Supplementary Information

Guided supramolecular polymerization of oligo(*p*-phenylenevinylene) functionalized bismelamines

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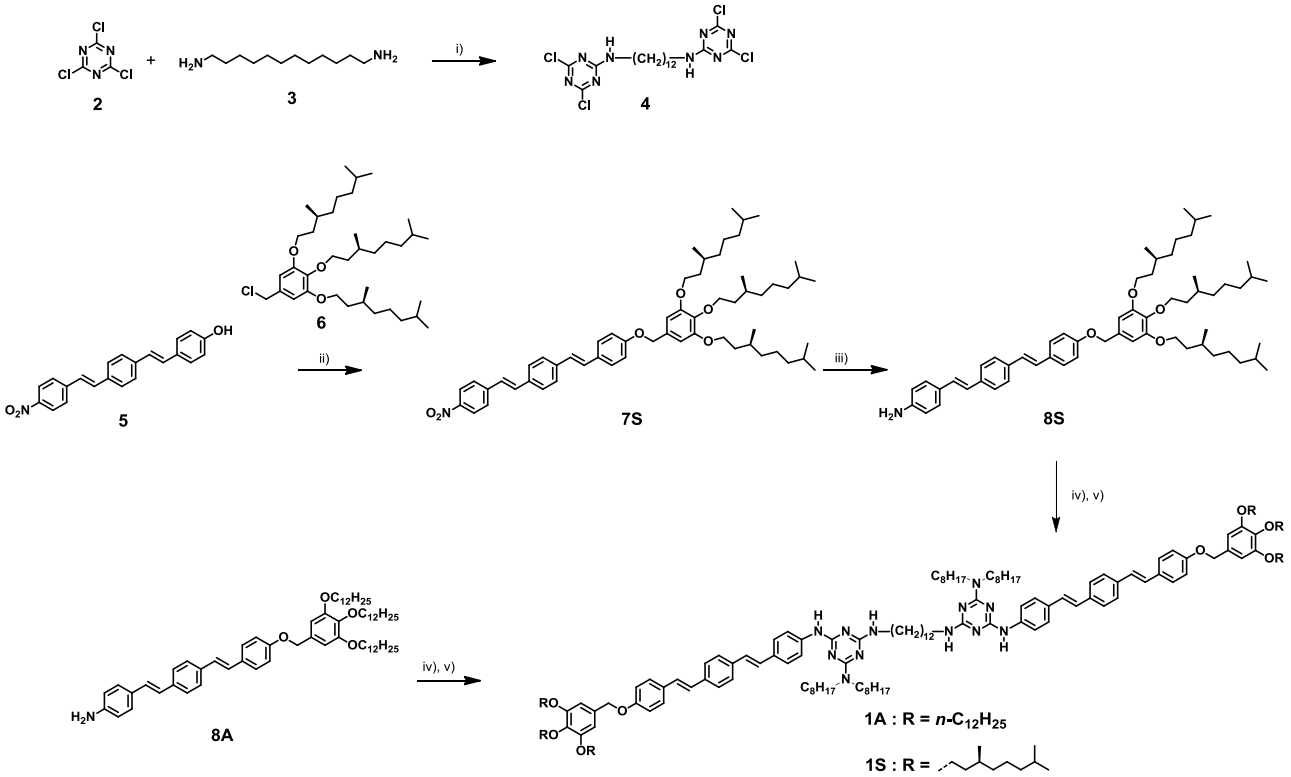
Materials and Methods

Column chromatography was performed using 63–210 μm silica gel. All other commercially available reagents and solvents were of reagent grade and used without further purification. The solvents for the preparation of the assemblies were all spectral grade and used without further purification. ^{1}H NMR spectra were recorded on a JEOL LA400 or a LA500 NMR spectrometers and chemical shifts are reported in ppm (δ) with the signal of TMS as internal standard. FAB-MS and ESI-MS spectra were measured on a JEOL JMS-AX500 and an Exactive (Thermo Fisher), respectively. UV/vis and circular dichroism (CD) spectra were recorded on a JASCO V660 spectrophotometer and JASCO J840 spectropolarimeter, respectively, with Peltier device temperature-control unit. AFM images were acquired under ambient conditions using Multimode 8 Nanoscope V (Bruker Instruments) in Peak Force Tapping (Scanasyst) mode. Silicon cantilevers (SCANASYST-AIR) with a spring constant of 0.4 N/m and frequency of 70 kHz (nominal value, Bruker, Japan) were used. The samples were prepared by spin-coating of MCH solutions onto freshly cleaved highly-oriented pyrolytic graphite (HOPG). Dynamic light scattering measurements

