

## Supporting Information

### **Controlled Self-Assembly Triggered by Olefin Metathesis: Crosslinked Graphitic Nanotubes from an Amphiphilic Hexa-*peri*-hexabenzocoronene**

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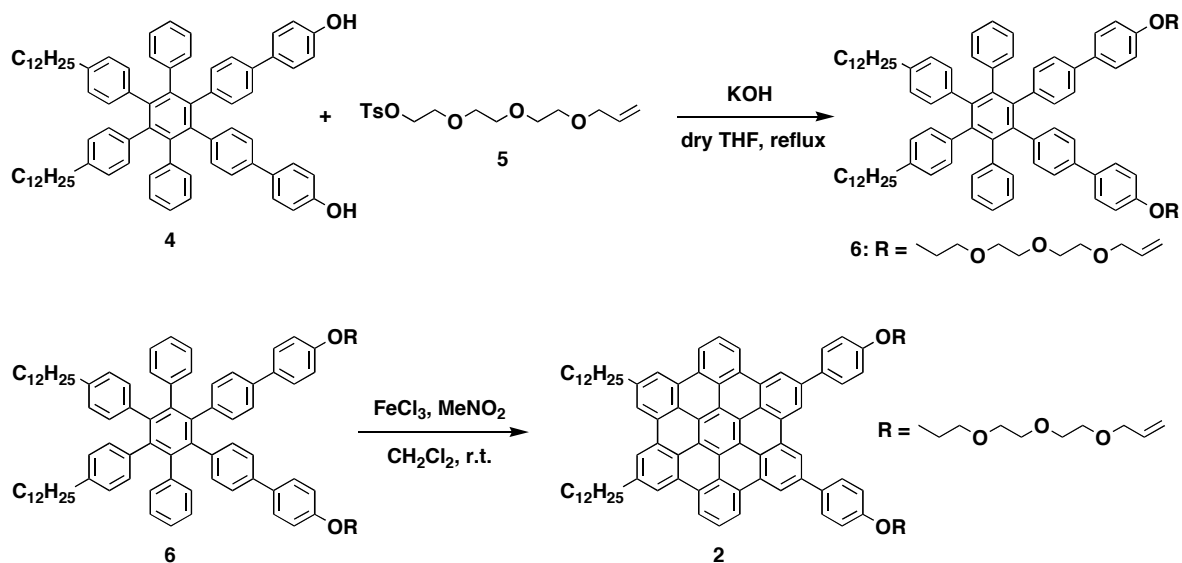
## 1. Measurements

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 298 K on a JEOL model NM-Excalibur 500 spectrometer, operating at 500 and 125 MHz, respectively, using partially or non-deuterated solvent residues as internal references. Electronic absorption spectra were recorded on a JASCO model V-560 UV/VIS spectrophotometer using a quartz cell of 0.1-mm path length. Infrared (IR) spectra were recorded at 25 °C on a JASCO model FT/IR-660<sub>plus</sub> Fourier transform infrared spectrometer. Differential scanning calorimetry (DSC) was performed on a Mettler–Toledo model DSC 822<sup>e</sup> differential scanning calorimeter, where temperature and enthalpy were calibrated with In (430 K, 3.3 J mol<sup>-1</sup>) and Zn (692.7 K, 12 J mol<sup>-1</sup>) standard samples using sealed Al sample pans. Cooling and heating profiles were recorded and analyzed using the Mettler–Toledo STAR<sup>e</sup> software system. X-ray diffraction (XRD) patterns were recorded at room temperature on a Rigaku model RINT–2500 counter diffractometer with a Cu K $\alpha$  radiation source. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI–TOF MS) was performed on an Applied Biosystems BioSpectrometry Workstation<sup>TM</sup> model Voyager-DE<sup>TM</sup> STR spectrometer using dithranol as a matrix. Scanning electron microscopy (SEM) was performed on a JEOL model JSM-6700F FE-SEM operating at 5 kV. Transmission electron micrographs (TEM) were recorded on a Philips model Tecnai F20 electron microscope operating at 120 kV. Contact angle measurements were performed on a Kyowa Interface Science Solid/Liquid Interface Analyzer model DropMaster500.

