

# Ultra-Large Sheet Formation by 1D to 2D Hierarchical Self-Assembly of A “Rod-Coil” Graft Copolymer with Polyphenylene Backbone

## Electronic Supplementary Information

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# Contributed Equally

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### 1. Materials.

Materials were purchased from J&K, Alfa Aesar, Admas-beta and Sigma-Aldrich suppliers and used as received, unless otherwise mentioned.

### 2. Instrumentation and Methods

**Analytical thin layer chromatography (TLC)** was carried out on silica gel coated substrates “60 F254” from Merck.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in deuterated solvents on a Mercury Plus 400 (400 MHz for proton, 100 MHz for carbon) spectrometer with tetramethylsilane as the internal reference. Chemical shifts are reported in ppm with the solvent proton or carbon signal as the internal standard. Data are reported via chemical shift, integration and multiplicity (Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet).

Molecular weights of the polymers were measured by **gel permeation chromatography (GPC)** using tetrahydrofuran (THF) as the eluent and polystyrene (PS) as the standard with a refractive index detector (Shimadzu RID-10A).

The polymers were purified by **Recycling GPC** with Shodex K-2003 GPC columns using chloroform as the eluent.

**Elemental analysis (EA)** of the solid samples was recorded on Vario-EL Cube.

**Fourier transform infrared (FTIR)** spectra were obtained on a Spectrum 100 (Perkin Elmer, Inc., USA) spectrometer.

**Ultraviolet-Visible (UV-Vis)** absorption spectra were obtained on a HITACHI U-4100 spectrometer.

**Photoluminescence (PL)** spectra were recorded with a FluoroMax-4 spectrophotometer.

**Differential scanning calorimetry (DSC)** curves were scanned on a DSC-204F1 Calorimeter.

**Transmission electron microscopy (TEM)** observations were performed on a JEM-2100 (JEOL Ltd., Japan) with an accelerating voltage of 200 kV. TEM samples were obtained by dropping the solutions of the polymer assemblies onto carbon-coated copper grids, followed by freeze-drying or vacuum-drying for 6 h, and no staining treatment was performed.

**Atomic force microscopy (AFM)** measurements were conducted on a scanning probe microscope (Multimode Nanoscope, USA) operated via tapping mode by using silicon nitride cantilevers with a force constant of 0.12 N/m. The samples were prepared via dip coating method on mica sheets and then dried at room temperature (RT) under vacuum for 6 h.

**Scanning electron microscopy (SEM)** measurements were carried out on an FEI Sirion-200 field emission SEM. The samples were prepared by drop-casting the aggregate solution onto silicon wafers.



temperature until the red color of I<sub>2</sub> disappeared (ca. 2 minutes). Methyl-1,1-bromoundecanoate (5.0 mL, 20.72 mmol) was added and the mixture was stirred at 80 °C for 24h. Subsequently, the mixture was cooled to room temperature, then 2.0 g (1.46 mmol) compound **1** and 140 mg PdCl<sub>2</sub>(dppf) were added. The mixture was stirred at 80 °C again for 7 h. Afterwards, the reaction mixture was quenched with 10 mL H<sub>2</sub>O. Then 40 mL ethyl acetate was added and the mixture was filtered. The obtained filtrate was washed with brine, and dried with MgSO<sub>4</sub>. Finally, the mixture was filtered, evaporated and purified by silica column chromatography (eluent: hexane/ethyl acetate 7:1, v/v) to give compound **2** as a white solid (1.52 g, 56 % yield).

<sup>1</sup>H NMR (400 MHz, Dichlorobenzene-*d*<sub>4</sub>, 170 °C, Figure S1): δ 7.54–7.44 (s, 2H), 7.26–7.24 (s, 2H), 7.20–7.01 (m, 16H), 6.93–6.74 (m, 10H), 6.74–6.62 (m, 8H), 6.61–6.43 (m, 10H), 3.70–3.62 (s, 12H), 2.38–2.32 (t, 16H, J = 7.5 Hz), 1.66–1.56 (m, 16H), 1.24–1.02 (m, 48H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, Figure S2): δ 174.47, 142.12, 139.97, 139.59, 139.45, 139.23, 137.67, 137.37, 133.85, 132.60, 131.56, 131.29, 130.92, 130.13, 127.84, 127.84, 127.63, 127.05, 126.73, 126.27, 125.19, 109.99, 51.60, 35.54, 35.47, 34.33, 31.35, 29.77, 29.68, 29.48, 29.38, 29.03, 28.96, 25.83, 25.19.

