Supplementary Information for

Non-charged, water soluble dendronized polymers

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Synthetic procedures and analytical data

N-hydroxysuccinimidyl-3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)-ethoxy)benzoate (**1**):

To a well-stirred solution of 3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)-ethoxy)benzoic acid (1.00 g, 1.64 mmol) in dichloromethane (35 mL) was added N-hydroxysuccinimide (HOSu; 0.23 g, 1.97 mmol) at room temperature. The mixture was stirred for 15 min then dicyclohexylcarbodiimide (DCC, 0.42 g, 2.05 mmol) was added at −10 °C. The reaction mixture was gradually warmed to room temperature and stirred over night. After removal of the formed white precipitate by suction filtration, the filtrate was concentrated *in vacuo*. The residue was dissolved in isopropanol, and after cooling to −20 °C, a faint yellow oil precipitated from solution which was separated by decanting. This procedure was repeated 3-4 times to give the oily product (0.96 g, 83%). ^{1}H NMR (300 MHz, MeOD): δ = 2.87 (s, 4H, CH_2CO), 3.27-3.32(m, 9H, CH_3O), 3.47-3.50 (m, 6H, CH_2O), 3.55-3.70 (m, 19H, CH_2O), 3.77-3.80 (m, 2H, CH_2O), 3.83-3.86 (m, 4H, CH_2O), 4.20-4.23 (m, 4H, CH_2O), 4.27-4.30 (m, 2H, CH_2O), 7.43 (s, 2 H, CH); ^{13}C NMR(125 MHz, MeOD): δ = 24.27, 56.79, 67.97, 68.40, 69.03, 69.20, 69.28, 69.40, 69.48, 70.61, 71.44, 108.39, 118.44, 143.30, 151.77, 160.64, 169.48. HRMS: m/z calcd, 728.3106; found, 728.3100 $[M + Na]^+$. Elemental analysis (%) calcd for $C_{32}H_{51}NO_{16}$: C 54.46, H 7.28, N 1.98; found: C 54.01, H 7.00, N 2.61.

h-PG2

To a well-stirred solution of ***de*-PG1** (50 mg, 0.091 mmol) in 20 mL DMF was added triethylamine (TEA) (22 mg, 0.22 mmol) and 4-dimethylaminopyridine (DMAP)

(0.010 g, 0.082 mmol) at −10 °C. A solution of OEG dendron active ester **1** (0.642 g, 0.91 mmol) in DMF (2 mL) was added in 3 portions over 10 days. During the addition of each portion, the reaction mixture was cooled to −10 °C, then slowly warmed to rt and stirred for 1-2 days. After the addition of **1**, the reaction mixture was concentrated *in vacuo*. The residue was dissolved in dichloromethane (10 mL) and precipitated into cold diethyl ether to yield a white solid. The same precipitation step was repeated 3 times then the resulting solid was lyophilized to yield a powdery white solid as the product ***h*-PG2** (0.126 g, 92%). ^{1}H NMR (300 MHz, MeOD): δ = 1.22-1.24 (br, 2H), 1.36-1.38 (br, 2H), 1.76-1.78 (br, 1H), 1.89-1.93 (br, 2 H), 2.85-3.05 (br, 6H), 3.30-3.40 (br, 26 H), 3.53-3.93 (br, 59H), 4.18-4.37 (br, 10 H), 6.45 (br, 1H), 7.02-7.04 (br, 1H), 7.22 (br, 2H), 7.51 (br, 1H), 8.15-8.17 (br, 1H). Elemental analysis (%) calcd for $(C_{73}H_{118}N_2O_{30})_n$: C 58.31, H 7.91, N 1.86; found: C 58.02, H 7.90, N 1.87.

***h*-PG3**

To a well-stirred solution of ***de*-PG2** (50 mg, 0.039 mmol) in 20 mL DMF was added triethylamine (TEA) (20 mg, 0.20 mmol) and 4-dimethylaminopyridine (DMAP) (0.010 g, 0.082 mmol) at −10 °C. A solution of OEG dendron active ester **1** (0.564 g, 0.800 mmol) in DMF (2 mL) was added in 3 portions over 15 days. During the addition of each portion, the reaction mixture was cooled to −10 °C, then slowly warmed to rt and stirred for 3-4 days. After the addition of **1**, the reaction mixture was concentrated *in vacuo*. The residue was dissolved in dichloromethane (10 mL) and precipitated into cold diethyl ether to yield a white solid. The same precipitation step was repeated 3 times and the resulting solid was lyophilized to yield a powdery white solid as the product ***h*-PG3** (0.116 g, 93%). ^{1}H NMR (300 MHz, MeOD): δ = 1.20-1.35 (br, 1H), 1.68-2.25 (br, 10H), 2.52 (br, 7H), 2.71 (br, 12H), 2.83 (br, 15H), 3.28-

3.45 (br, 36H), 3.50-3.79 (br, 94H), 4.17-4.35 (br, 19 H), 6.45 (br, 1H), 7.01 (br, d, 2H, Ph), 7.20 (br, 4H), 7.48 (br, 1H), 8.14 (br, d, 2H), 8.23 (br, 1H), 8.46 (br, 1H). Elemental analysis (%) calcd for $(C_{155}H_{246}N_6O_{62})_n$: C 58.44, H 7.78, N 2.64; found: C 57.93; H, 7.66; N, 2.61.