## 2. Materials

Unless otherwise noted, all commercial reagents were used as received from Aldrich Chemical Co. Ltd. [ $\text{FeCl}_3$  (99%) and  $\text{MeNO}_2$  (99%)], STREM CHEMICALS Co. Ltd. [bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride, Grubbs Catalyst, 1st generation].  $\text{CH}_2\text{Cl}_2$  was dried over  $\text{CaH}_2$  under argon and freshly distilled prior to use. Tetrahydrofuran (THF) was refluxed over a mixture of Na and benzophenone ketyl under argon and distilled just before use.

### 3. Synthesis of HBC Amphiphile 2



#### 2,3-Bis(4'-hydroxy-4-biphenyl)-5,6-di(4-dodecylphenyl)-1,4-diphenylbenzene (4).

Compound **4** was synthesized in a manner similar to that reported previously.<sup>1</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.28 (d,  $J$  = 8.5 Hz, 4H), 7.04 (d,  $J$  = 8.5 Hz, 4H), 6.89–6.79 (m, 14H), 6.75 (d,  $J$  = 8.5 Hz, 4H), 6.67 (d,  $J$  = 8.5 Hz, 4H), 6.61 (d,  $J$  = 8.0 Hz, 4H), 2.33 (t,  $J$  = 7.5 Hz, 4H), 1.40–1.35 (m, 4H), 1.30–1.19 (m, 34H), 1.08 (br., 4H), 0.87 (t,  $J$  = 7.5 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 154.58, 140.75, 140.60, 140.33, 139.64, 139.24, 139.20, 137.80, 136.77, 133.53, 131.82, 131.44, 131.16, 127.84, 126.49, 126.47, 124.91, 124.57, 115.30, 35.37, 32.00, 31.22, 29.80, 29.75, 29.59, 29.45, 28.87, 22.77, 14.20. MALDI–TOF MS: calcd for C<sub>78</sub>H<sub>86</sub>O<sub>2</sub> [M + H]<sup>+</sup>:  $m/z$  = 1054.66; found: 1054.89.

#### 2,3-Bis(4'-{2-[2-(2-allyloxyethoxy)ethoxy]ethoxy}-4-biphenyl)-5,6-di(4-dodecylphenyl)-1,4-diphenylbenzene (6).

To a THF solution (10 mL) of a mixture of **4** (890 mg, 0.84 mmol) and 2-[2-(2-allyloxyethoxy)ethoxy]ethyl *p*-tosylate (**5**)<sup>2</sup> (727 mg, 2.11 mmol) was added KOH (118 mg, 2.11 mmol), and the resulting suspension was refluxed for 14 h under argon. The reaction mixture was allowed to cool to room temperature and

evaporated to dryness. A CH<sub>2</sub>Cl<sub>2</sub> solution of the residue was washed with water, dried over anhydrous MgSO<sub>4</sub>, and evaporated to dryness. The residue was subjected to column chromatography (SiO<sub>2</sub>, ethyl acetate/CH<sub>2</sub>Cl<sub>2</sub> 1/4) to allow isolation of **6** as colorless solid (900 mg) in 76% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 50 °C): δ (ppm) 7.32 (d, *J* = 8.5 Hz, 4H), 7.05 (d, *J* = 8.5 Hz, 4H), 6.86–6.80 (m, 18H), 6.67 (d, *J* = 8.5 Hz, 4H), 6.62 (d, *J* = 8.5 Hz, 4H), 5.92–5.85 (m, 2H), 5.26–5.22 (m, 2H), 5.16–5.14 (m, 2H), 4.09 (t, *J* = 8.0 Hz, 4H), 4.00–3.99 (m, 4H), 3.82 (t, *J* = 5.0 Hz, 4H), 3.72–3.57 (m, 12H), 2.33 (t, *J* = 7.5 Hz, 4H), 1.39–1.36 (m, 4H), 1.29–1.20 (m, 32H), 1.08 (br, 4H), 0.87 (t, *J* = 7.0 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 50 °C): δ (ppm) 158.06, 140.87, 140.67, 140.45, 139.76, 139.31, 139.25, 137.94, 137.00, 134.80, 133.69, 131.88, 131.53, 131.26, 127.63, 126.51, 126.48, 124.94, 124.65, 116.76, 114.85, 72.23, 70.95, 70.77, 69.85, 69.58, 67.75, 35.42, 32.04, 31.21, 29.80, 29.75, 29.59, 29.44, 28.91, 22.76, 14.13. MALDI–TOF MS: Calcd. for C<sub>96</sub>H<sub>118</sub>O<sub>8</sub> [M + H]<sup>+</sup>: *m/z* = 1399.96; Found: 1399.43.

