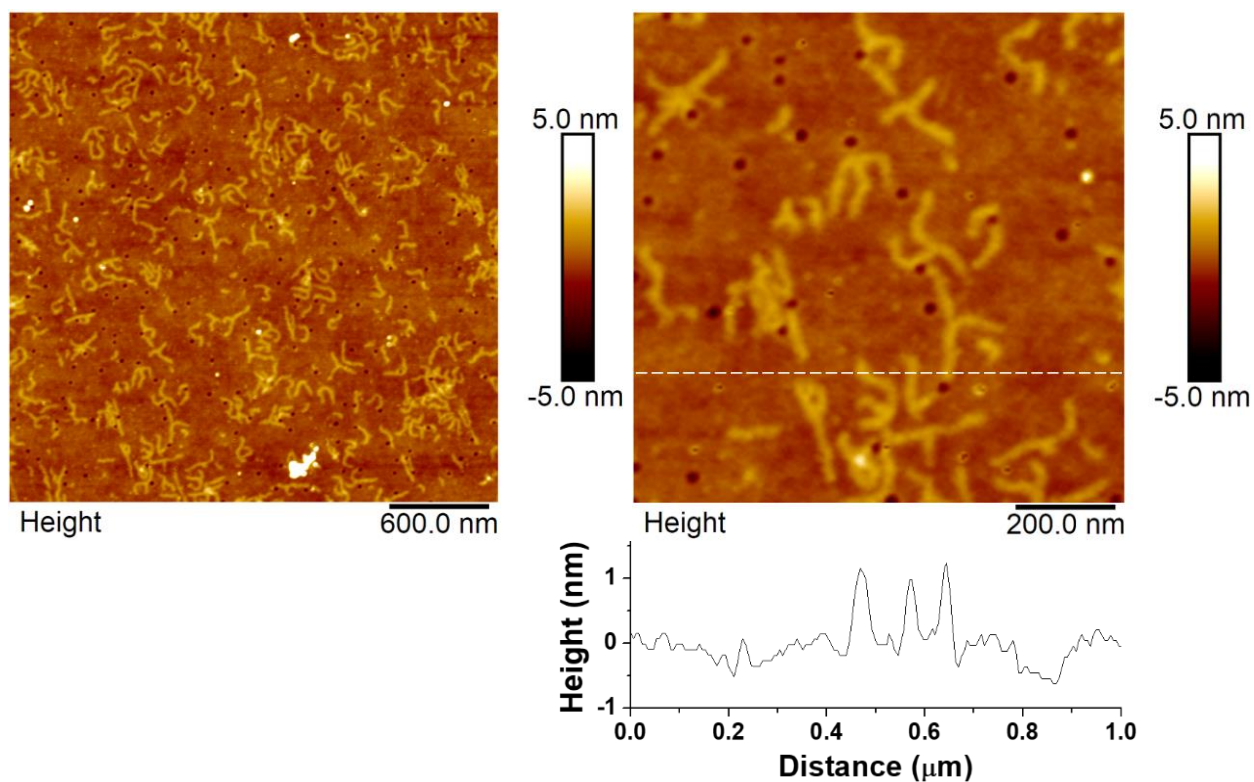
**Figure S5.** (A)  $^1\text{H}$  NMR spectrum of purified SMB-22 in  $\text{CDCl}_3$  and (B) SEC trace of purified SMB-22 obtained from a GPC-MALS system using DMF with 0.10 M LiBr as the eluent.



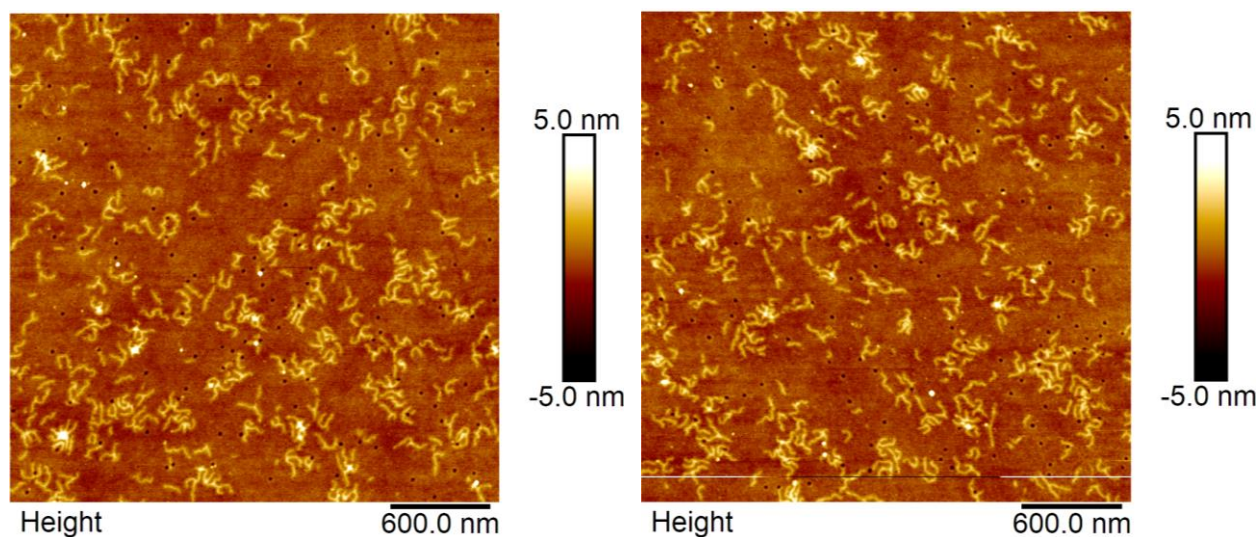
**Figure S6.** Hydrodynamic size distributions of 0.2 mg/g SMB-11 (A) and SMB-22 (B) in acidic water with a pH of 4.50 obtained from dynamic light scattering measurements at 25 °C.

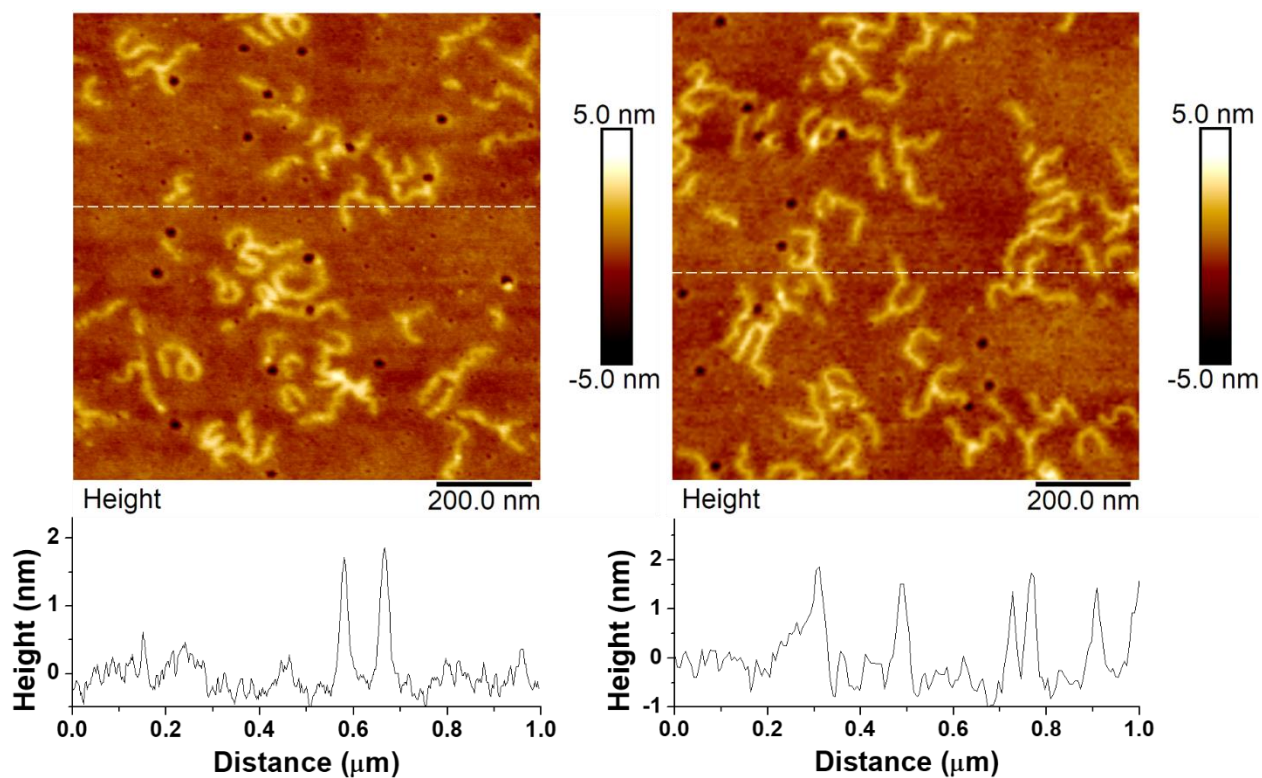


**Figure S7.** Atomic force microscopy (AFM) height images (top:  $3 \times 3 \mu\text{m}$  and bottom:  $1 \times 1 \mu\text{m}$ ) of SMB-11 spin cast onto bare mica from THF at a brush polymer concentration of  $0.05 \text{ mg/g}$  at room temperature ( $\sim 20 \text{ }^\circ\text{C}$ ), with a cross-sectional height profile corresponding to the dashed line in each of bottom  $1 \times 1 \mu\text{m}$  images.