were conducted on Beckmann Coulter N5 particle analyzer equipped with 25 mW He-Ne laser. The sample solutions were filtered with Millipore membrane filter (pore size = 0.2 μm) before measurements to remove dust. The scattering angle was set to 90°.

Synthesis and analytical data

OPV dimer **1A** and **1S** were synthesized according to Scheme S1. Synthesis of compound **6**,[S1] **5**[S2] and **8A**[S2] were reported previously.



Scheme S1. Synthesis of **1A** and **1S**. i) diisopropylethylamine, THF, 0 °C, 0.5 h; ii) K_2CO_3, DMF, 65 °C, 6 h; iii) Na_2S, H_2O, 1,4-dioxane, 100 °C, 3 h; iv) diisopropylethylamine, THF, reflux, 12 h; v) dioctylamine, THF, reflux, 12 h.

4: To a dry THF solution (40 mL) of the mixture of 1,3,5-trichlorotriazine (1.0 g, 5.4 mmol) and diisopropylethylamine (1.0 mL) cooled to 0 °C, 1,12-diaminododecane (540 mg, 2.7 mmol) was slowly added under N_2. After stirring for 0.5 h, the solvent was removed by evaporation, and the residue was dissolved in chloroform and washed with water and brine, and the organic phase was

dried over Na_2SO_4. After removing the solvent by evaporation, the residue was purified by recrystallization (chloroform/hexane) to obtain **4** as a colorless solid (0.92 g, 1.9 mmol, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.04 (s, 2H), 3.48 (q, J = 6.7 Hz, 4H), 7.71 (s, 1H), 1.65-1.55 (m, 4H), 1.40-1.22 (m, 20H); MS (FAB): 495 $[M+H]^+$.

7S: To a dry DMF solution (10 mL) of the mixture of **5** (86 mg, 0.25 mmol) and K_2CO_3 (1.0 g, 7.1 mmol) heated to 65 °C, **6** (150 mg, 0.25 mmol) was added under N_2. After stirring for 6 h, the mixture was poured into ice water and the resulting precipitates were collected by filtration. The residue was reprecipitated from chloroform/methanol mixture to obtain **7S** as a yellow solid (160 mg, 0.17 mmol, 71% yield). Due to poor solubility, this compound was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (d, J = 8.9 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 7.56-7.50 (m, 4H), 7.47 (d, J = 9.2 Hz, 2H), 7.27 (d, J = 16 Hz, 1H), 7.15 (d, J = 16.4 Hz, 1H), 7.11 (d, J = 16 Hz, 1H), 7.02-6.96 (m, 3H), 6.63 (s, 2H), 4.98 (s, 2H), 4.06-3.98 (m, 6H), 1.90-1.80 (m, 3H), 1.75-1.65 (m, 3H), 1.65-1.47 (m, 6H), 1.40-1.10 (m, 18H), 0.94-0.92 (m, 9H), 0.87 (d, J = 6.7 Hz, 18H).

8S: To a dry 1,4-dioxane solution (10 mL) of the mixture of **7S** (170 mg, 0.18 mmol) heated to 65 °C, a mixture of 1,4-dioxane (6.0 mL), water (2.0 mL) and Na_2S (250 mg, 3.35 mmol) was added slowly under N_2, and the solution was stirred at 100 °C for 3 h. After cooling to r.t., 1,4-dioxane was removed by evaporation, and the resulting precipitates was dissolved in chloroform and washed with water and brine, and the organic phase was dried over Na_2SO_4. After evaporation, the residue was reprecipitated from chloroform/methanol mixture to obtain **8S** as a yellow solid (120 mg, 0.13 mmol, 71% yield). Due to poor solubility, this compound was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.42 (m, 6H), 7.34 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 6.64 (s,2H), 4.97 (s, 2H), 4.06-3.98 (m, 6H), 3.75 (s, 2H), 1.90-1.80 (m, 3H), 1.75-1.65 (m, 3H), 1.65-1.47 (m, 6H), 1.40-1.10 (m, 18H), 0.94-0.92 (m, 9H), 0.87 (d, J = 6.7 Hz, 18H); MS (FAB): 872 $[M+H]^+$.