**2,5-Bis(4'-{2-[2-(2-allyloxyethoxy)ethoxy]ethoxy}phenyl)-11,14-didodecyl-hexa-*peri*-hexabenzocoronene (2).** A MeNO<sub>2</sub> (10 mL) solution of anhydrous FeCl<sub>3</sub> (1.78 g, 10.94 mmol) was slowly added to a dry CH<sub>2</sub>Cl<sub>2</sub> (150 mL) solution of **6** (850 mg, 0.61 mmol) under bubbling with Ar through a glass capillary. After being stirred for 1.5 h, the reaction mixture was poured into MeOH (400 mL). The resulting yellow precipitate was isolated by filtration and subjected to column chromatography (SiO<sub>2</sub>, hot THF), followed by precipitation from THF, to give **2** as yellow sticky solid (600 mg) in 71% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 50 °C): δ (ppm) 8.19 (s, 2H), 8.11 (s, 2H), 7.96 (s, 2H), 7.92 (s, 2H), 7.80 (s, 2H), 7.76 (s, 2H), 7.62 (d, *J* = 7.5 Hz, 4H), 7.24 (br., 2H), 7.14 (d, *J* = 7.5 Hz, 4H), 5.95–6.03 (m, 2H), 5.34 (d, *J* = 17.0 Hz, 2H), 5.23 (d, *J* = 11.0 Hz, 2H), 4.36 (m, 4H), 4.12–4.07 (m, 8H), 3.92–3.71 (m, 16H), 2.74 (br, 4H), 1.51–1.25 (m, 36H), 0.89 (t, *J* = 4.5 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 50 °C): δ (ppm) 158.45, 143.11, 141.26, 138.99, 134.95, 129.18, 129.03, 128.94, 128.76, 128.65, 128.48, 124.72, 120.45, 120.35, 118.78, 118.72, 118.54, 118.39, 118.30, 116.89, 115.11, 72.35, 71.16, 70.95, 70.14, 69.74, 67.92,

37.07, 32.09, 32.03, 30.16, 30.08, 30.02, 30.01, 29.99, 29.89, 29.55, 22.82, 14.18.

MALDI-TOF MS: Calcd. for  $C_{96}H_{106}O_8$   $[M + H]^+$ :  $m/z = 1387.86$ ; Found: 1387.82.