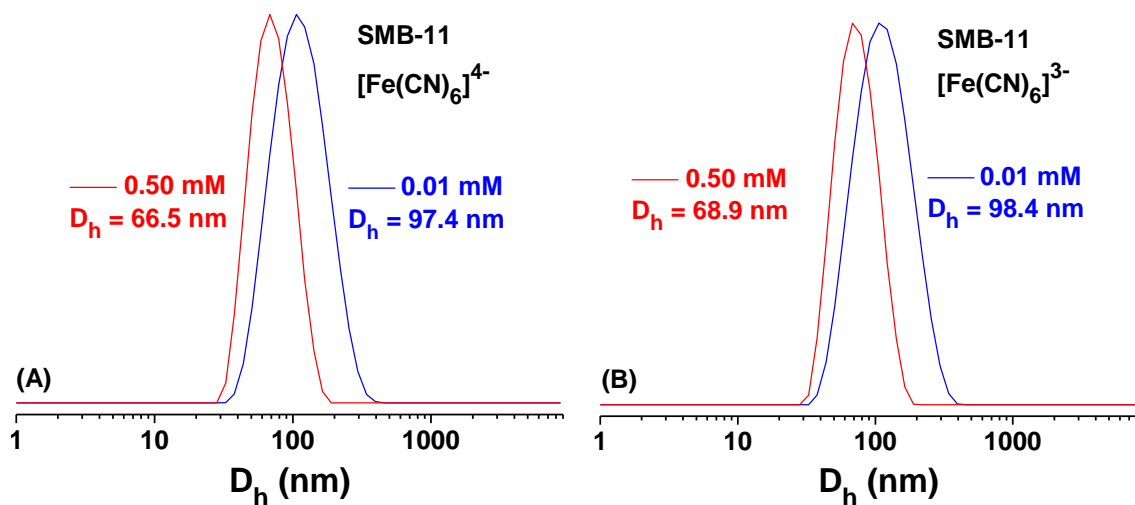


**Figure S8.** Atomic force microscopy (AFM) height images of SMB-11 drop cast on glass disks from a 0.050 mg/g SMB-11 solution in pH 4.50 water at room temperature ( $\sim 20\text{ }^\circ\text{C}$ ), with a cross-sectional profile along the dashed line of the  $1 \times 1\text{ }\mu\text{m}$  image.

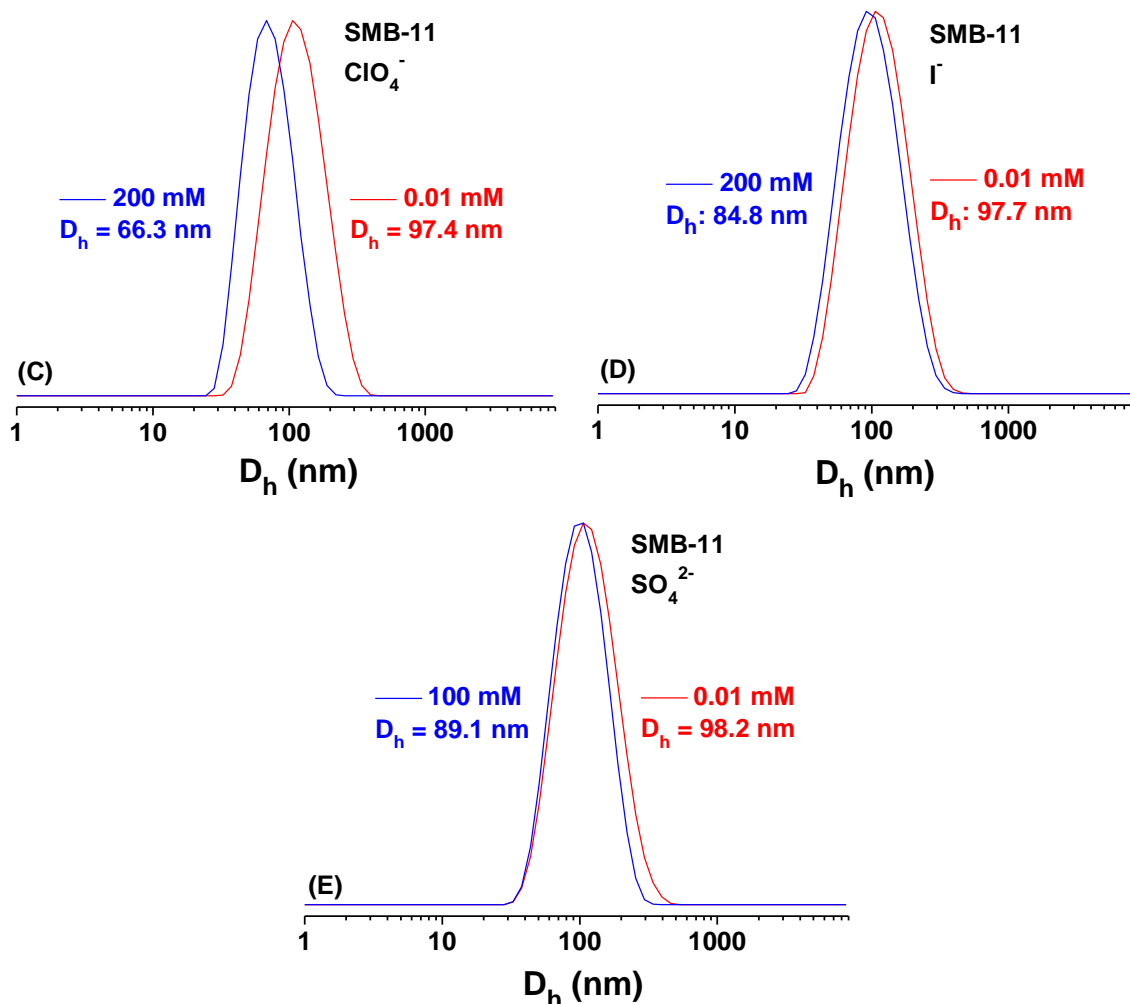




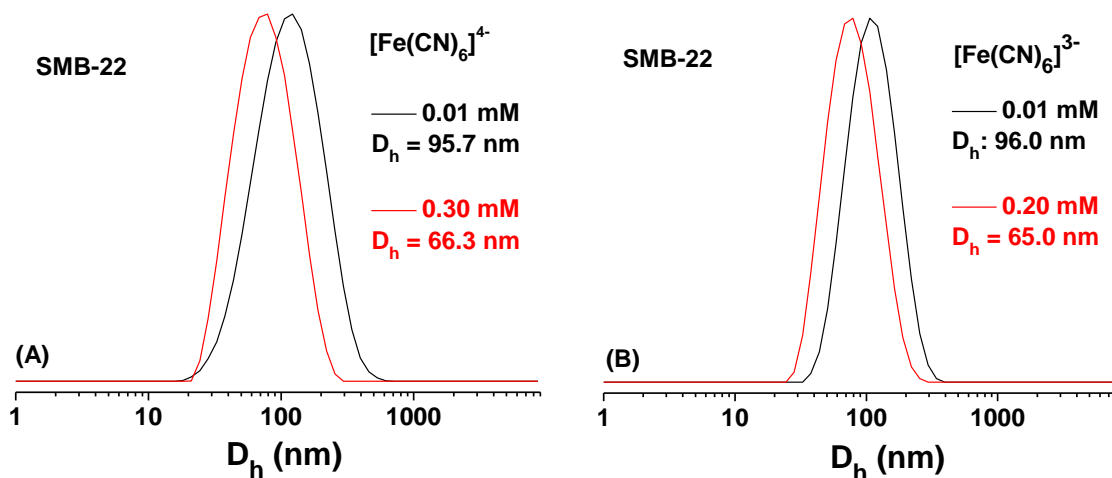
**Figure S9.** Atomic force microscopy (AFM) height images of SMB-22 drop cast on glass disks from a 0.050 mg/g SMB-22 solution in pH 4.50 water at room temperature ( $\sim 20^\circ\text{C}$ ), with a cross-sectional profile along the dashed line in each of the bottom  $1 \times 1 \mu\text{m}$  images.