1A: To a THF solution (20 mL) of the mixture of compound **4** (17 mg, 0.036 mmol) and

diisopropylethylamine (0.030 mL) heated to 80 °C, compound **11A** (70 mg, 0.073 mmol) was added under N_2. After stirring for 12 h, dioctylamine (17 mg, 0.073 mmol) was added at 80 °C and the mixture was stirred for 12 h at the same temperature. After cooling the reaction mixture to r.t., the solvent was removed by evaporation, and the residue was dissolved in chloroform and washed with water and 2% HCl aq., and the organic phase was dried over Na_2SO_4. After evaporation, the residue was purified by column chromatography over silica gel (hexane:ethyl acetate = 4: 1) to obtain **1A** as a yellow solid (75 mg, 0.027 mmol, 75% yield). ^{1}H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 100 °C): δ = 7.56 (d, J = 8.5 Hz, 4H), 7.41-7.37 (m, 16H), 7.04-6.90 (m, 12H), 6.61 (s, 2H), 6.58 (s, 4H), 4.94 (s, 4H), 4.73 (s, 2H), 3.97-3.91 (m, 12H), 3.48 (t, J = 6.0 Hz, 8H), 3.34 (q, J = 6.7, 2H), 1.77-1.67 (m, 12H), 1.65-1.52 (m, 12H), 1.48-1.37 (m, 24H), 1.36-1.22 (m, 152H), 0.89-0.83 (m, 30H); MS (ESI): *m/z* calcd for $C_{180}H_{286}O_8N_{12}Cl$ 2779.2036 $[M+Cl]^-$, found 2779.1953.