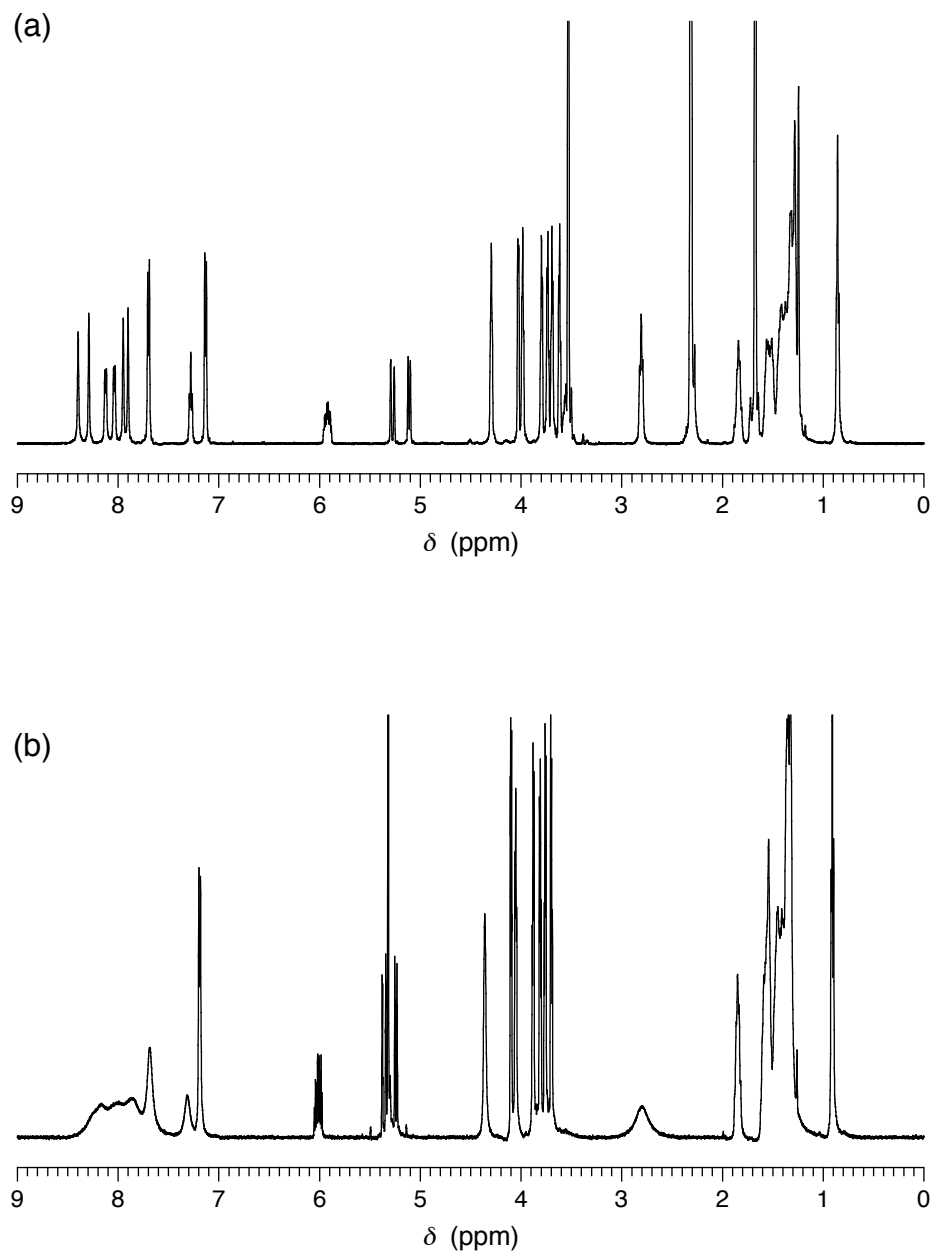
#### 4. Procedure for ADMET of HBC Amphiphile **2** in $CH_2Cl_2$

ADMET of **2** was carried out at 25 °C under an argon atmosphere in dry, degassed (freeze-pump-thaw cycles)  $CH_2Cl_2$  under anhydrous conditions. A  $CH_2Cl_2$  solution (5 mL) of Grubbs catalyst **3** (41.1 mg, 0.05 mmol) was added via a syringe to a  $CH_2Cl_2$  solution (35 mL) of **2** (138.7 mg, 0.1 mmol), whereupon the brown solution became turbid within 10 min, and produced a large amount of precipitates. Stirring was continued at 25 °C for 3 days until the reaction mixture showed a complete disappearance of the peak due to **2** in MALDI-TOF MS spectrometry. Then, the insoluble fraction was isolated from the reaction mixture by filtration, washed successively with  $CH_2Cl_2$  and MeOH, and dried overnight under a reduced pressure at 25 °C, affording a polymeric material as yellowish green solid (97 mg) in 71% yield based on **2**.