***h*-PG4**

To a well-stirred solution of ***de*-PG3** (50 mg, 0.018 mmol) in 20 mL DMF was added triethylamine (TEA) (18 mg, 0.18 mmol) and 4-dimethylaminopyridine (DMAP) (0.010 g, 0.082 mmol) at −10 °C. A solution of OEG dendron active ester **1** (0.564 g, 0.80 mmol) in DMF (2 mL) was added in 3 portions over 25 days. During the addition of each portion, the reaction mixture was cooled to −10 °C, then slowly warmed to rt and stirred for 7-8 days. After the addition of **1**, the reaction mixture was concentrated *in vacuo*. The residue was dissolved in dichloromethane (10 mL) and precipitated into cold diethyl ether to yield a white solid. The same precipitation step was repeated 3 times then the resulting solid was lyophilized to yield a powdery white solid as the product ***h*-PG4** (0.098 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29-1.36 (br, 48 H), 1.51-1.80 (br, 13 H), 1.88-2.09 (br, 12H), 2.81-2.99 (br, 25H), 3.34-3.87 (br, 208 H), 4.18-4.28 (br, 30 H), 6.66-6.68 (br, 6H), 7.38 (br, 18 H), 8.20 (br, 4H). Elemental analysis (%) calcd for $(C_{319}H_{502}N_{14}O_{126})_n$: C 58.50, H 7.73, N 2.99; found: C 58.14, H 7.70, N 2.96.

***h*-PG5**

To a well-stirred solution of ***de*-PG4** (50 mg, 0.0089 mmol) in 20 mL DMF was added triethylamine (TEA) (22 mg, 0.22 mmol) and 4-dimethylaminopyridine (DMAP) (0.010g, 0.082 mmol) at −10 °C. A solution of OEG dendron active ester **1**

(0.624 g, 0.885 mmol) in DMF (2 mL) was added in 3 portions over 6 days. During the addition of each portion, the reaction mixture was cooled to −10 °C, then slowly warmed to rt and stirred for 1-2 days. After the addition of all the active ester **1**, the reaction mixture was concentrated *in vacuo*. The residue was dissolved in dichloromethane (10 mL) and precipitated into cold diethyl ether to yield white solid. The same precipitation step was repeated 3 times to yield a powdery white solid as the product ***h*-PG5** (0.116 g, 99%). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.04 (br, 7H), 1.29-1.36 (br, 8H), 1.92-2.15 (br, 10H), 2.82 (br, 19H), 3.15-3.82 (br, 108H), 4.18 (br, 12H), 6.69 (br, 2H, Ph), 7.26-7.43 (br, 9H), 7.61-7.74 (br, 7H), 8.20 (br, 2H). Elemental analysis (%) calcd for $(C_{647}H_{1014}N_{30}O_{254})_n$ $(13268.7351)_n$: C 58.53, H 7.70, N 3.16; found: C 58.01, H 7.68, N 3.14.

Quantitative determination of coverage

Sample preparation: To a well-stirred solution of *h***PG3** (17.6 mg) in 20 mL DMF was added

Sanger's reagent (97 μL, 8×10^{-4} mol, 40 eq. per amine group). The yellow mixture was stirred at room temperature for 20 min, the directly subjected to the UV measurements. A solution containing Sanger's reagent (97 μL, 8×10^{-4} mol) in DMF (20 mL) was prepared at the same time and then used as the background reference solution in the UV-vis measurements. The controlled experiments using *de***PG2** was performed by the same procedure.

Measurements: The quantitative UV-vis experiments were performed on UV/Vis/NIR spectrophotometer (V-670, Jasco Inc., Tokyo, Japan) using 2 mm quartz cells. The extinction coefficient (ε) of 2,4-diphenylaniline moiety follows the ε value of an earlier reported reference compound as 1.64×10^4.[1] The absorption of the UV-

labeled polymer was measured then normalized to the solvent/Sanger reagent background (Fig. S1). The calculation of the coverage follows the same procedure reported earlier [2] and the values are mentioned in the main text.