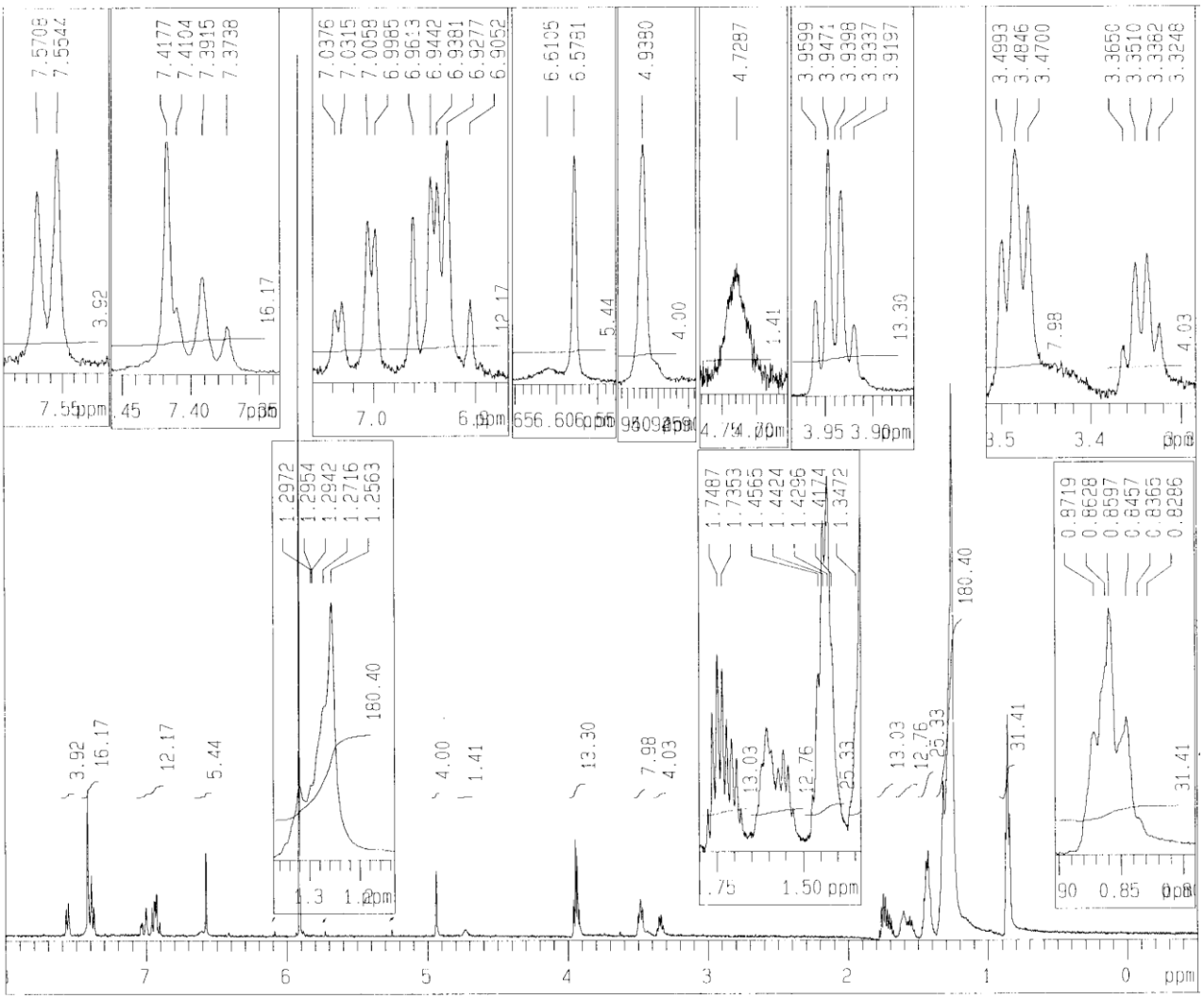


Chart S1. ^{1}H NMR spectrum of **1A** in 1,1,2,2-tetrachloroethane-d_2 at 100 °C.

1S: This compound was obtained as a yellow solid (58 mg, 0.022 mmol, 62% yield) from **4** and **8S** according to the same procedure for **1A**. ^{1}H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 100 °C): δ = 7.56 (d, J = 8.5 Hz, 4H), 7.41-7.37 (m, 16H), 7.04-6.90 (m, 12H), 6.59 (s, 2H), 6.59 (s, 4H), 4.95 (s, 4H), 4.72 (s, 2H), 4.01-3.96 (m, 12H), 3.48 (t, J = 6.0 Hz, 8H), 3.34 (q, J = 6.7, 2H), 1.85-1.73 (m, 6H), 1.70-1.63 (m, 6H), 1.66-1.50 (m, 24H), 1.37-1.20 (m, 80H), 1.20-1.10 (m, 12H), 1.36-1.22 (m, 164 H), 0.95-0.90 (m, 18H), 0.88-0.85 (m, 48H); MS (ESI): *m/z* calcd for $C_{168}H_{262}O_8N_{12}Cl$ 2611.0158 $[M+Cl]^-$, found 2611.0017.