#### 5. References

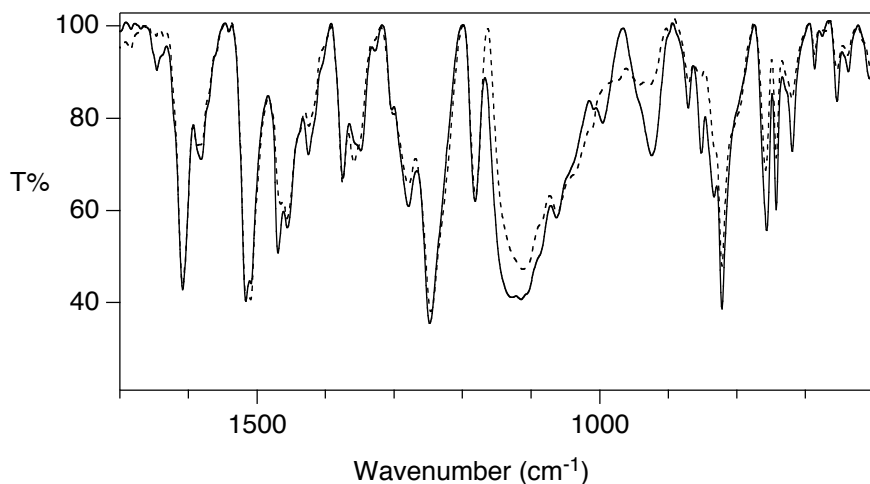
1. Hill, J. P.; Jin, W.; Kosaka, A.; Fukushima, T.; Ichihara, H.; Shimomura, T.; Ito, K.; Hashizume, T.; Ishii, N.; Aida, T. *Science* **2004**, *304*, 1481–1483.
2. Delgado, M.; Martín, J. D. *J. Org. Chem.* **1999**, *64*, 4798–4816.

## 6. $^1\text{H}$ NMR Spectroscopy of HBC Amphiphile **2**



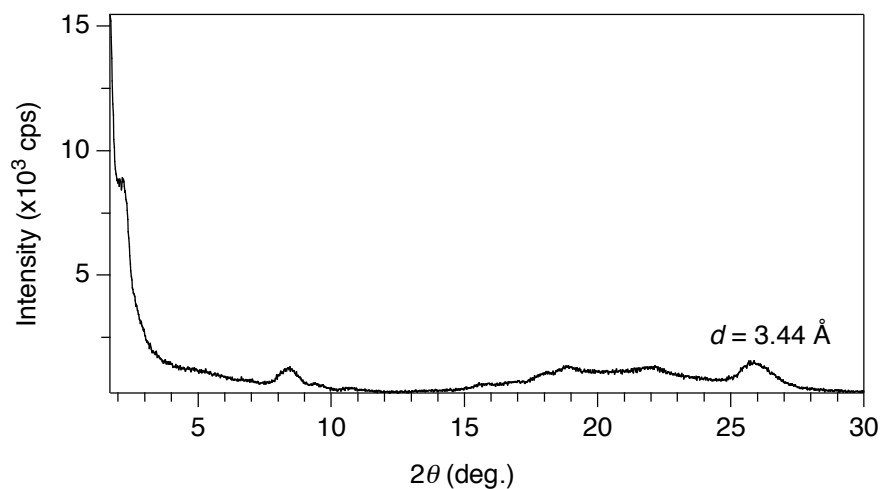
**Figure S1.**  $^1\text{H}$  NMR spectra of **2** in (a)  $\text{THF-}d_8$  at 50 °C and (b)  $\text{CD}_2\text{Cl}_2$  at 25 °C.