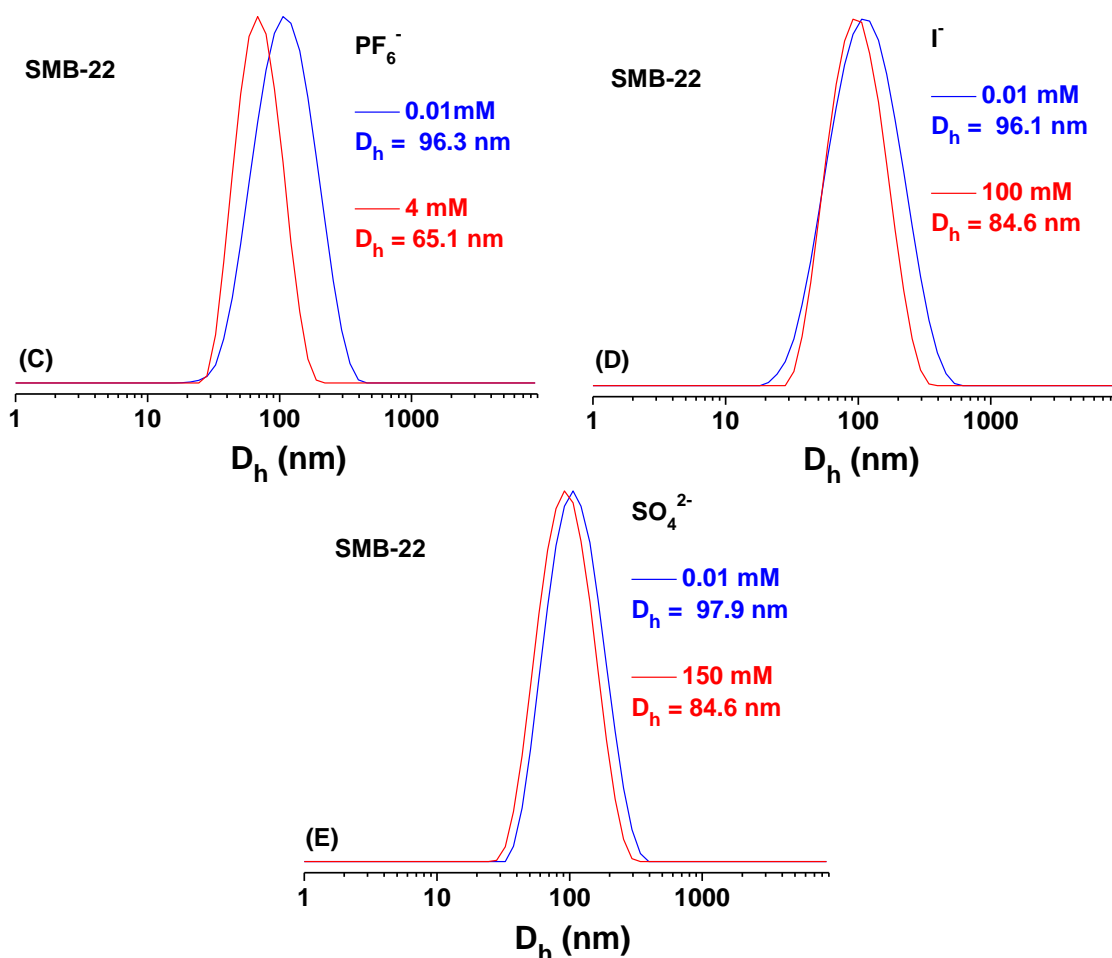




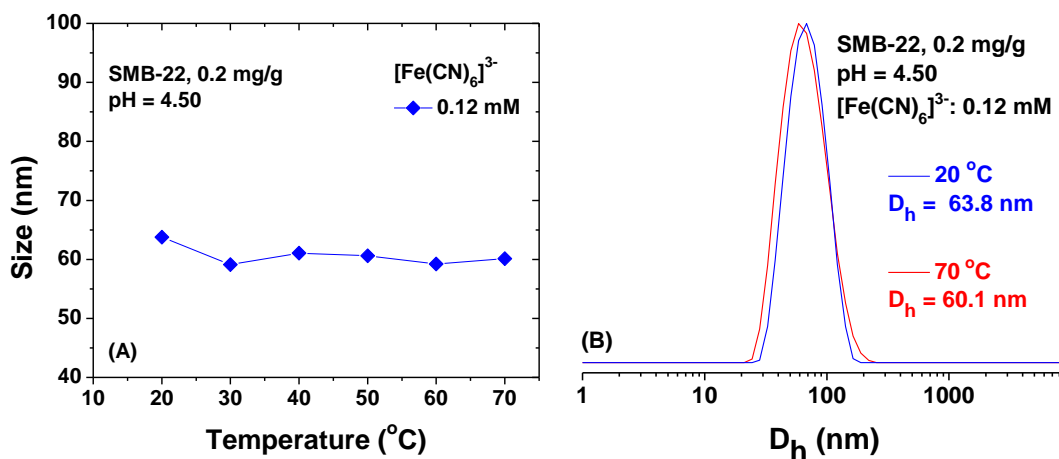


**Figure S10.** Hydrodynamic size distributions of 0.2 mg/g SMB-11 in pH 4.50 water in the presence of  $\text{Na}_4[\text{Fe}(\text{CN})_6]$  (A),  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (B),  $\text{NaClO}_4$  (C),  $\text{NaI}$  (D), and  $\text{Na}_2\text{SO}_4$  (E) at one low and one high concentration, obtained from DLS measurements at 25 °C. These size distributions are for the corresponding data points in Figure 2A.

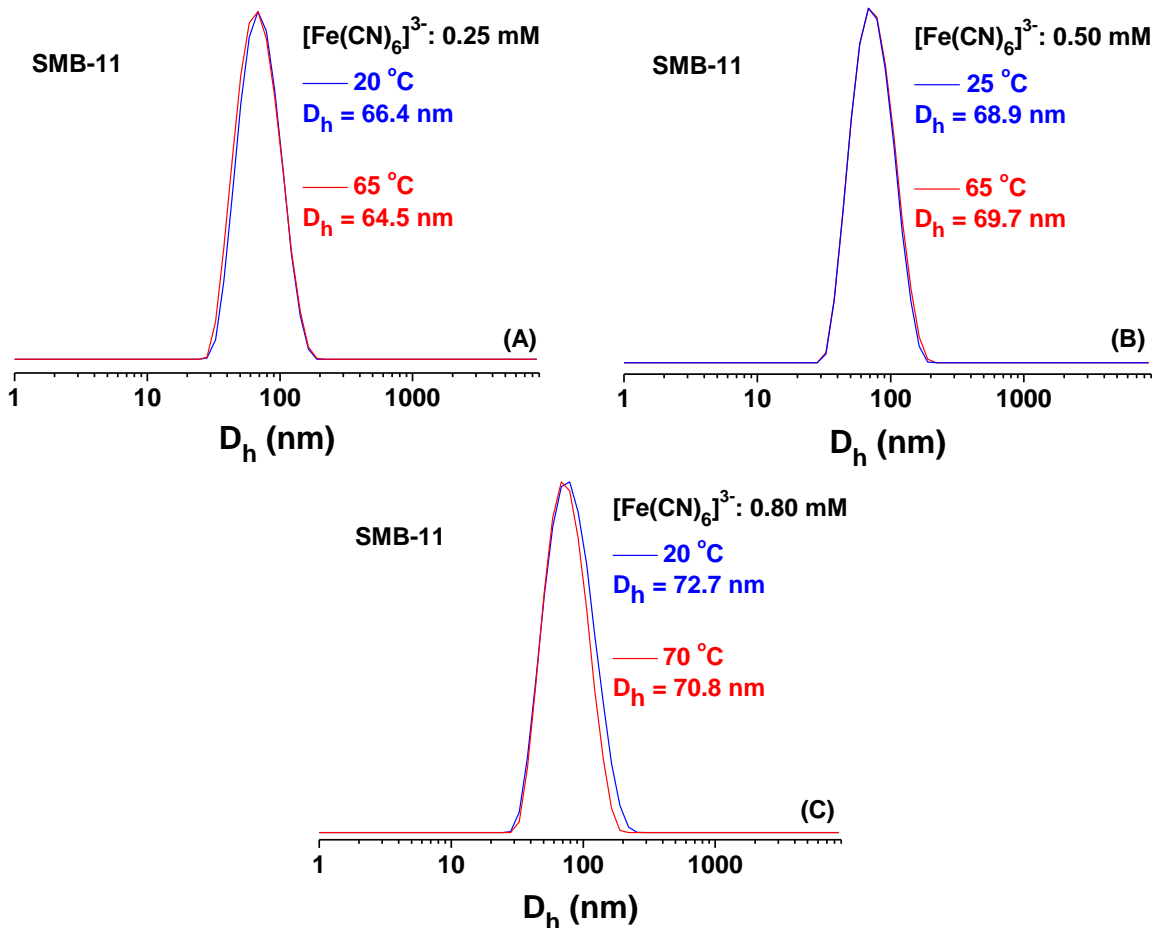




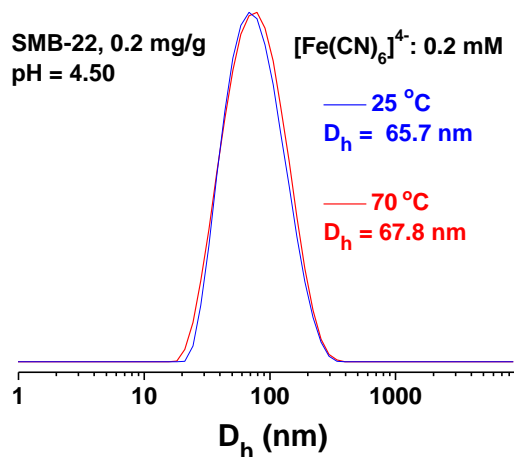
**Figure S11.** Hydrodynamic size distributions of 0.2 mg/g SMB-22 in pH 4.50 water with (A)  $\text{Na}_4[\text{Fe}(\text{CN})_6]$ , (B)  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , (C)  $\text{NaPF}_6$ , (D)  $\text{NaI}$ , and (E)  $\text{Na}_2\text{SO}_4$  at one low and one high concentration at 25 °C. These size distributions are for the corresponding data points in Figure 2B.