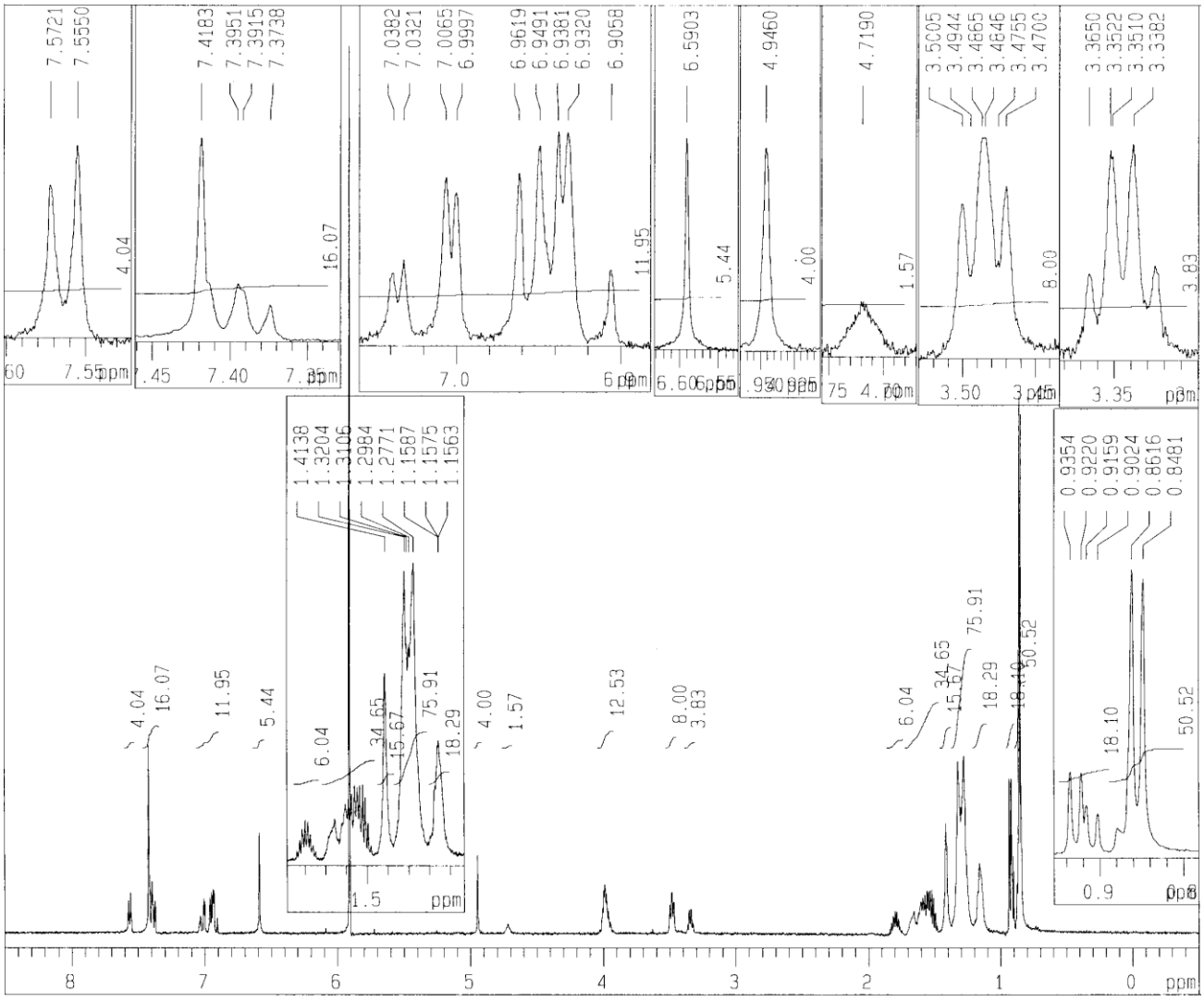


Chart S2. ^{1}H NMR spectrum of **1S** in 1,1,2,2-tetrachloroethane-d_2 at 100 °C.

Supporting Figures

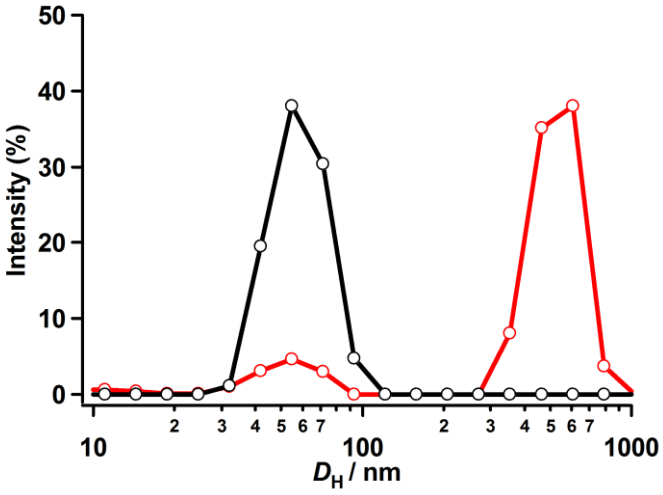


Figure S1. Dynamic light scattering of MCH solutions (c = 1.0 × 10^{-4} M) of **1A** (black line) and **1A·dCA** (red line) measured at 20 ºC.