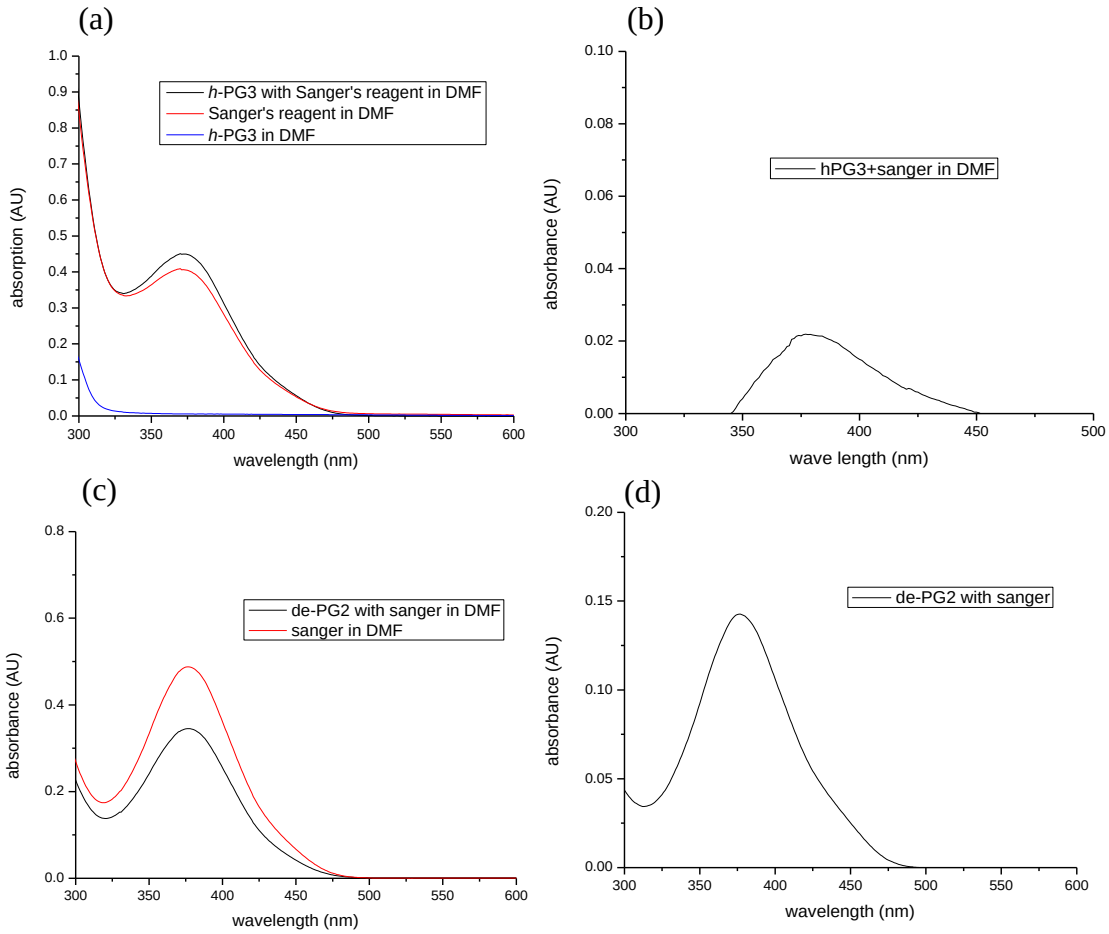

Figure S1. Quantitative UV measurements of ***h*PG3** and *de*-**PG2** in DMF. (a) UV absorption of ***h*PG3**, Sanger's reagent and ***h*PG3** plus Sanger's reagent; (b) UV absorption of labeled ***h*PG3**, after substraction of the absorption of Sanger's reagent and ***h*PG3**; (c) UV absorption of Sanger's reagent and *de*-**PG2** plus Sanger's reagent; (d) UV absorption of labeled *de*-**PG2**, after substraction of the absorption of Sanger's reagent (the absorption of *de*-**PG2** is negligible).