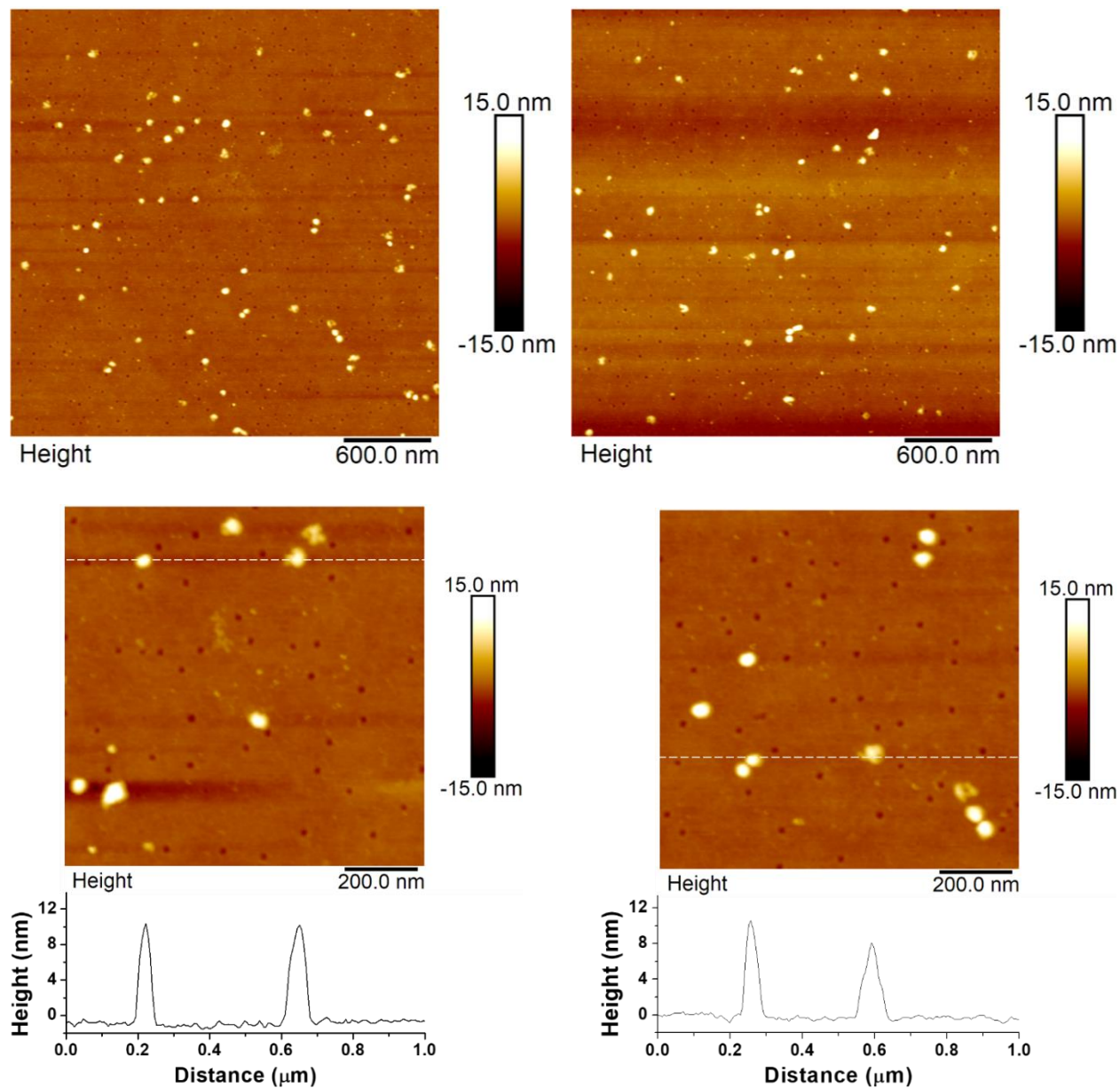
**Figure S12.** (A) Apparent hydrodynamic size ( $D_h$ ) of 0.2 mg/g SMB-22 in pH 4.50 water in the presence of 0.12 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  as a function of temperature. (B) Hydrodynamic size distributions of 0.2 mg/g SMB-22 in pH 4.50 water with 0.12 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  at 20 and 70 °C.



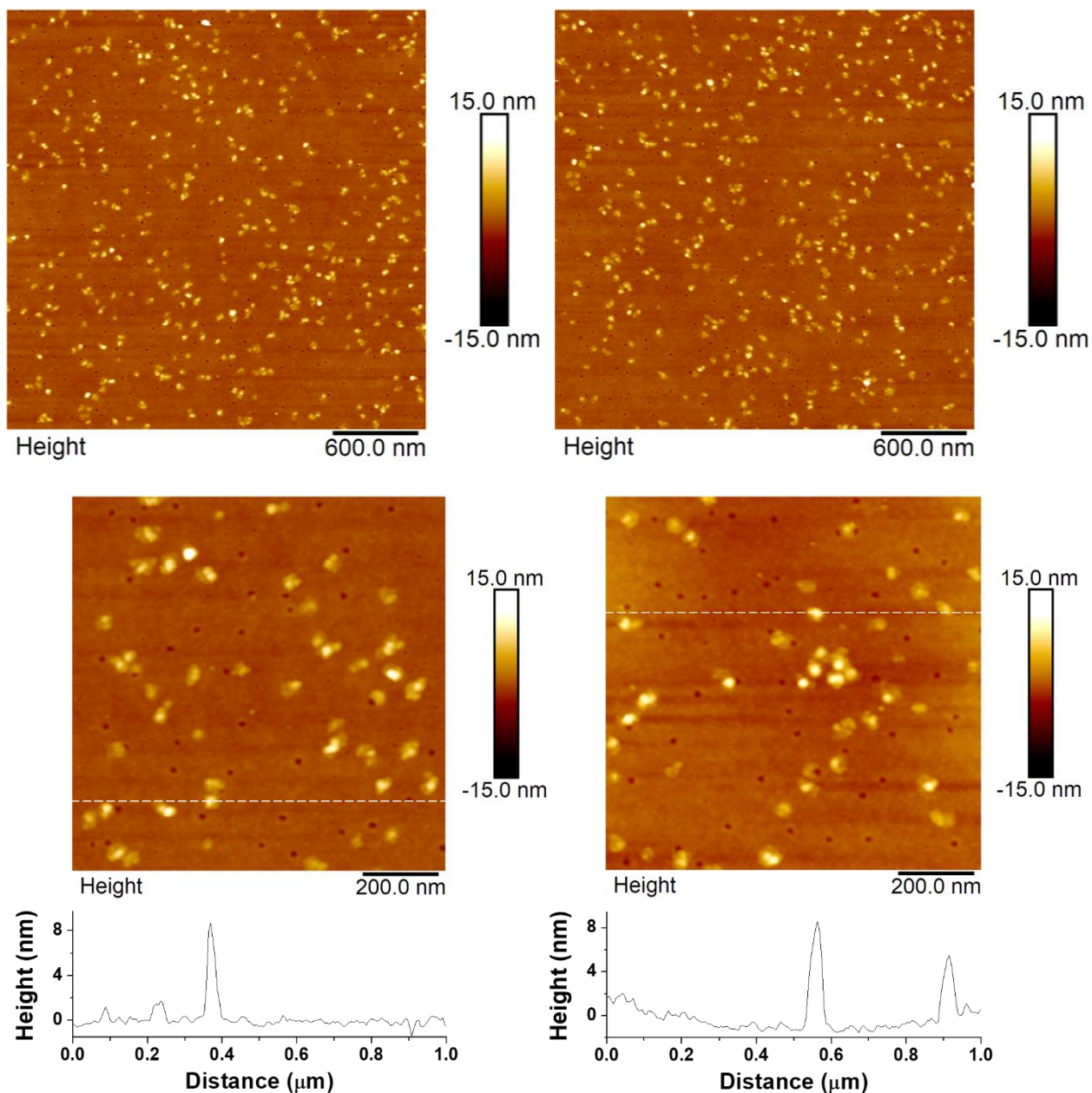
**Figure S13.** Hydrodynamic size distributions of 0.2 mg/g SMB-11 in pH 4.50 water in the presence of 0.25 mM (A), 0.50 mM (B), and 0.80 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (C) at one low and one high temperature. These size distributions are for the corresponding data point in Figure 3A.



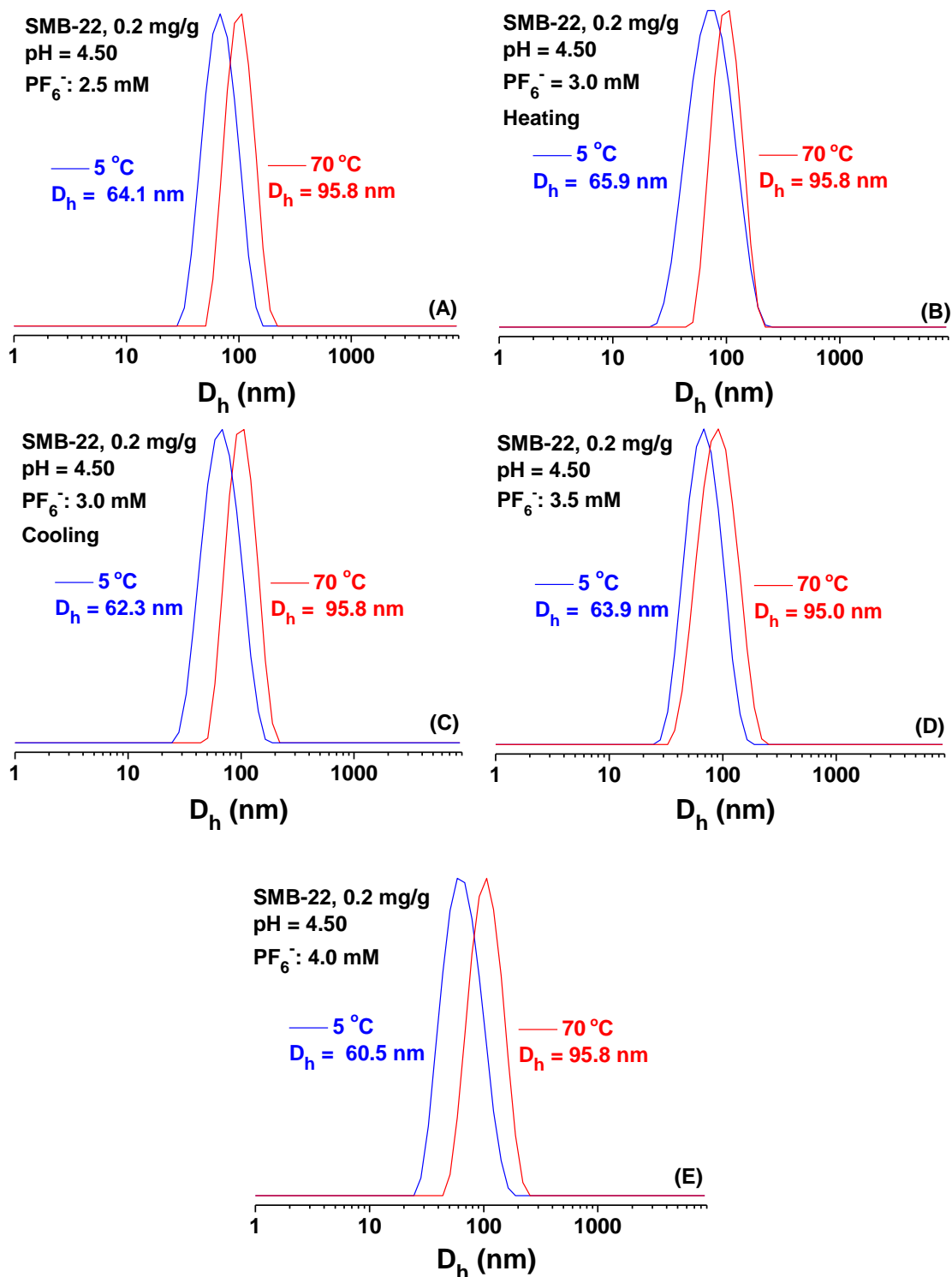
**Figure S14.** Hydrodynamic size distributions of 0.2 mg/g SMB-22 in pH 4.50 water in the presence of 0.2 mM  $\text{Na}_4[\text{Fe}(\text{CN})_6]$  at 25 and 70 °C.