Elemental Analysis: Calculated: C 81.65, H 7.63, O 6.91, Cl 3.83; Found: C 82.09, H 7.73, O 6.85.

MS (FD, 8 kV): m/z (%): 1851 (100) [M<sup>+</sup>] (calcd. C<sub>126</sub>H<sub>140</sub>Cl<sub>2</sub>O<sub>8</sub> = 1851)

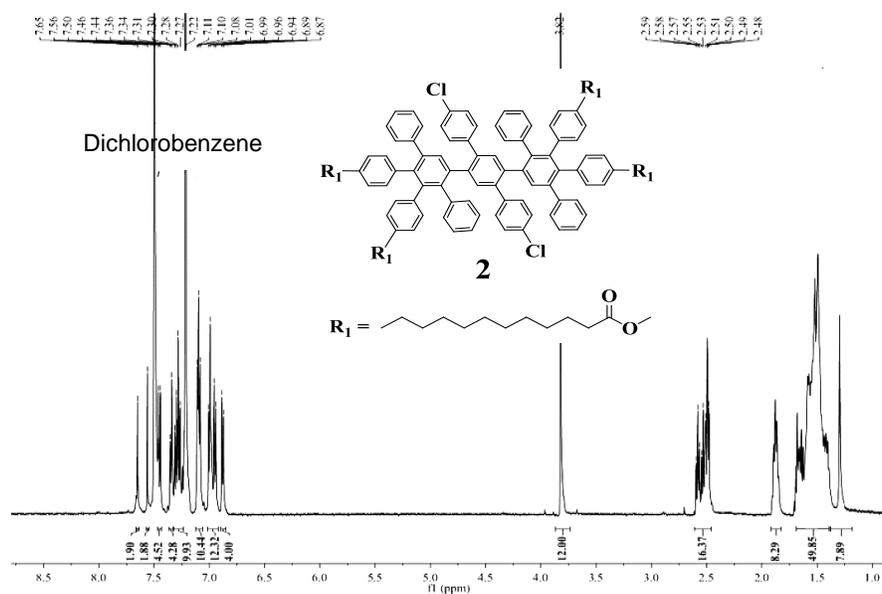
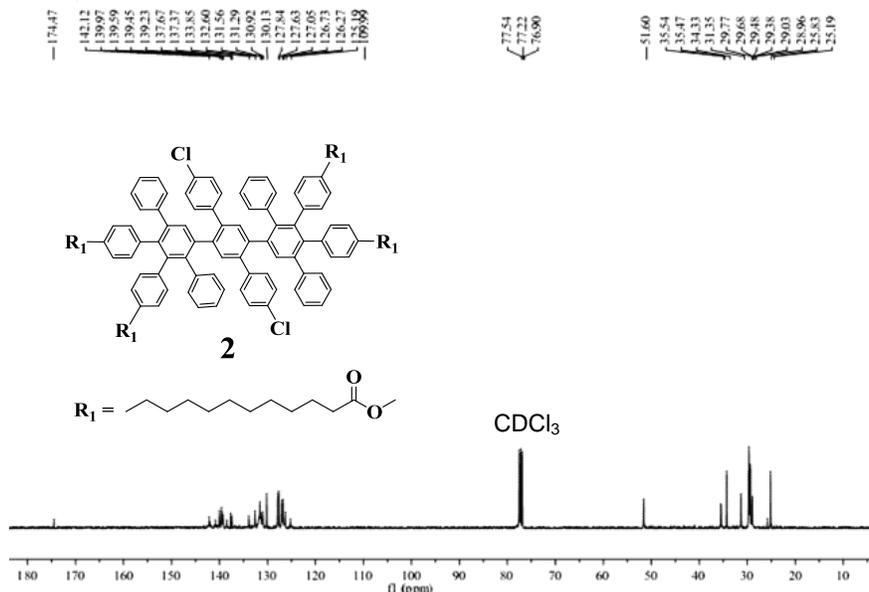