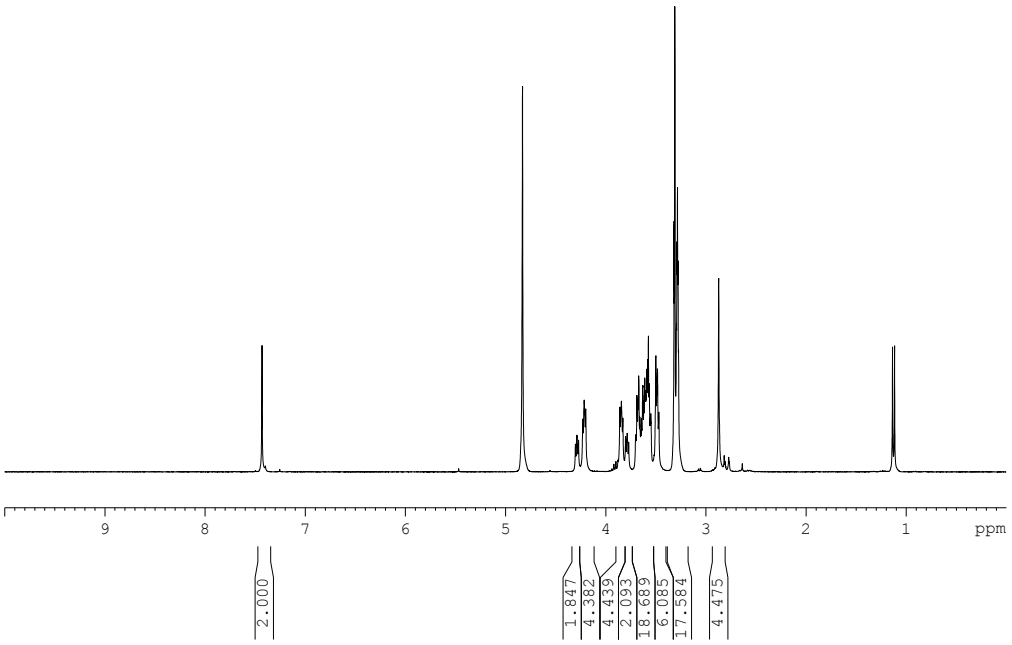

Figure S2. ^{1}H NMR spectrum of compound **1** in MeOD.

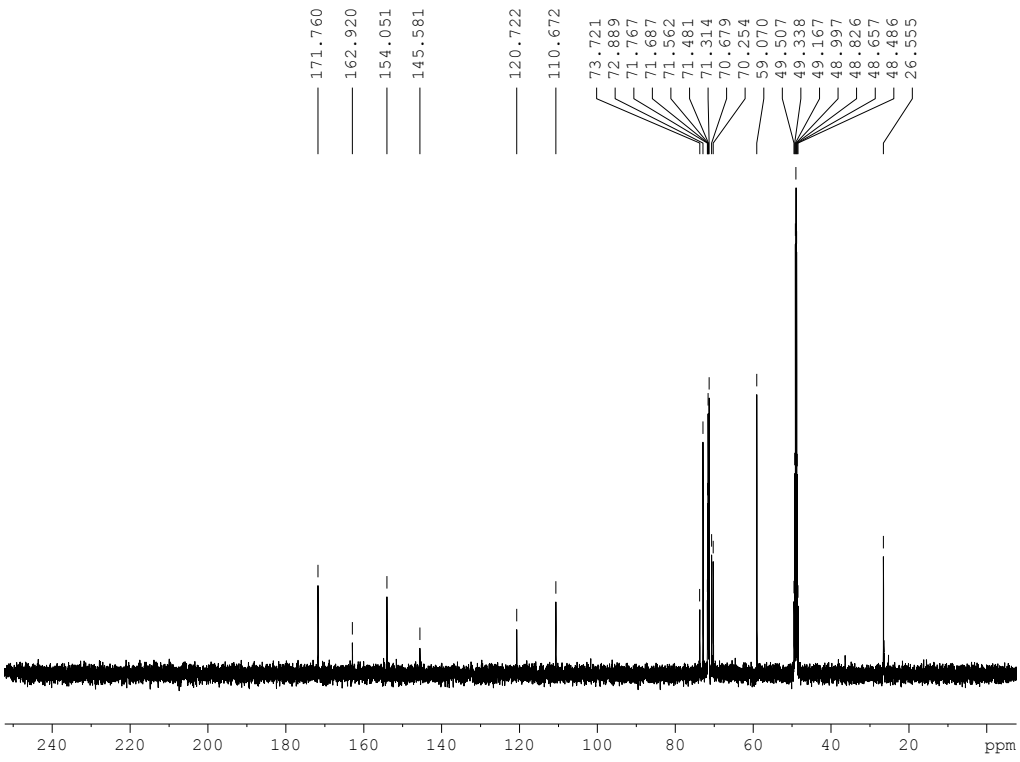

Figure S3. ^{13}C NMR spectrum of compound **1** in MeOD.