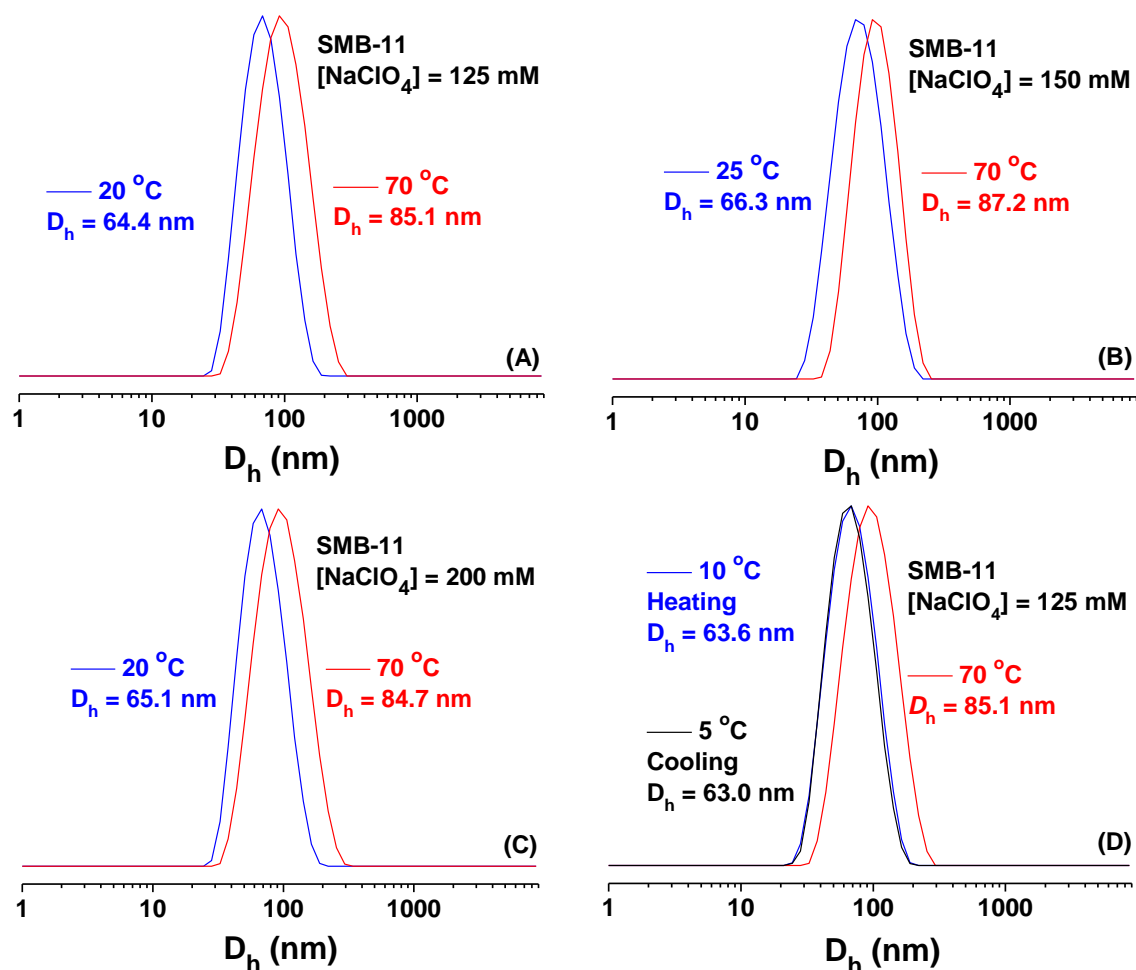
**Figure S15.** Atomic force microscopy height images (top:  $3 \times 3 \mu\text{m}$  and bottom:  $1 \times 1 \mu\text{m}$ ) of SMB-11 drop cast on glass disks at  $20^\circ\text{C}$  from a  $0.050 \text{ mg/g}$  SMB-11 in pH 4.50 water in the presence of  $0.075 \text{ mM K}_3[\text{Fe}(\text{CN})_6]$ , with a cross-sectional profile along the dashed line in each of the bottom images. The solution used to prepare AFM samples was diluted from a  $0.2 \text{ mg/g}$  solution of SMB-11 in pH 4.50 water with  $0.30 \text{ mM K}_3[\text{Fe}(\text{CN})_6]$  using pH 4.50 water.



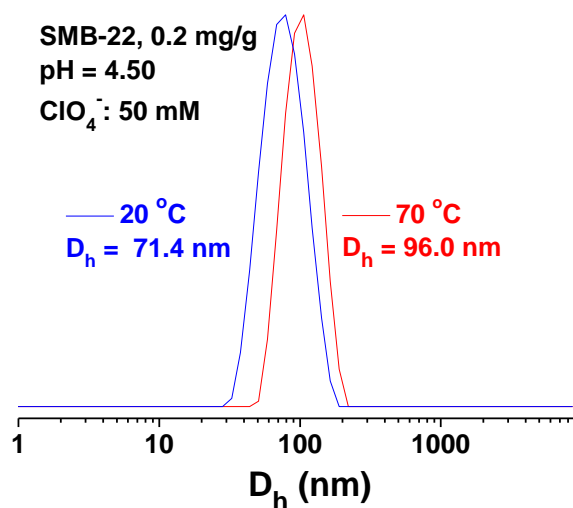
**Figure S16.** Atomic force microscopy height images of SMB-11 drop cast on glass disks at 70 °C from a 0.050 mg/g SMB-11 in pH 4.50 water in the presence of 0.075 mM  $K_3[Fe(CN)_6]$ , with cross-sectional profiles along the dashed lines in the  $1 \times 1 \mu\text{m}$  images. The solution used to prepare AFM samples was diluted from a 0.2 mg/g solution of SMB-11 in pH 4.50 water with 0.30 mM  $K_3[Fe(CN)_6]$  using pH 4.50 water.



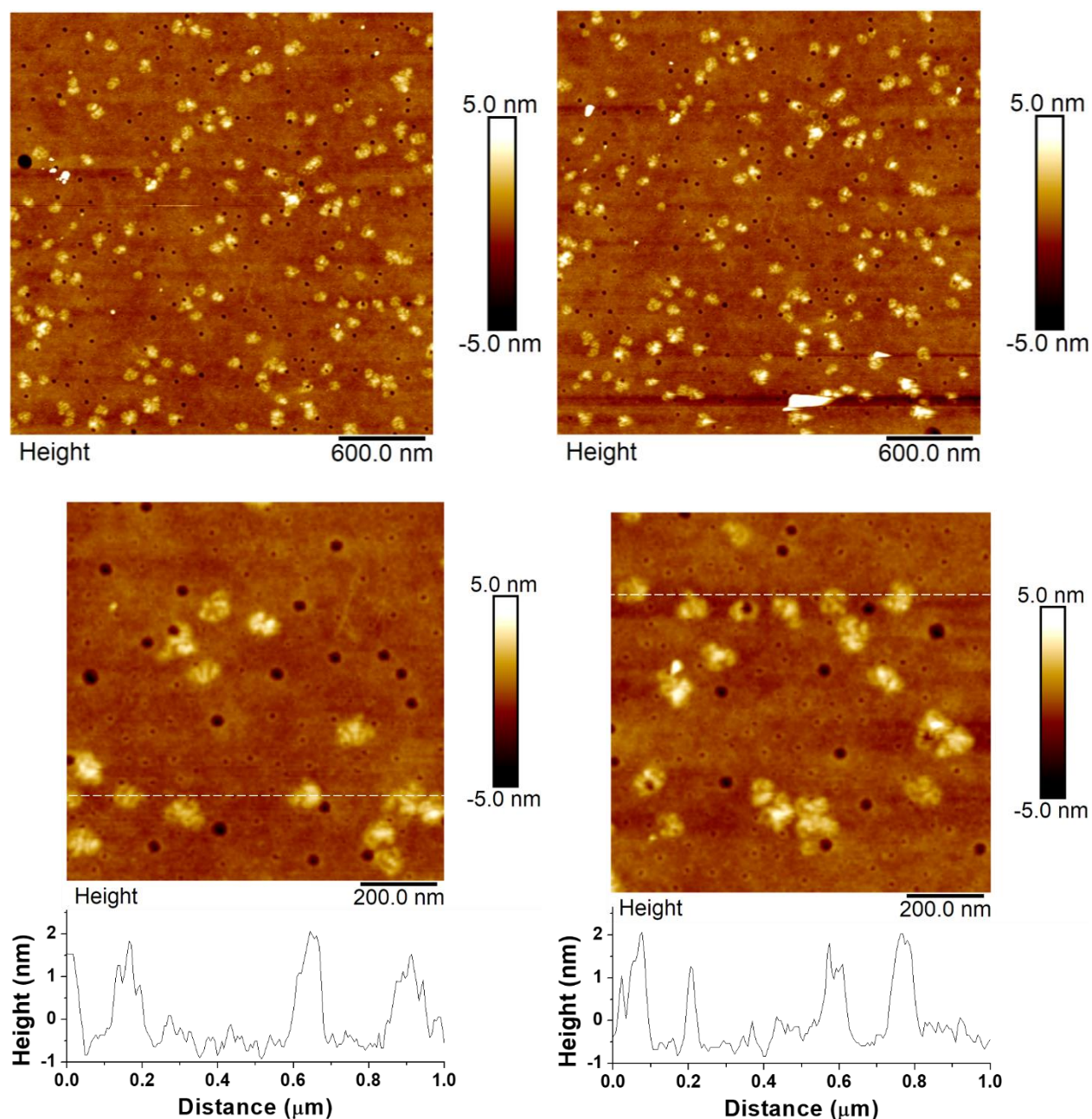
**Figure S17.** Hydrodynamic size distributions of 0.2 mg/g SMB-22 in pH 4.50 water in the presence of (A) 2.5 mM, (B) 3.0 mM (heating), (C) 3.0 mM (cooling), (D) 3.5 mM, and (E) 4.0 mM NaPF<sub>6</sub> at 5 and 70 °C, obtained from DLS measurements. These size distributions are for the corresponding data points in Figure 5C and D.