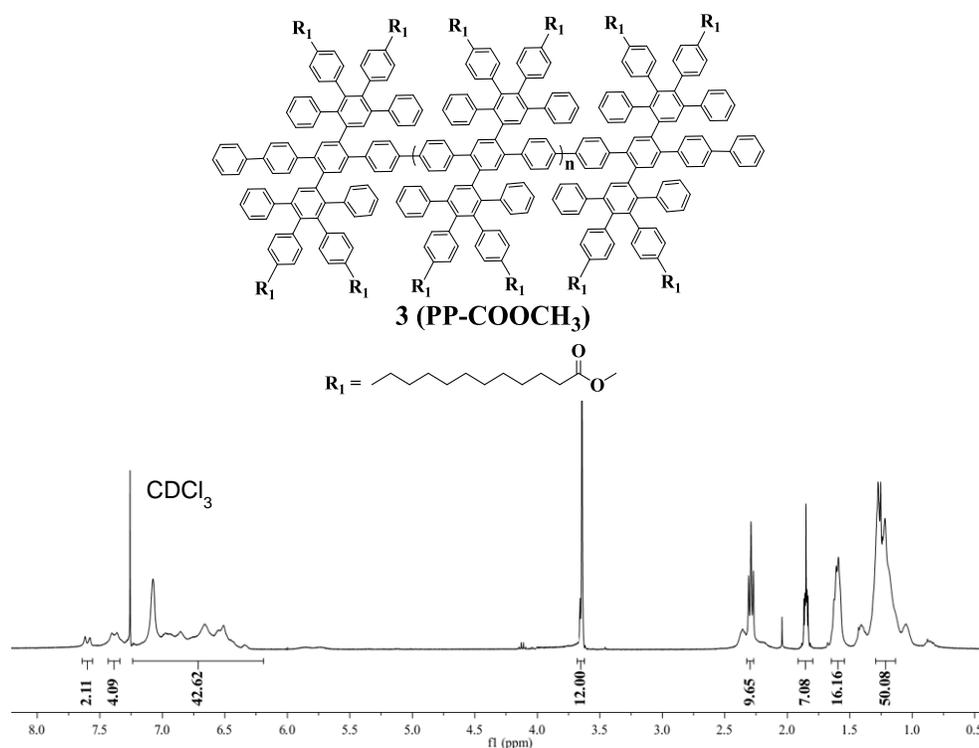
Figure S1. <sup>1</sup>H NMR spectrum of compound **2**



**Figure S2.**  $^{13}\text{C}$  NMR spectrum of compound **2**

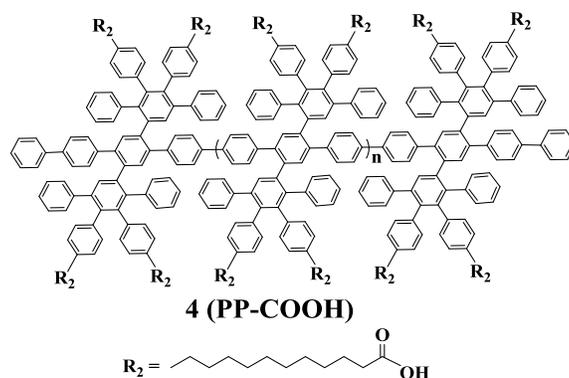
### 3.2 Synthesis of polymer (PP-COOCH<sub>3</sub>, **3**)<sup>2,3</sup>

The synthesis procedures of PP-COOCH<sub>3</sub> were similar to those described in previous publications.<sup>2,3</sup> Typically, a mixture of bis(cyclooctadiene)nickel(0) (72 mg, 0.25 mmol), cyclooctadiene (0.065 ml, 0.25 mmol), and 2,2'-bipyridine (38 mg, 0.25 mmol) were dissolved into the mixed solvent of dimethyl formamide (DMF) (0.50 ml) and toluene (2.0 ml). The resulting catalyst solution was stirred at 60 °C for 30 min. Then, a solution of compound **2** (100 mg, 0.054 mmol) dissolved in 0.5 ml DMF and 1.0 ml toluene was added. The reaction mixture was stirred at 80 °C for 72 h in dark. Subsequently, 0.5 mL anhydrous chlorobenzene was added and the mixture was stirred for another 2 h. After reaction, the reaction mixture was cooled down to room temperature and passed through a silica column (eluent: THF) to remove the catalyst. The obtained solution was evaporated to remove most of THF and then the residue was dropwise added into methanol, yielding white precipitate. The precipitate was collected by filtration, followed by vacuum drying, giving rise to an off-white solid product (81 mg, 84 % yield). The product was further purified by recycling GPC to obtain PP-COOCH<sub>3</sub> (**3**) with a narrow molecular weight distribution (Figure S4B).