## 7. IR Spectroscopy before and after ADMET of HBC Amphiphile **2**



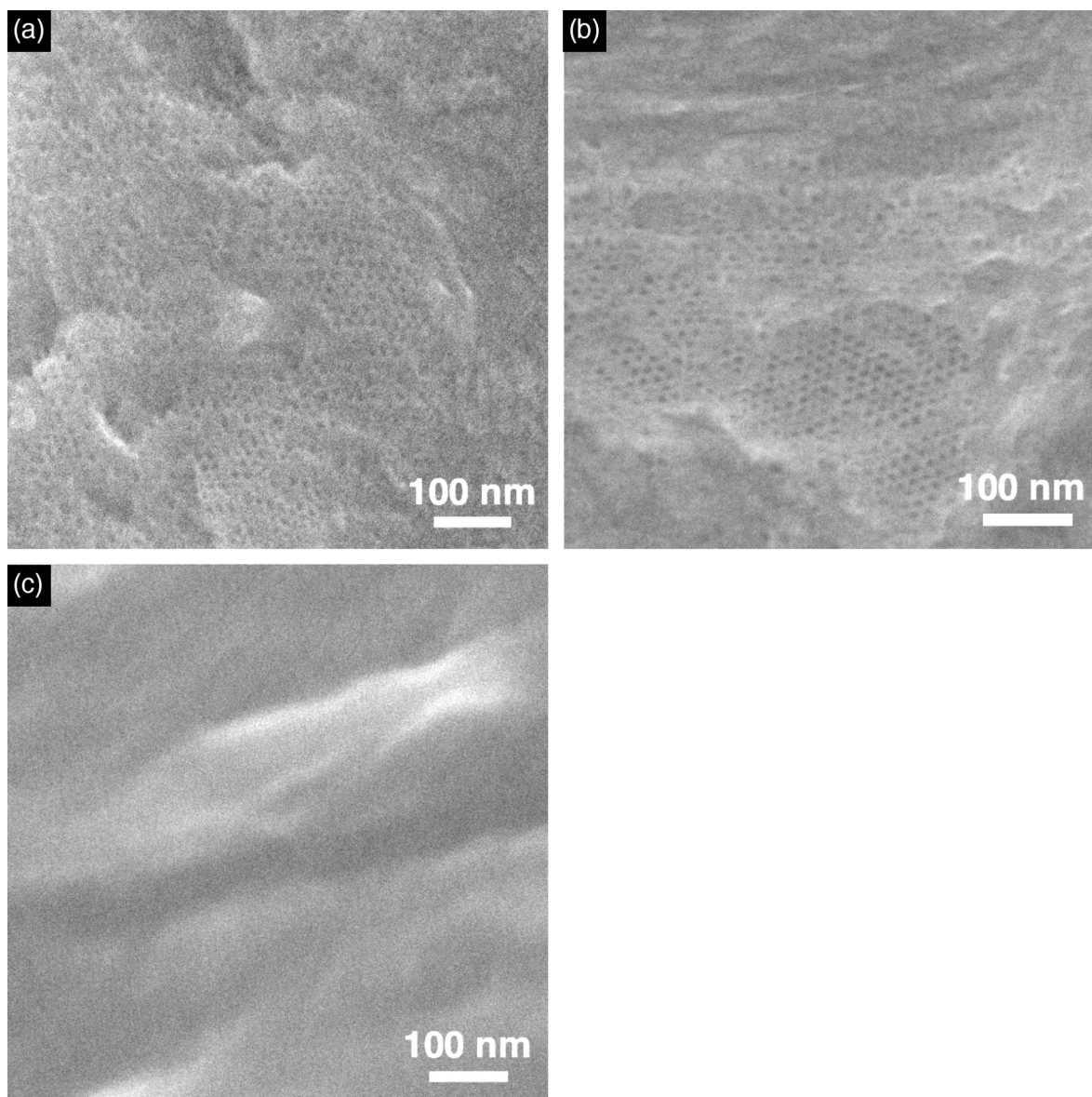
**Figure S2.** IR spectra (KBr) of **2** (solid curve) and a solid product isolated from the reaction mixture of **2** and **3** in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C for 3 days (broken curve).

## 8. X-Ray Diffraction (XRD) Analysis of HBC Amphiphile **2** after ADMET



**Figure S3.** XRD pattern of a solid product isolated from the reaction mixture of **2** and **3** in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C for 3 days.