**Figure S18.** Hydrodynamic size distributions of 0.2 mg/g SMB-11 in pH 4.50 water in the presence of NaClO<sub>4</sub> with various concentrations at one low and one high temperature, corresponding to the data points in Figure 6A and B.

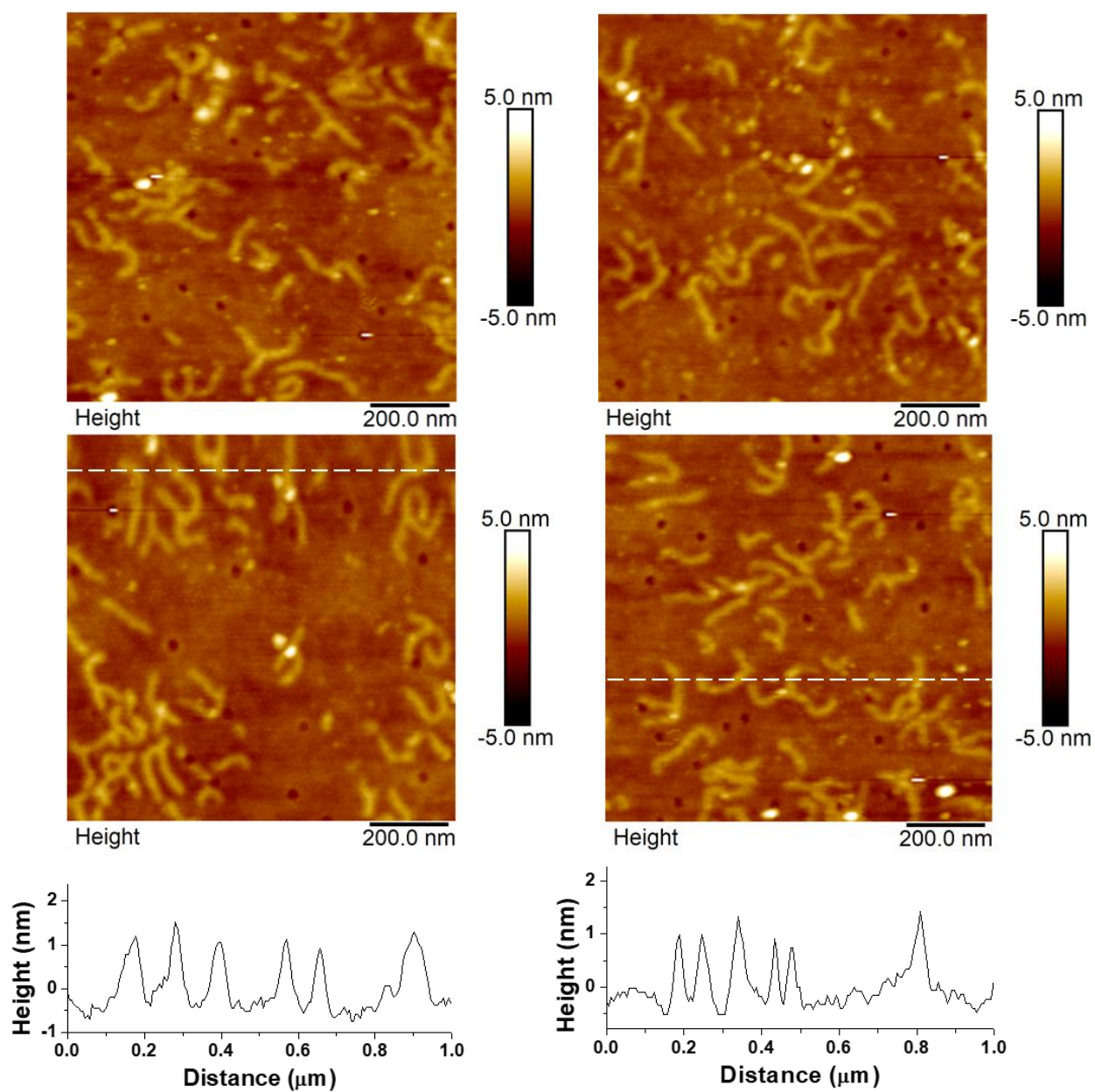


**Figure S19.** Hydrodynamic size distributions of 0.2 mg/g SMB-22 in pH 4.50 water in the presence of 50 mM NaClO<sub>4</sub> at 20 and 70 °C for the corresponding data points in Figure 6C.

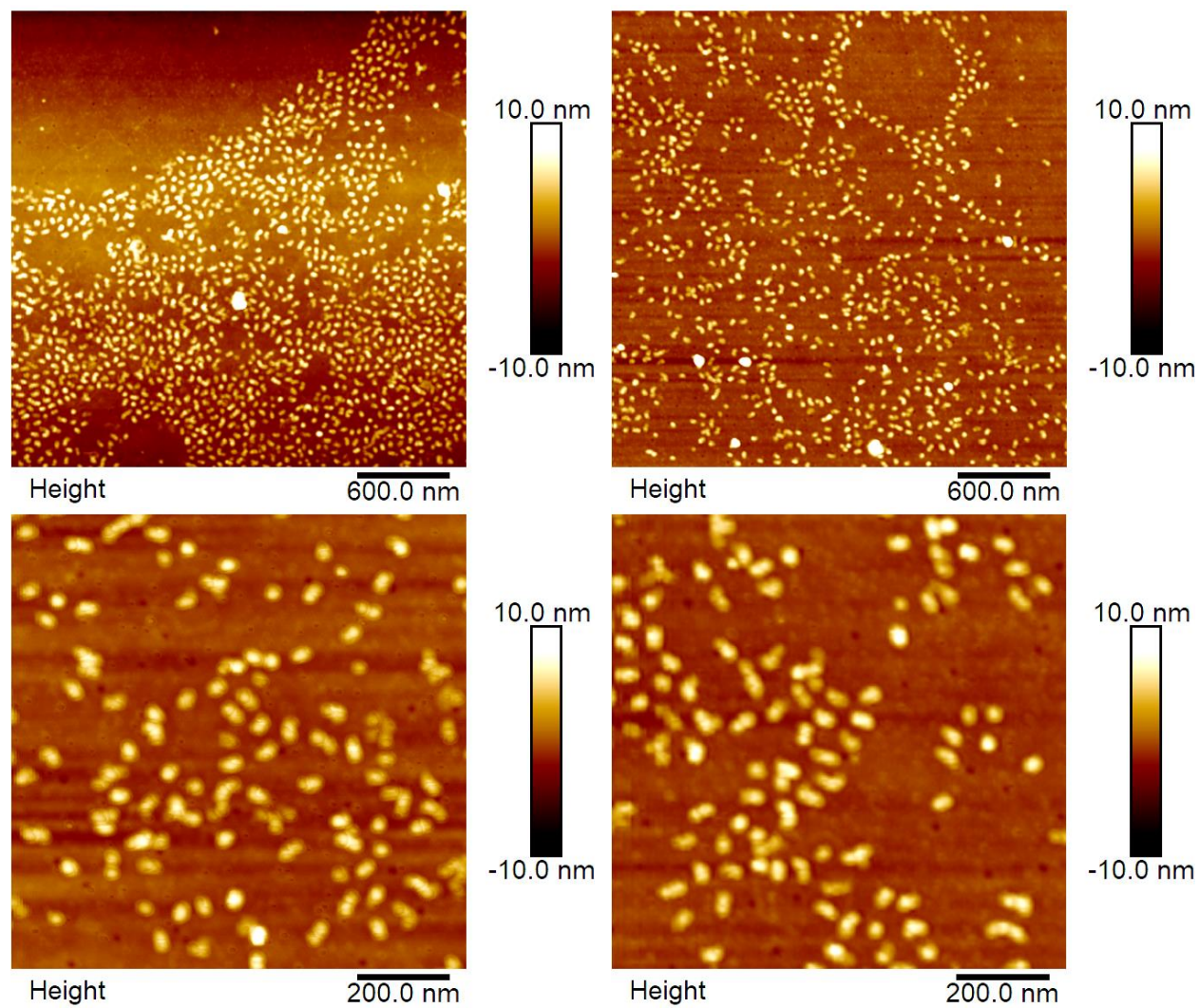


**Figure S20.** AFM height images (top:  $3 \times 3 \mu\text{m}$  and bottom:  $1 \times 1 \mu\text{m}$ ) of SMB-11 drop cast on glass disks from a solution of 0.050 mg/g SMB-11 in pH 4.50 water in the presence of 1.5 mM  $\text{NaPF}_6$  at 20 °C, with a cross-sectional profile along the dashed line in each of the bottom two  $1 \times 1 \mu\text{m}$  images.. The solution was diluted from a pH 4.50 solution of 0.2 mg/g SMB-11 with 6 mM  $\text{NaPF}_6$  using pH 4.50 water.