**Figure S3.** <sup>1</sup>H NMR spectrum of PP-COOCH<sub>3</sub>

### 3.3 Synthesis of PP-COOH (4)

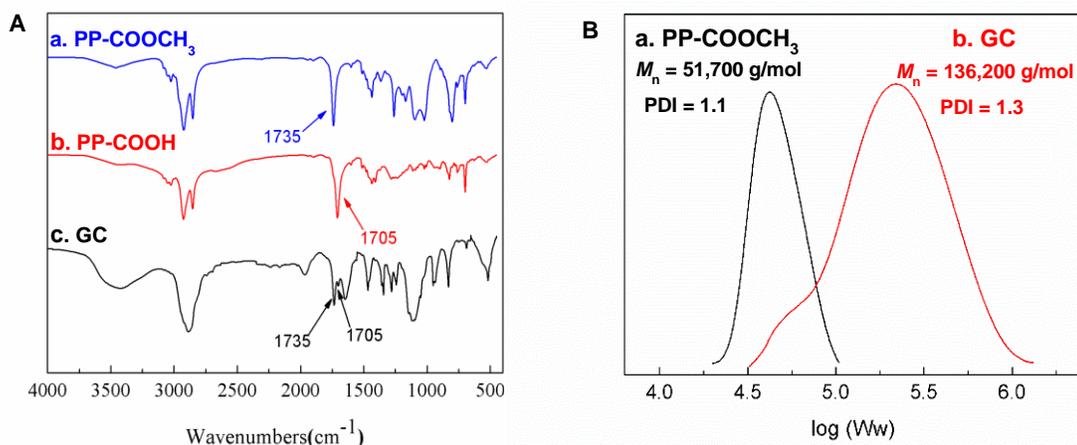


PP-COOCH<sub>3</sub> (**3**) (30 mg) and potassium hydroxide (0.9 g) were dissolved in a mixed solvent of 30 mL THF, 2 mL methanol and 2 mL water. The mixture was refluxed for 24 h and then cooled down to room temperature. Then the neutralization of the mixture with 2 M HCl aqueous

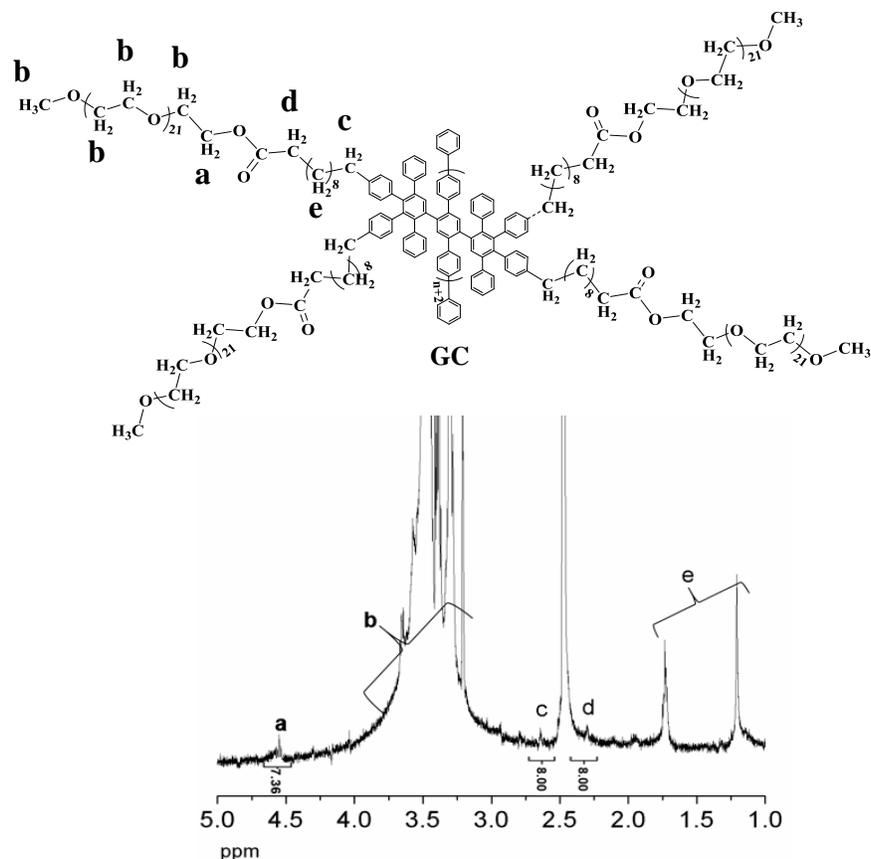
solution was carried out. The grey precipitate was collected and washed with water and methanol. After vacuum drying at room temperature, 29 mg PP-COOH (**4**) was obtained (~97% yield).