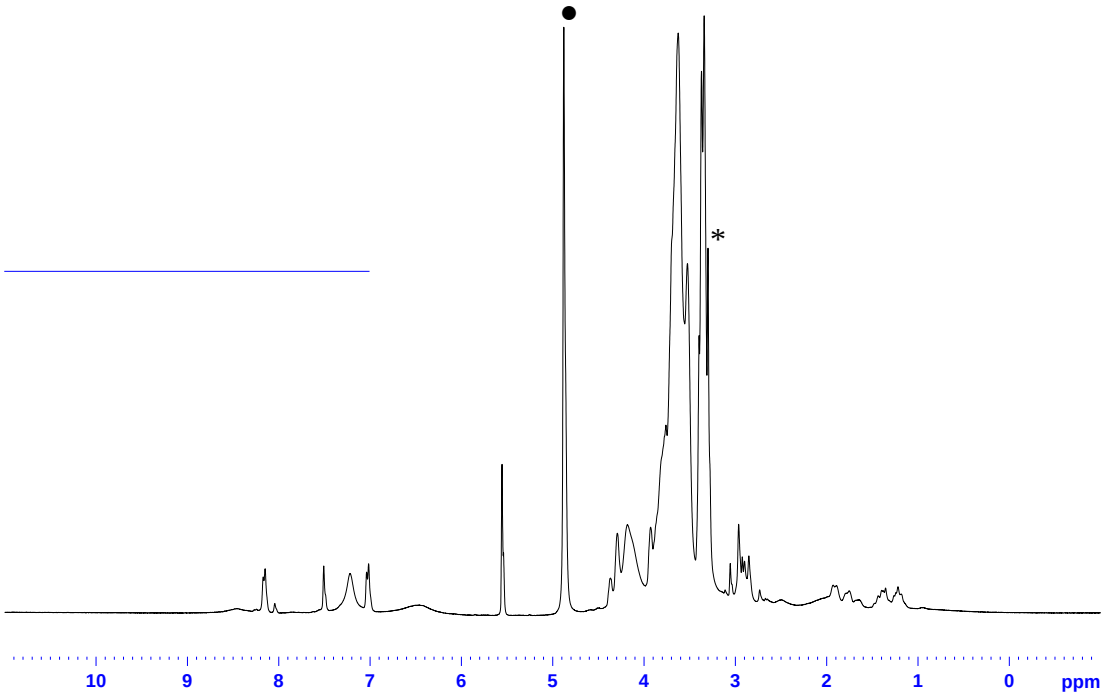

Figure S4. ^{1}H NMR spectrum of ***h*PG2** in MeOD-d_4 (300 MHz) (● H_2O, * MeOH).

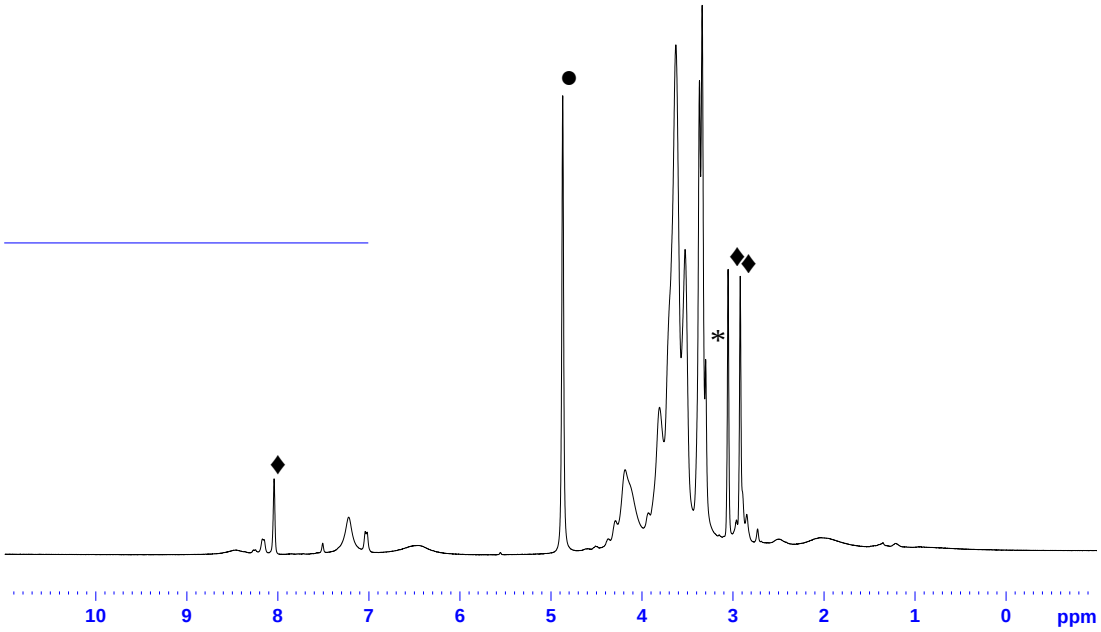

Figure S5. ^{1}H NMR spectrum of ***h*PG3** in MeOD-d_4 (300 MHz) (● H_2O, ♦DMF, *MeOH).