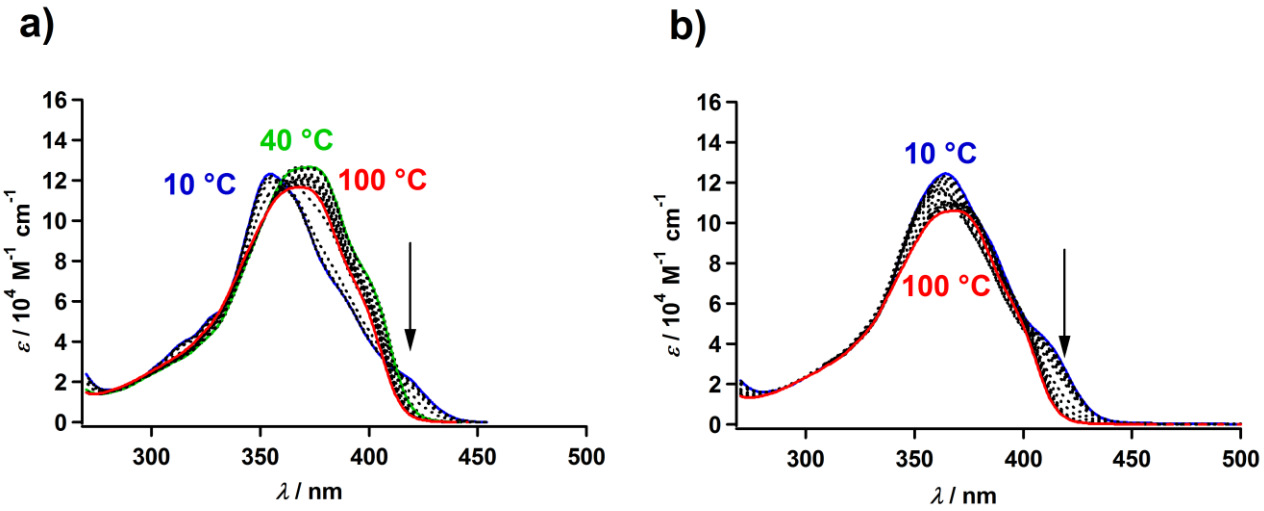


Figure S2. Temperature-dependent UV/vis spectra of a) **1A** in MCH (c = 1.0 × 10^{-5} M) and b) **1A·dCA** in MCH (c = 1.0 × 10^{-5} M). Both assemblies showed reversible changes between aggregated (420 nm for **1A**, 415 nm for **1A·dCA**) upon varying the solution temperatures between 10 and 90 °C. The molar fraction of aggregated molecules (α) used for the plots shown in Figure 1b is calculated according to the following equation: $\alpha = 1 - (\varepsilon_{max} - \varepsilon) / (\varepsilon_{max} - \varepsilon_{min})$ at given wavelengths.