### 3.4 Synthesis of graft copolymers (GC, **5**)

A mixed solvent of dry THF (12 mL) and DMF (6 mL) were added into a dry 100 mL Schlenk tube containing PP-COOH (**4**) (10 mg,  $5.5 \times 10^{-3}$  mmol) and poly(ethylene oxide) (PEO,  $M_n$  1000, 110 mg, 0.11 mmol). Dimethylaminopyridine (DMAP, 0.4 mg,  $8.4 \times 10^{-4}$  mmol) was added after the two polymers dissolved completely and the mixture was stirred for several minutes. Then the mixture was cooled to 0 °C, followed by the addition of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 5 mg,  $6.6 \times 10^{-3}$  mmol). The mixture was stirred at 0 °C for 30 min and then at room temperature for 3 days. Afterwards, the mixture was dialyzed against pure water by changing the external water for more than 10 times over a period of 3 days. The cutoff (14 kDa) of the dialysis membrane ensures the removal of the residual unreacted PEO chains and small molecules. At last, the resulting mixture was freeze-dried to yield the GC sample, which was further purified by recycling GPC with chloroform as eluent.



**Figure S4.** (A) FTIR spectra of PP-COOCH<sub>3</sub> (a), PP-COOH (b) and GC (c), the appearance of a peak at 1705 cm<sup>-1</sup> along with the disappearance of the signal at 1735 cm<sup>-1</sup> in the spectrum of PP-COOH proves the successfully conversion of -COOCH<sub>3</sub> to -COOH groups after hydrolysis. (B) GPC curve (THF, PS standard) of PP-COOH (a) and GC (b). Based on  $M_n$ , the polymerization degree (DP) of PP-COOCH<sub>3</sub> is calculated to be ~29 and the value of n in the schematic illustration of PP-COOCH<sub>3</sub>, PP-COOH, and the GC in Scheme S1 is 27. GC shows an increased  $M_n$  compared with that of PP-COOCH<sub>3</sub>, which demonstrates the successful grafting of PEO chains.



**Figure S5.**  $^1\text{H}$  NMR spectrum of **GC**

The grafting percentage ( $GP$ ) of the graft copolymer were estimated based on the  $^1\text{H}$  NMR spectra *via* the following Equation (1):

$$GP = \frac{I_a}{I_c} \times 100\% \quad (1)$$

Where  $I_a$  is the integral area of the proton peak of **a** group marked in the spectrum,  $I_c$  represents the integral area of the proton peak of **c** labeled in the spectrum. The  $GP$  of GC sample was calculated to be ~92% according to Equation (1).

**Elemental analysis.** C 63.48 %, O 26. 68%, H 9.84 %. The  $GP$  of the GC can also be calculated according to Equation (2):

$$(126x + 44y) = \frac{a}{12}$$

$$(8x + 23y) = \frac{b}{16}$$

$$GP = \frac{y}{4x} \times 100\% \quad (2)$$

where  $a$  and  $b$  represent the weight contents of C and O in a repeating unit of the GC, respectively; 126 and 8 are the total numbers of C and O in the hydrophobic part of a repeating unit of the GC, respectively; 45 and 22 denote the total numbers of C and O in each PEO chain (1K g/mol), respectively;  $x$  is the mole number of repeating units of GC;  $y$  expresses the total mole number of PEO chains. Suppose we have 1 g of GC, the  $GP$  of GC based on Equation (2), is calculated to be ~87%. The result approximates the datum that was obtained by NMR as described above.