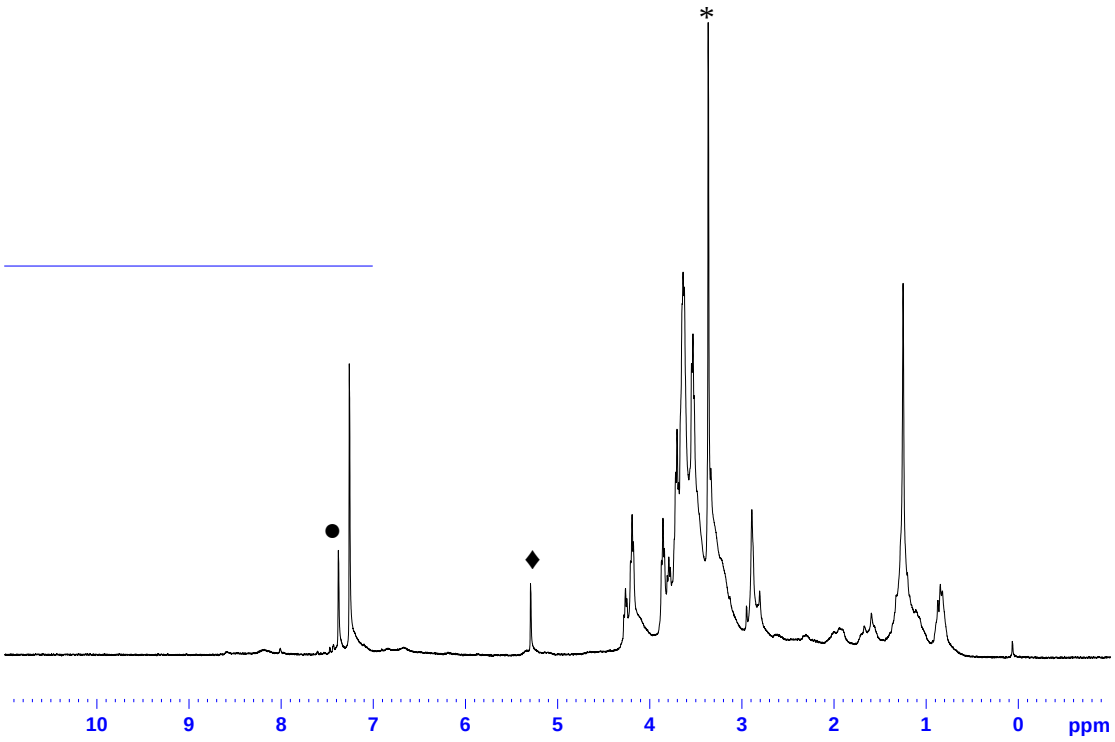

Figure S6. ^{1}H NMR spectrum of ***h*PG4** in $CDCl_3$ (300 MHz) (● $CHCl_3$, ♦dichloromethane, *MeOH).

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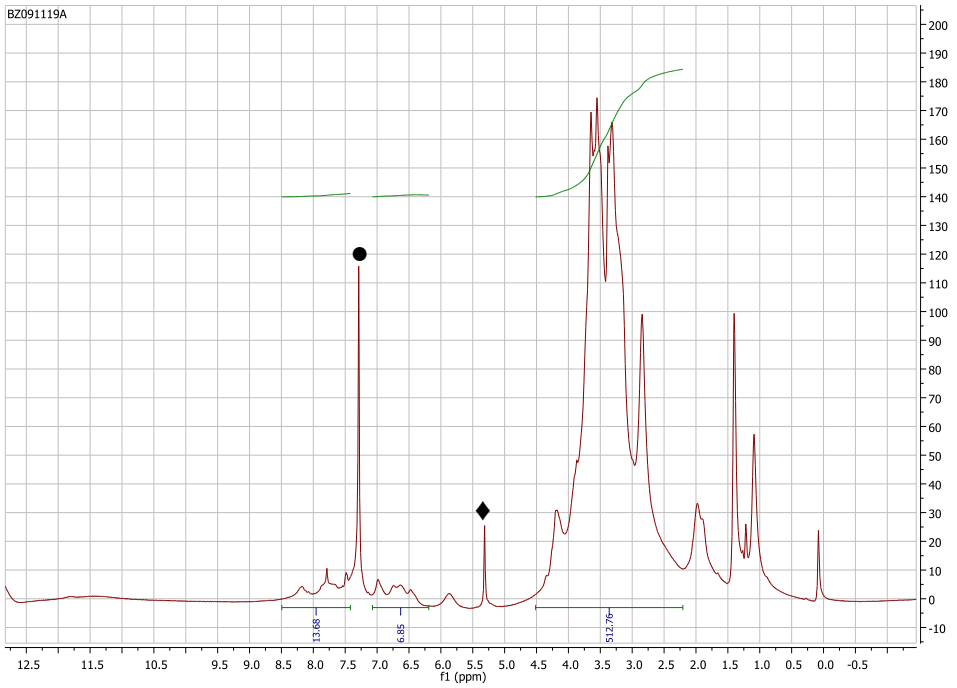

Figure S7. ^{1}H NMR spectrum of ***h*PG5** in $CDCl_3$ (700 MHz) (● $CHCl_3$, ♦dichloromethane).