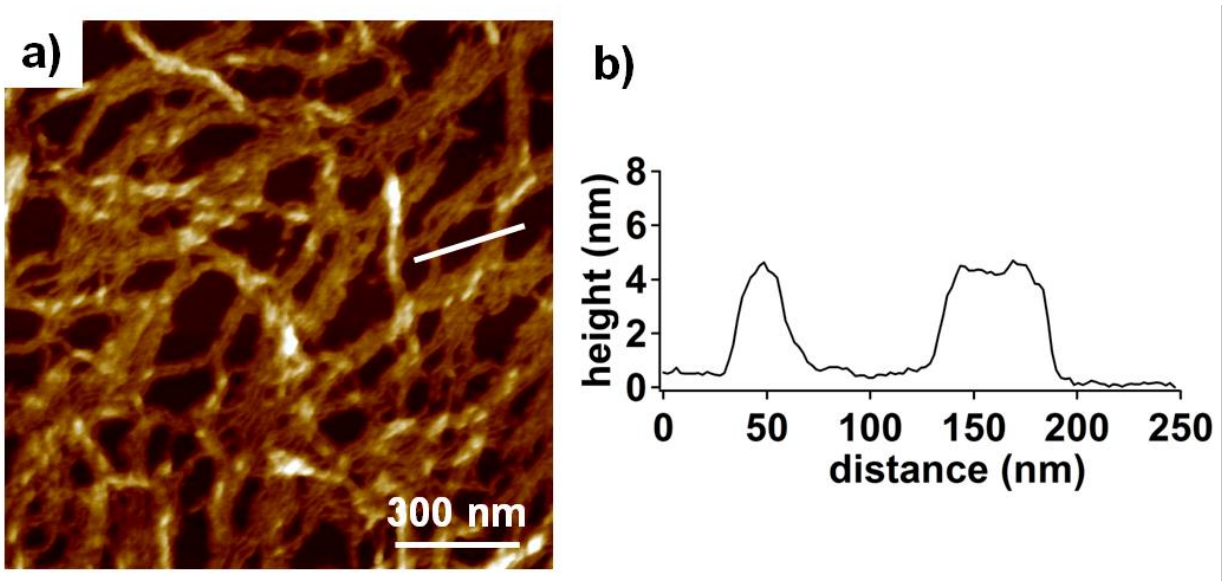


Figure S3. a) AFM height image of self-assemblies of **1A** spin-coated onto HOPG from a MCH solution (c = 4.0 × 10^{-4} M) at 20 ºC. b) Cross-sectional analysis along to the white line in a).

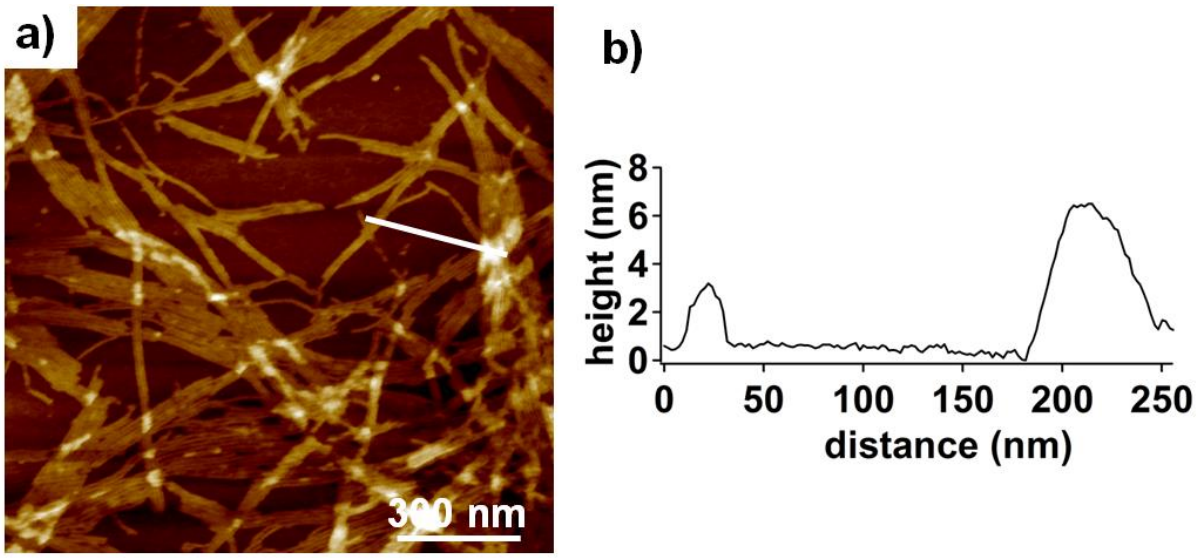


Figure S4. a) AFM height image of coassemblies of **1A** spin-coated onto HOPG from a MCH solution (c = 1.0 × 10^{-4} M) at 20 ºC. b) Cross-sectional analysis along to the white line in a).

References

[S1] V. Percec, M. R. Imam, M. Peterca, D. A. Wilson, and P. A. Heiney, *J. Am. Chem. Soc.*, 2009, **131**, 1294–1304.

[S2] S. Yagai, S. Kubota, T. Iwashima, K. Kishikawa, T. Nakanishi, T. Karatsu and A. Kitamura, *Chem. –Eur. J.*, 2008, **14**, 5246–5257.