#### **4. Self-assembly of the graft copolymer (GC)**

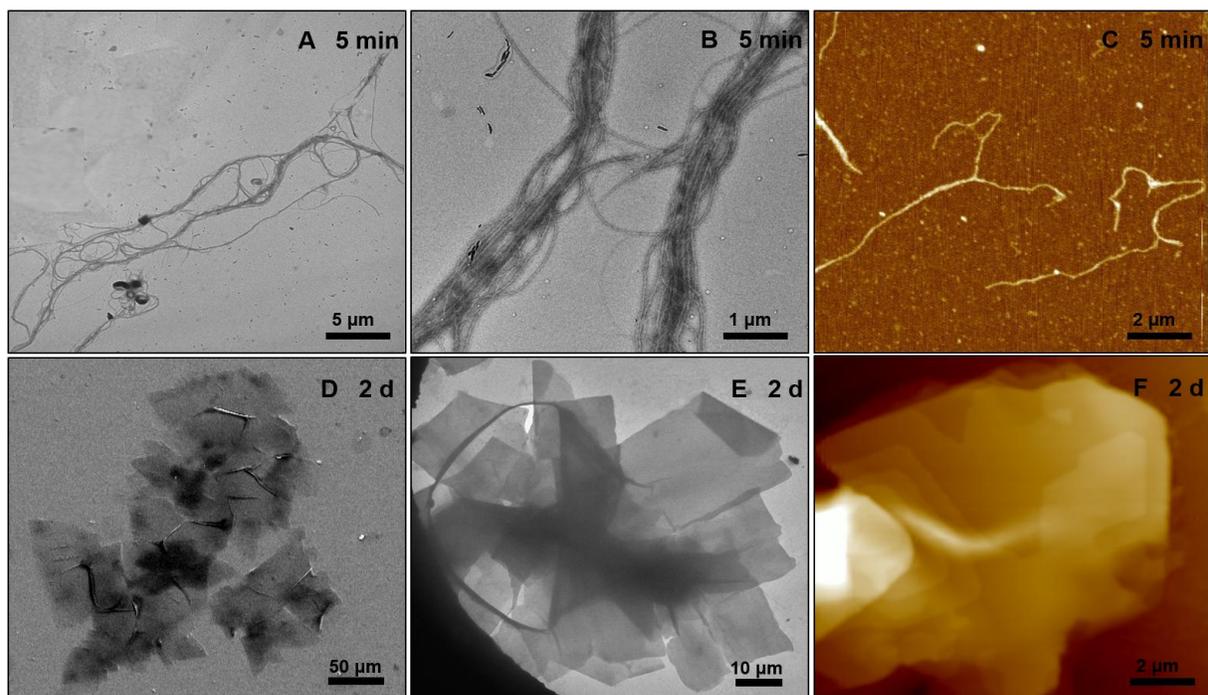
##### **4.1 Self-assembly procedures**

The self-assembly of GC was performed via a cosolvent method at RT (~20 °C). First, 0.1 mg GC was dissolved in 10 mL chloroform (CHCl<sub>3</sub>). Then, 1 mL of this CHCl<sub>3</sub> solution was added dropwise (60 μL/min) into 9 mL methanol (CH<sub>3</sub>OH) under gently stirring. At the end of the addition, the stirring was stopped and a bluish solution was obtained, indicating the formation of polymer aggregates. The as-obtained solution was incubated for a period of days.

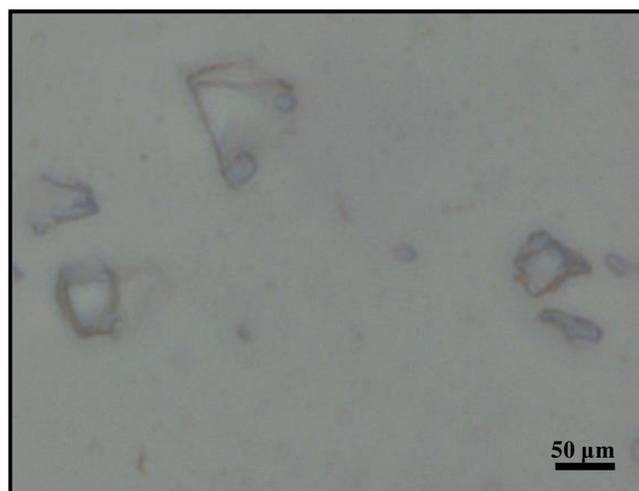
TEM samples were prepared by dropping the aggregate solutions onto carbon-coated copper grids, followed by vacuum-drying at RT or freeze-drying for 6 h. No staining treatment was performed.

The AFM samples were prepared via dip coating method with mica sheets and then dried under vacuum at RT for 6 h.