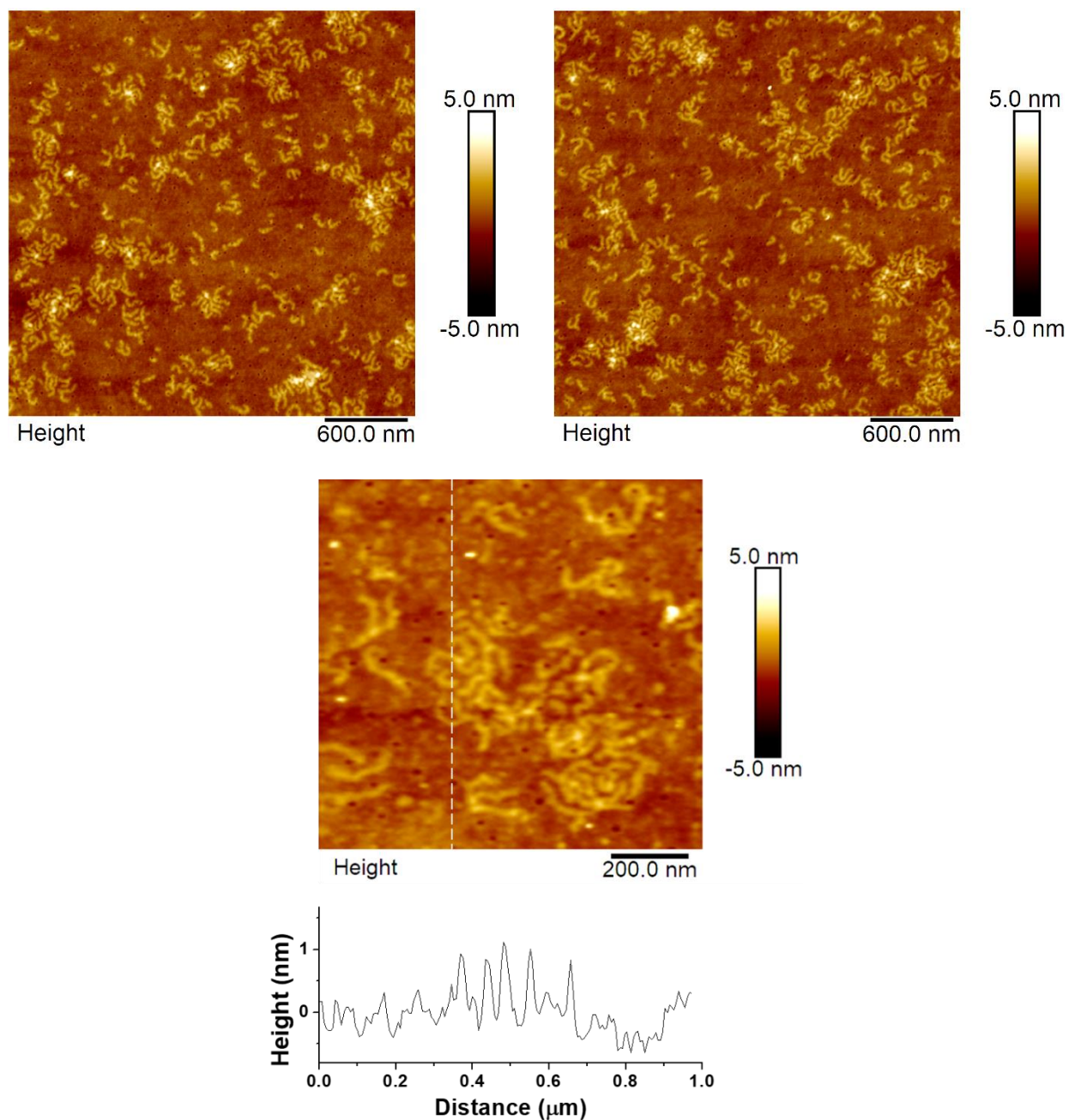




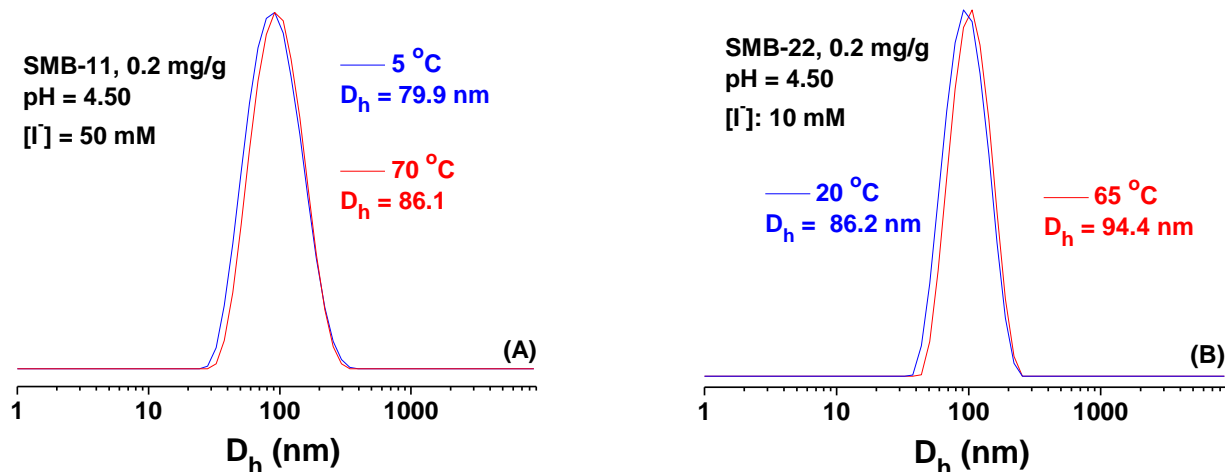
**Figure S21.** AFM height images ( $1 \times 1 \mu\text{m}$ ) of SMB-11 drop cast on glass disks from a solution of 0.050 mg/g SMB-11 in pH 4.50 water in the presence of 1.5 mM  $\text{NaPF}_6$  at 70 °C, with cross-sectional profiles along the dashed lines in the bottom two images. The solution was diluted from a pH 4.50 solution of 0.2 mg/g SMB-11 with 6 mM  $\text{NaPF}_6$  using pH 4.50 water.



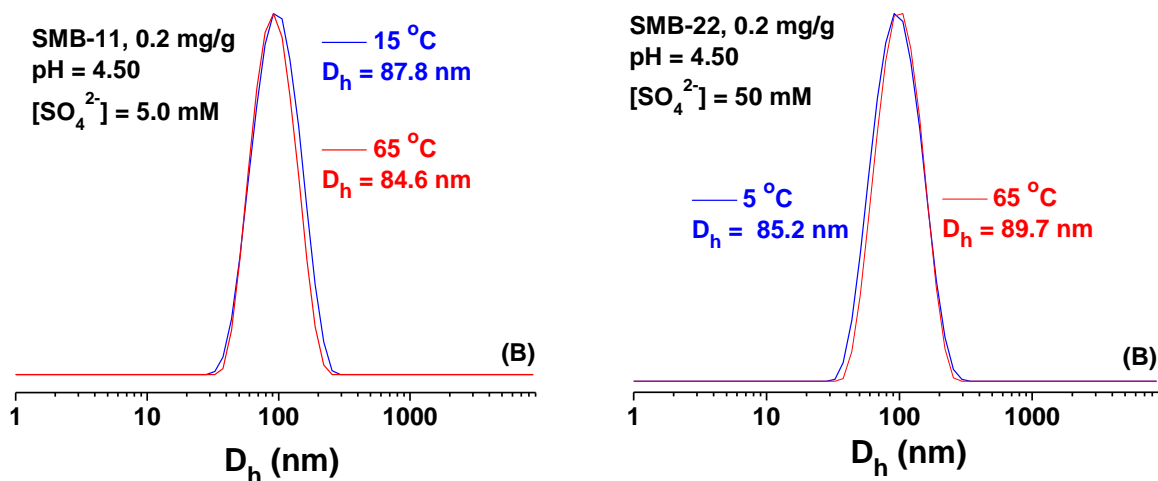
**Figure S22.** AFM height images of SMB-22 drop cast on glass disks from a 0.050 mg/g solution of SMB-22 in pH 4.50 water in the presence of 1.0 mM  $\text{NaPF}_6$  at 0 °C. The solution was diluted from a pH 4.50 solution of 0.2 mg/g SMB-22 with 4 mM  $\text{NaPF}_6$  using pH 4.50 water.