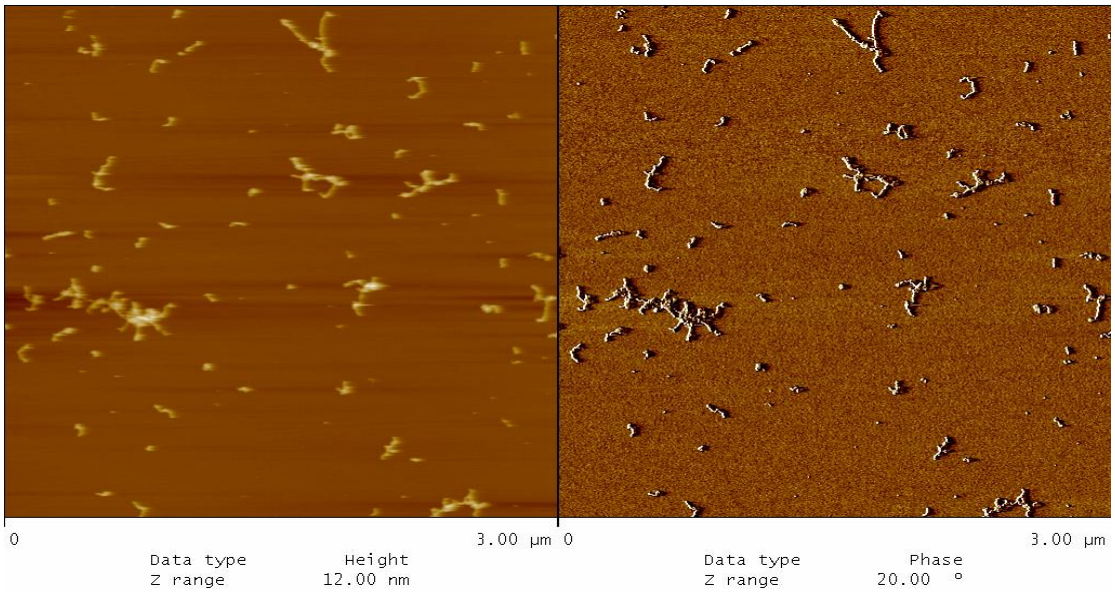

Figure S8. Tapping mode AFM image of ***h*PG4** on mica after spin-coating from chloroform. h_{AFM}(***h*PG4**) was determined as 2.1 ± 0.3 nm (average of 6 analyses).

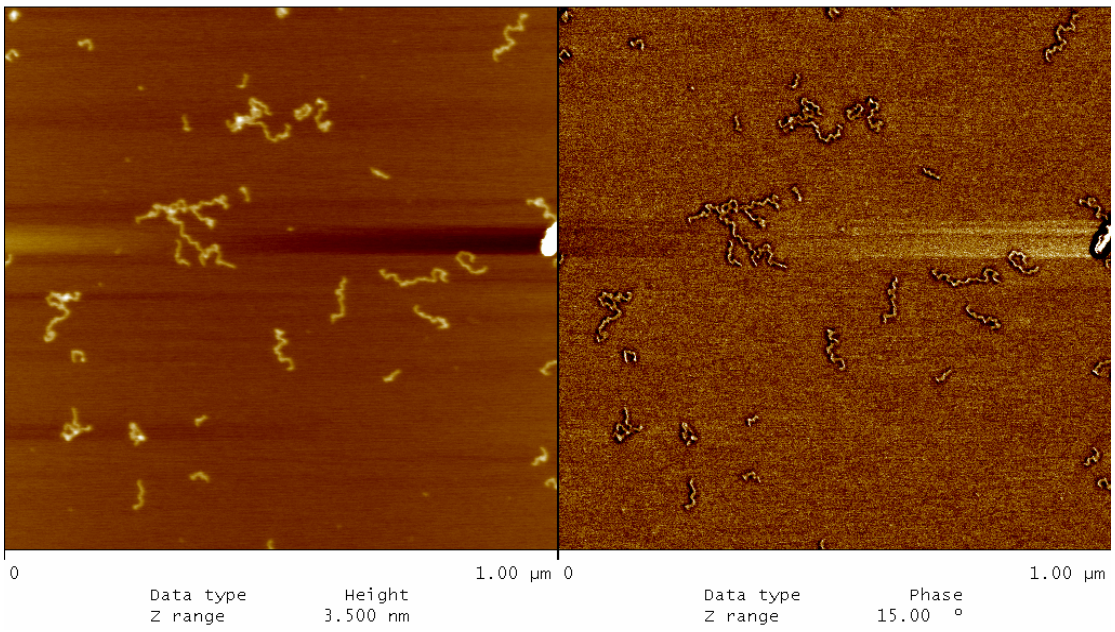

Figure S9. AFM image of ***h*PG2** after spin-coating from chloroform (8 mg/L) and air drying for 3 d. h_{AFM}(***h*PG4**) was determined as 0.7 ± 0.1 nm (average of 10 analyses).