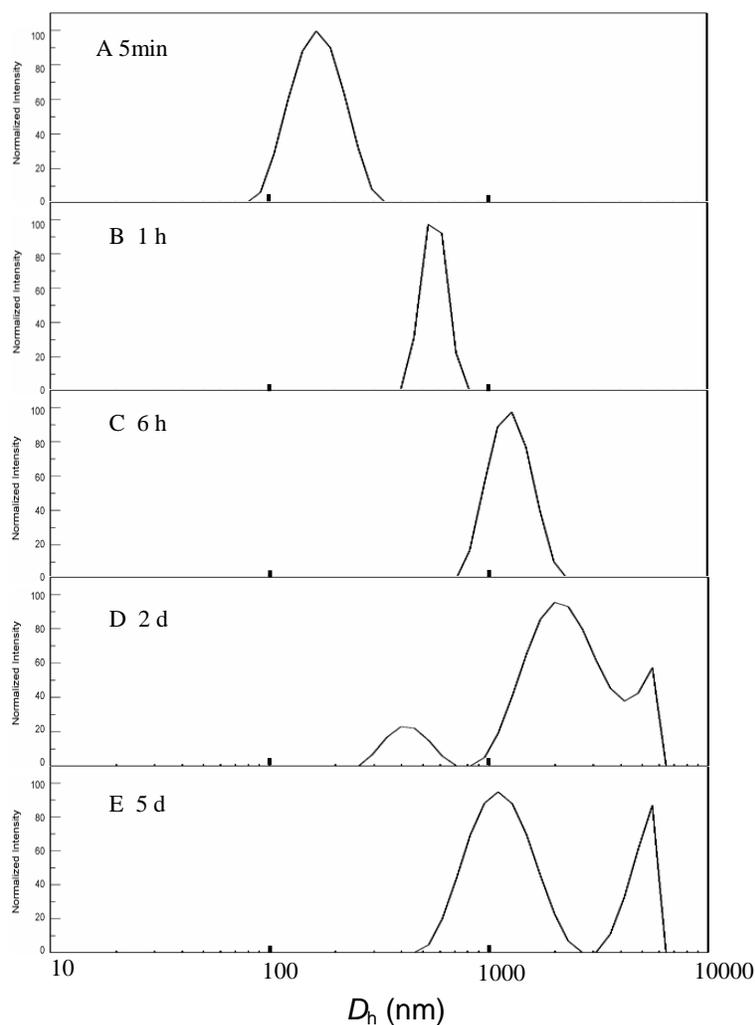
## 4.2 Supporting figures for the self-assembly of the graft copolymer (GC)



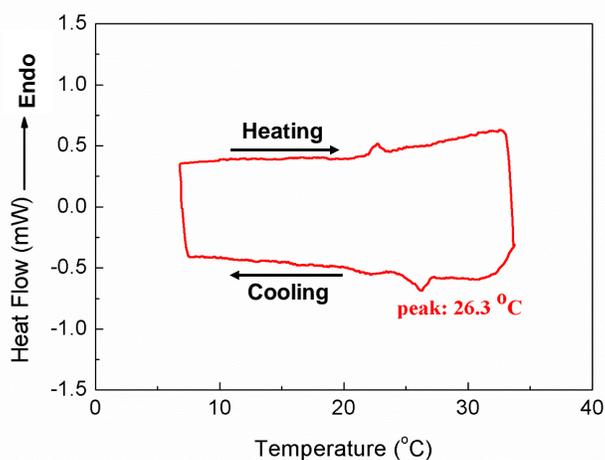
**Figure S6.** TEM (A, B and E), SEM (D) and AFM (C, F) images of the helices and nanosheets formed by the GC in  $\text{CHCl}_3\text{-CH}_3\text{OH}$  (v/v 1:9).



**Figure S7.** A photo of the ultralarge sheets suspended in the  $\text{CHCl}_3\text{-CH}_3\text{OH}$  solution obtained by an optical microscope.



**Figure S8.** DLS plots of the GC assemblies in the  $\text{CHCl}_3\text{-CH}_3\text{OH}$  (v/v 1:9) solution at room temperature after (A) 5 min, (B) 1 h, (C) 6 h, (D) 2 days and (E) 5 days. The appearance of double or triple peaks is likely attributed to the growth of small size assemblies to larger ones or the size anisotropy of 1D and 2D assemblies determined by DLS in solution.<sup>4</sup> The difference between hydrodynamic diameters and dimensions obtained by TEM is frequently seen for 1D and 2D assemblies, probably due to the size anisotropy of 1D and 2D structures determined by DLS in solution.<sup>4</sup>



**Figure S9.** A typical  $\mu$ DSC curve of the GC aggregates (5 mg/mL) in the  $\text{CHCl}_3$ - $\text{CH}_3\text{OH}$  (v/v 1:9) solvent; the scan rate was 1 °C/min. Estimated from the heat enthalpy, the exothermal peak on the cooling curve at  $\sim 26$  °C is attributed to the crystallization of the grafted PEO chains.<sup>2</sup>