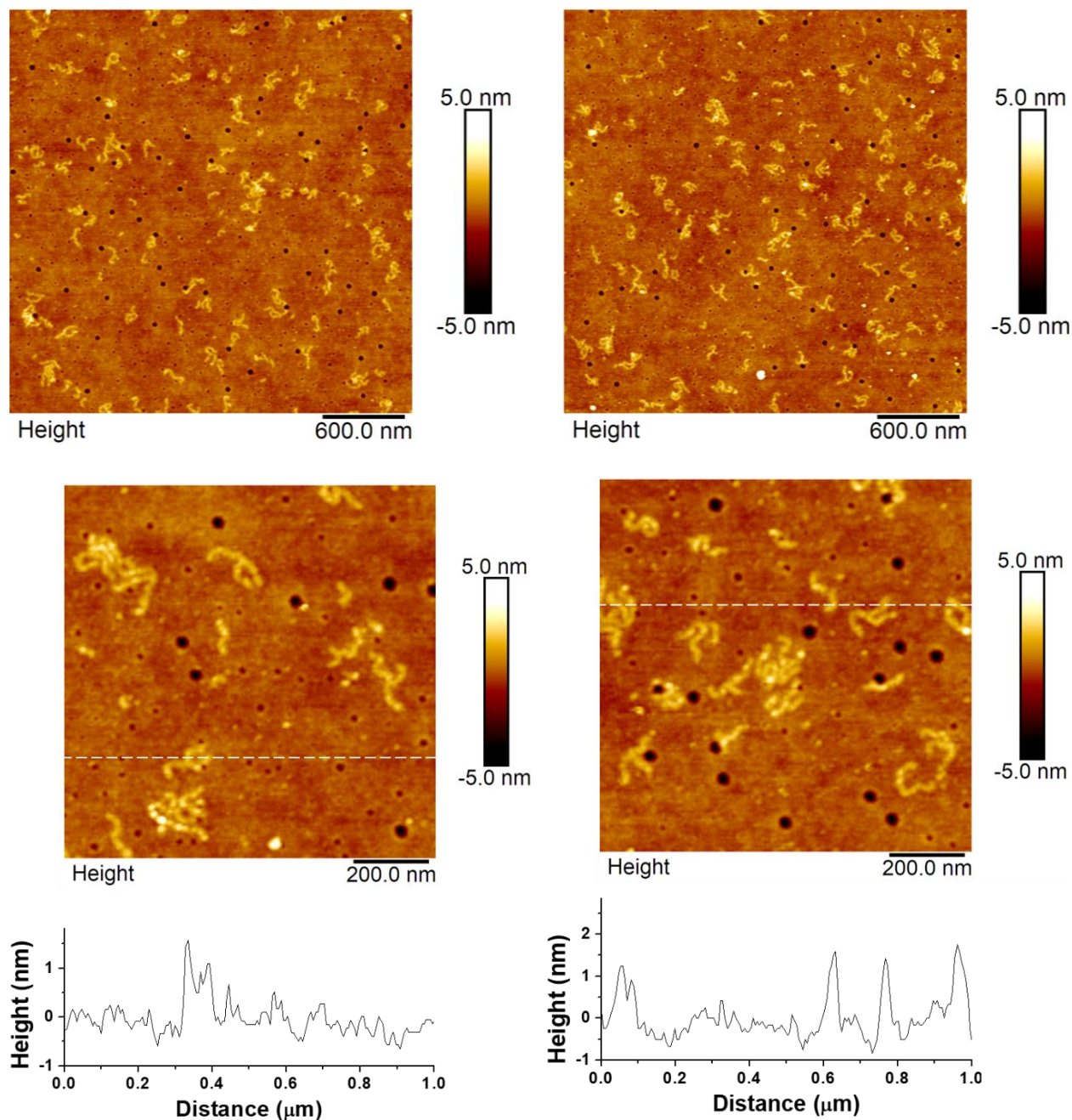
**Figure S23.** AFM height images of SMB-22 drop cast on glass disks from a solution of 0.050 mg/g SMB-22 in pH 4.50 water in the presence of 1.0 mM  $\text{NaPF}_6$  at 70  $^\circ\text{C}$ , with cross-sectional profiles along the dashed lines in the bottom two images. The solution was diluted with pH 4.50 water from a 0.2 mg/g solution of SMB-22 with a pH of 4.50 in the presence of 4 mM  $\text{NaPF}_6$ .



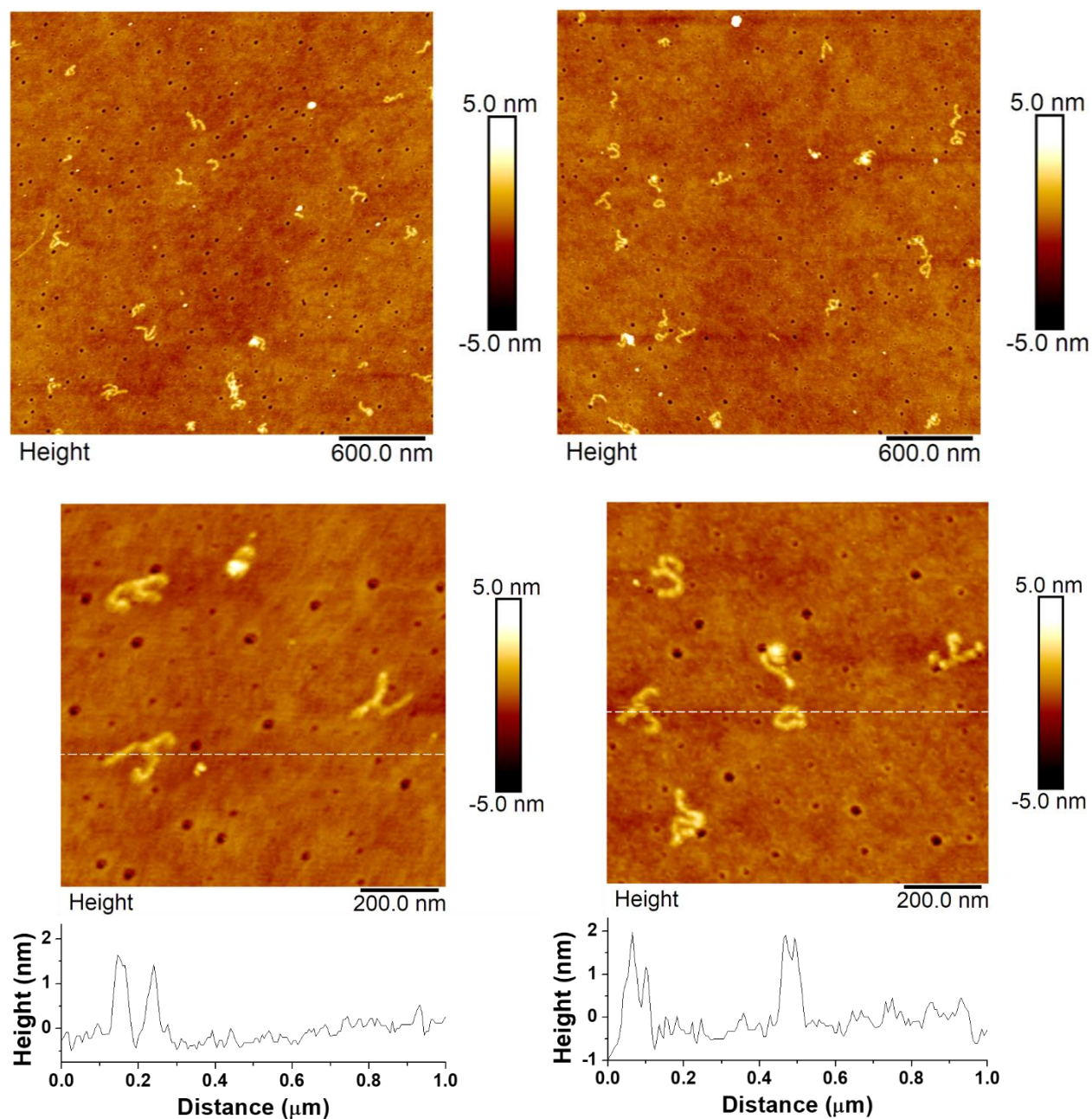
**Figure S24.** Hydrodynamic size distributions of (A) 0.2 mg/g SMB-11 in pH 4.50 water in the presence of 50 mM NaI at 5 and 70 °C for the corresponding data points in Figure 9A and (B) 0.2 mg/g SMB-22 in pH 4.50 water in the presence of 10 mM NaI at 20 and 65 °C for the corresponding data points in Figure 9B.



**Figure S25.** Hydrodynamic size distributions of (A) 0.2 mg/g SMB-11 in pH 4.50 water in the presence of 5 mM NaSO<sub>4</sub> at one low (15 °C) and one high temperature (65 °C) for the corresponding data points in Figure 10A and (B) 0.2 mg/g SMB-22 in pH 4.50 water in the presence of 50 mM Na<sub>2</sub>SO<sub>4</sub> at 5 and 65 °C for the corresponding data points in Figure 10B.



**Figure S26.** AFM height images (top:  $3 \times 3 \mu\text{m}$  and bottom:  $1 \times 1 \mu\text{m}$ ) of SMB-11 drop cast on a glass disk from a solution of 0.050 mg/g SMB-11 in pH 4.50 water with 2.5 mM  $\text{Na}_2\text{SO}_4$  at 20 °C, with a cross-sectional profile along the dashed line in each of the bottom two  $1 \times 1 \mu\text{m}$  images.. The solution was diluted from a 0.2 mg/g solution of SMB-11 in pH 4.50 water with 10 mM  $\text{Na}_2\text{SO}_4$  using pH 4.50 water.



**Figure S27.** AFM height images (top:  $3 \times 3 \mu\text{m}$  and bottom:  $1 \times 1 \mu\text{m}$ ) of SMB-11 drop cast on glass disks from a solution of 0.050 mg/g SMB-11 in pH 4.50 water with 2.5 mM  $\text{Na}_2\text{SO}_4$  at 70 °C, with a cross-sectional profile along the dashed line in each of the two bottom images. The solution was diluted from a 0.2 mg/g solution of SMB-11 in pH 4.50 water with 10 mM  $\text{Na}_2\text{SO}_4$  using pH 4.50 water.