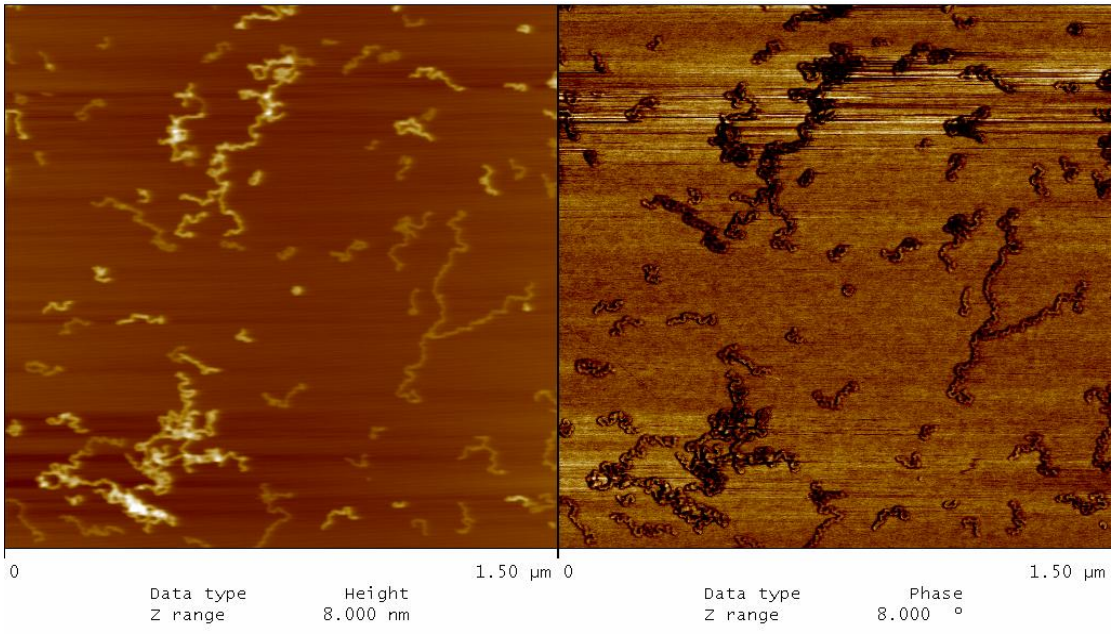

Figure S10. AFM co-imaging of **PG3** and ***h*PG3**. To a freshly cleaved mica was spin-coated a solution of *h*-**PG3** in chloroform, followed by a solution of **PG3** in chloroform. h_{AFM}(**PG3**) and h_{AFM}(***h*PG3**) was determined as 1.7 ± 0.3 nm 0.8 ± 0.2 nm, respectively (average of 10 analyses).

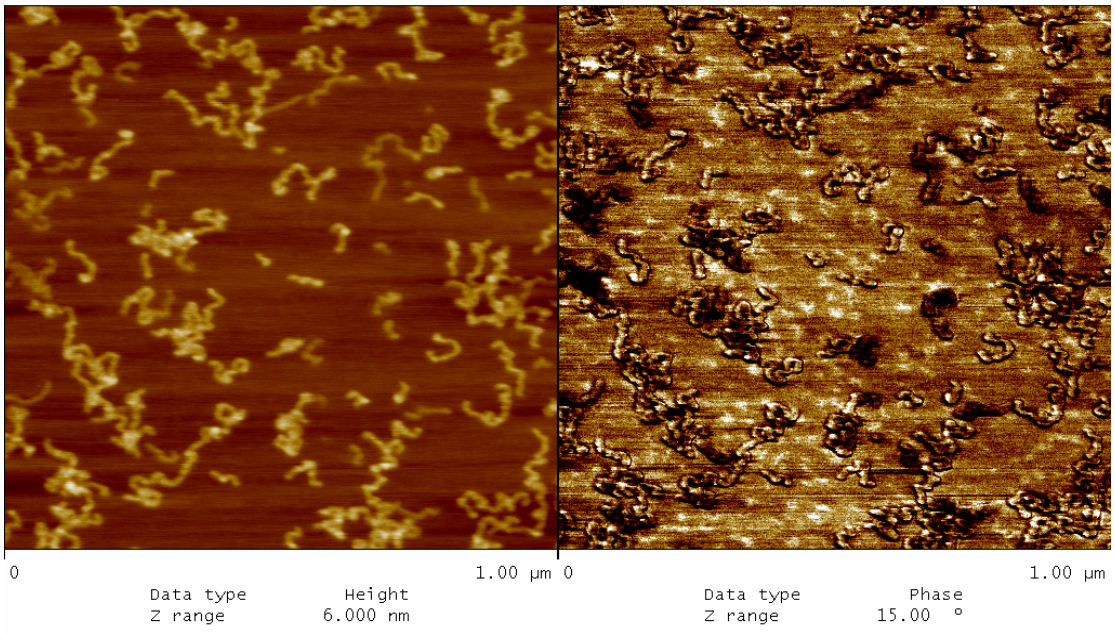

Figure S11. AFM co-imaging of **PG2** and ***h*PG2** after spin-coating of *h*-**PG2** from chloroform, followed by **PG3** from chloroform. h_{AFM}(**PG2**) and h_{AFM}(***h*PG2**) was determined as 1.2 ± 0.2 nm 0.1 ± 0.2 nm, respectively (average of 10 analyses).

Reference

1 L. Shu, I. Gössl, J. P. Rabe, A. D.Schlüter, *Macromol. Chem. Phys*., 2002, **203**, 2540.
2 Y. Guo, J. van Beek, B. Zhang, M. Colussi, P. Walde, A. Zhang, M. Kröger, A. Halperin, A. D.Schlüter, *J. Am. Chem. Soc.*, 2009, **131**, 11841.