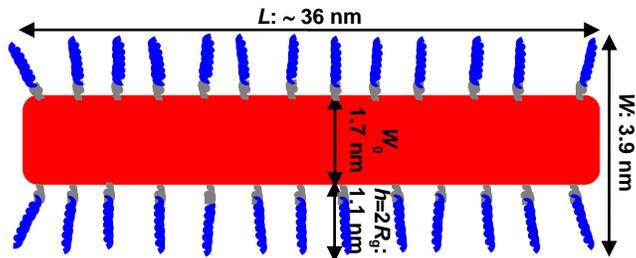
## 4.3 Supporting calculations

### 4.3.1. Estimation of the dimension of a single GC molecule in dry state.

The thickness of the nanowires, the rafts, or the single-layer nanosheets in dry state can be estimated by considering the dimension of a single graft copolymer molecule (see Figure S10). The Chembio3D ultra software gives that the polyphenylene backbone ( $\text{DP} = \sim 29$ ) has a length ( $L$ ) of  $\sim 36$  nm and a width ( $W_0$ ) of  $\sim 1.7$  nm. The thickness of the nanowires, the rafts, or the single-layer nanosheets in dry state equals the width ( $W$ ) of the GC, which can be estimated according to the Equation (3):

$$W = W_0 + 2h \quad (3)$$

Where  $h = 2R_g = (2n/3)^{1/2}l$  ( $R_g$  is the radius of gyration of a PEO chain in theta-condition, and  $R_g^2 = n^2/6$ ), in which  $n$  equals 77 (the total number of single-bonds in a PEO chain and an alkyl chain),  $l$  equals 0.154. Thus,  $R_g = 0.55$  nm,  $h = 1.1$  nm, and  $W = 3.9$  nm. Therefore, the thickness of the nanowires, the rafts, or the single-layer nanosheets in dry state equals  $\sim 4$  nm.



**Figure S10.** Schematic diagram of a GC molecule with dimensions indicated

#### 4.3.2. Estimation of the average distance between neighboring PEO chains on the rigid backbone after aggregation of GC molecules.

The average distance ( $d_1$ ) between neighboring PEO chains on the rigid backbone can be estimated according to Figure S11. For the GC molecules, the number of repeat units in the backbone is  $\sim 29$  and the GP of the PEO chains is 92% resulted from  $^1\text{H}$  NMR spectra, thus the number of PEO chains on one side of the backbone is  $\sim 54$  ( $29 \times 2 \times 0.92$ ). Therefore,  $d_1$  is  $36/54 = \sim 0.7$  nm.

The average distance ( $d_2$ ) between neighboring PEO chains on the other direction is considered to be less than 1 nm, since the average distance between neighboring polyphenylene backbones in aggregates is smaller than the largest distance ( $2 \times d_3/2 = d_3 \approx 1$  nm) if  $d_3$  segments would rotate perpendicularly to the backbone plane. While the average distance between neighboring aromatic backbones arranged via  $\pi$ - $\pi$  stacking are generally smaller than  $< 0.7$  nm.<sup>5,6</sup> Namely,  $d_2$  should be smaller than 0.7 nm. Thus,  $d_1$  was used to estimate the number density ( $\sigma$ ) of the tethered PEO chains at the surface of the GC aggregates ( $\sigma$  is defined to be the reciprocal average covering area of each chain<sup>7</sup>), and  $\sigma = \frac{1}{\pi(0.7/2)^2} = \sim 2.6$  nm<sup>-2</sup>.

The crystallization of tethered polymer chains at one surface depends on their reduced tethering density,  $\tilde{\sigma} = \sigma\pi R_g^2$ . If  $\tilde{\sigma} \geq 14.3$ , the polymer chains would be highly stretched and could crystallize.<sup>8</sup> For the GC aggregates,  $\sigma = \sim 2.6$  nm<sup>-2</sup>. Thus,  $\tilde{\sigma}$  equals  $\sim 18.4$  ( $> 14.3$ ) with an estimated  $R_g$  of  $\sim 1.5$  nm for the PEO coils in solution state.<sup>9</sup> This estimation manifests a high possibility for the crystallization of PEO chains in the GC assemblies below their  $T_c$ . Therefore, the unique molecular structure of GC molecule leads to the short average distance of adjacent PEO chains after aggregation, which favors the PEO crystallization and drives the sheet formation.



## References

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- (9) The  $R_g$  for a PEO chain at its end-free state in solution is estimated using  $R_g^2 = b^2 N_b / 6$  from: Rubenstein, M.; Colby, R. H. *Polymer Physics*; Oxford University Press: New York, **2004**, where  $b = 0.8$  nm for PEO.