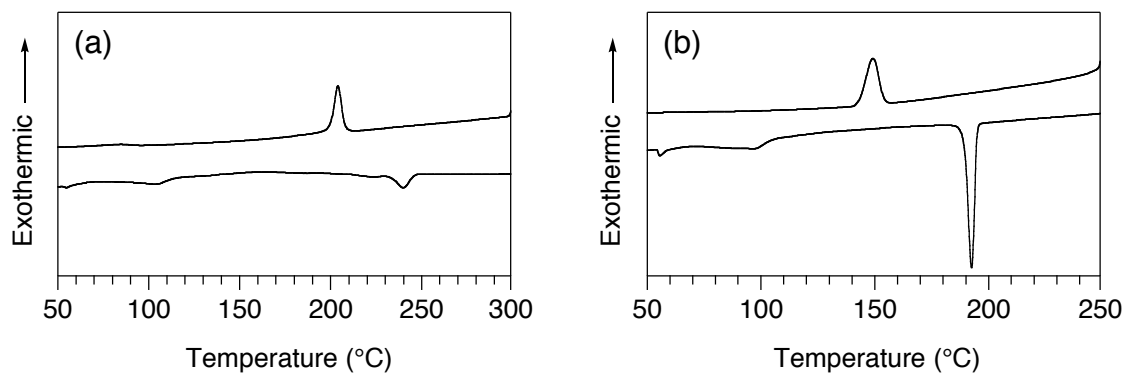
## 9. SEM Microscopy of Crosslinked and Uncrosslinked Nanotubes after Heating



**Figure S4.** SEM micrographs of crosslinked nanotubes after heated at 175 °C for (a) 24 h and (b) 3 days, and (c) uncrosslinked nanotubes after heated for 2 h at 175 °C.

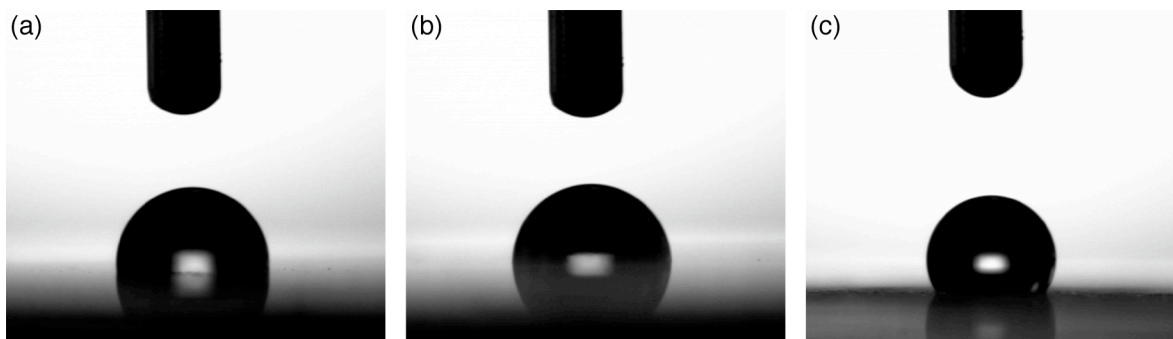


## 10. DSC Profiles of Crosslinked and Uncrosslinked Nanotubes



**Figure S5.** DSC thermographs (first heating/cooling cycle) of the nanotubes of **2** crosslinked with **3** (a) and uncrosslinked (b). Scan rate: 10 °C/min.

## 11. Contact Angle Measurements



**Figure S6.** Pictures of water droplets on glass substrates coated with (a) crosslinked nanotubes formed by ADMET of **2** in CH<sub>2</sub>Cl<sub>2</sub>, (b) uncrosslinked nanotubes formed by self-assembly of **2** in THF (1 mg/mL), and (c) **2** from its homogeneous CH<sub>2</sub>Cl<sub>2</sub> solution (1 mg/mL). The contact angles are (a) 94.4, (b) 87.2, and (c) 120.3 degrees at 24.3 °C in air with a 41.7% humidity.