Support Information for

Structural Complexity Induced by Topology Change in Hybrids with Hexa-*peri*-hexabenzocoronene and Polyhedral Oligomeric Silsesquioxane

Meng-Yao Zhang, Sheng Zhou, Hong-Bing Pan, Jing Ping, Wei Zhang, Xing-He Fan and Zhihao Shen*

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Center for Soft Matter Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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Experimental Section

Materials and Characterization Methods.

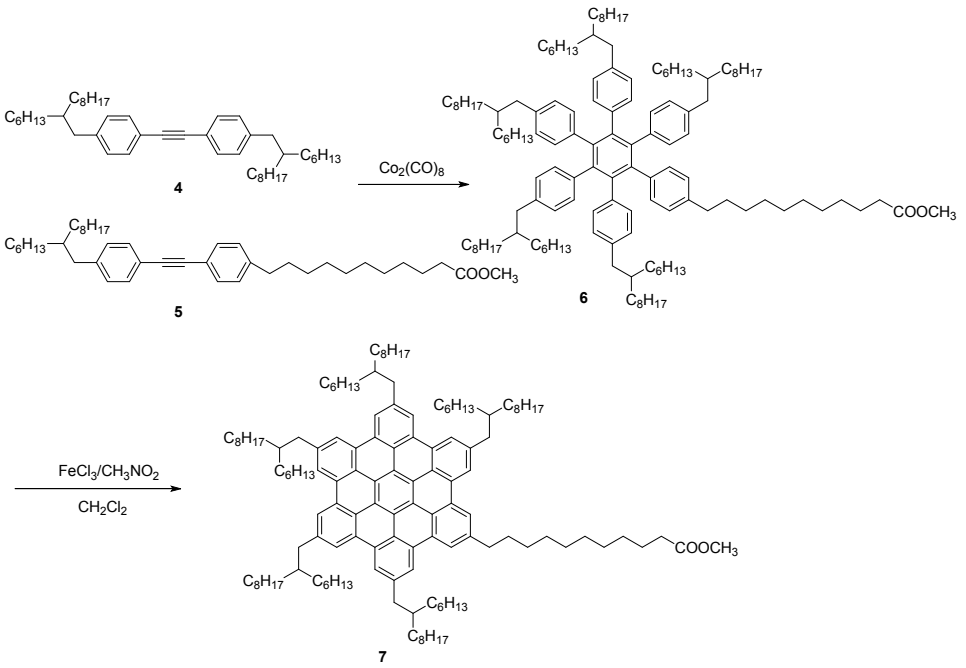
3-Hydroxypropylheptaisobutyl-POSS (POSS-OH) was purchased from Sigma Aldrich. 4-Dimethyl-aminopyridine (DMAP) and ferric chloride ($FeCl_3$) were purchased from J&K Chemical. *N*,*N*'-Diisopropylcarbodiimide (DIC) was purchased from Beijing Ouhe Technology Company Limited. Dichloromethane (CH_2Cl_2) was pretreated with the M. Braun solvent purification system. All other reagents were purchased from commercial sources and used as received unless otherwise noted.

All ^{1}H and ^{13}C NMR spectra were acquired in $CDCl_3$ (99.8% D with 0.03% TMS) using a Bruker 400 or 500 NMR spectrometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were measured using a Bruker Autoflex III MALDI-TOF spectrometer and alpha-cyano-4-hydroxycinnamic acid (CCA) as matrix. Elemental analysis was performed using an Elementar VARIO EL elemental analyzer. Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q600 analyzer under N_2 (10 ^{o}C/min). Differential scanning calorimetry (DSC) experiments were carried out on a TA DSC Q100 calorimeter in nitrogen. A sample of 2–3 mg was put into an aluminum DSC pan, and DSC measurements were operated with a rate of 10 ^{o}C/min during the heating and cooling cycles. Polarized light microscopy (PLM) observation was performed on a Nikon DS-Ri1 microscope with an Instec HCS302 hot stage. Small-angle X-ray Scattering (SAXS) experiments were performed on a SAXSess instrument (Anton Paar) using Cu Kα radiation at a wavelength of 0.154 nm. The working voltage and

current were 40 kV and 40 mA, respectively. The *d*-spacing (*d*) is given by $2\pi/q$. The synchrotron-radiation X-ray scattering experiments were performed on the Beamline 1W2A at BSRF[1] and Beamline BL15U1 at SSRF. For SAXS or synchrotron-radiation SAXS experiments, samples of about 15 mg were prepared by first dissolving in a mixed solvent of tetrahydrofuran (THF)/MeCN (v:v = 1:1). The solvent was then allowed to slowly evaporate at ambient temperature to give bulk powder samples, which were further dried in vacuum overnight. Then the dry powder samples were put into aluminum foil and annealed at temperatures near the transition temperatures for 24 h. The two-dimensional (2D) wide-angle X-ray diffraction (WAXD) experiments were performed on a Bruker D8Discover diffractometer with GADDS as a 2D detector. For 2D WAXD experiments, shear-oriented samples were obtained by mechanically shearing the samples of 3–4 mg at the temperatures near the transitions. Transmission electron microscopy (TEM) experiments were performed on JEM2100 at an accelerating voltage of 200 kV. Samples for TEM experiments were prepared by first embedding in the epoxy resin and then microtoming with a thickness of 30–80 nm.

Synthesis.

The synthesis of the precursor of HBC-1POSS-COO (**1E**) is illustrated in Scheme S1. The experimental details are described as follows.



Scheme S1. Synthetic route of the precursor of **1E**.

Synthesis of 1,2-bis(4-(2-hexyldecyl)phenyl)ethyne (4). Compound **4** was synthesized following the procedure in our previous report.[2] ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.42 (d, 4H), 7.11 (d, 4H), 2.52 (d, 4H), 1.60 (m, 2H), 1.24 (m, 42H), 0.88 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 142.27, 131.33, 129.23, 120.57, 89.02, 40.57, 39.68, 33.20, 33.17, 31.96, 31.94, 30.03, 29.71, 29.67, 29.39, 26.58, 22.74, 14.17, 14.16.

Synthesis of methyl 11-(4-((4-(2-hexyldecyl)phenyl)ethynyl)phenyl)undecanoate (5). Compound **5** was also synthesized following the procedure in our previous report.[2] ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.44–7.41 (dd, 4H), 7.15–7.10 (dd, 4H), 3.66 (s, 3H), 2.61(m, 2H), 2.52(d, 2H), 2.30(m, 2H), 1.60 (m, 5H), 1.25 (m, 36H), 0.88 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 174.30, 143.14, 142.25, 131.47, 131.33,

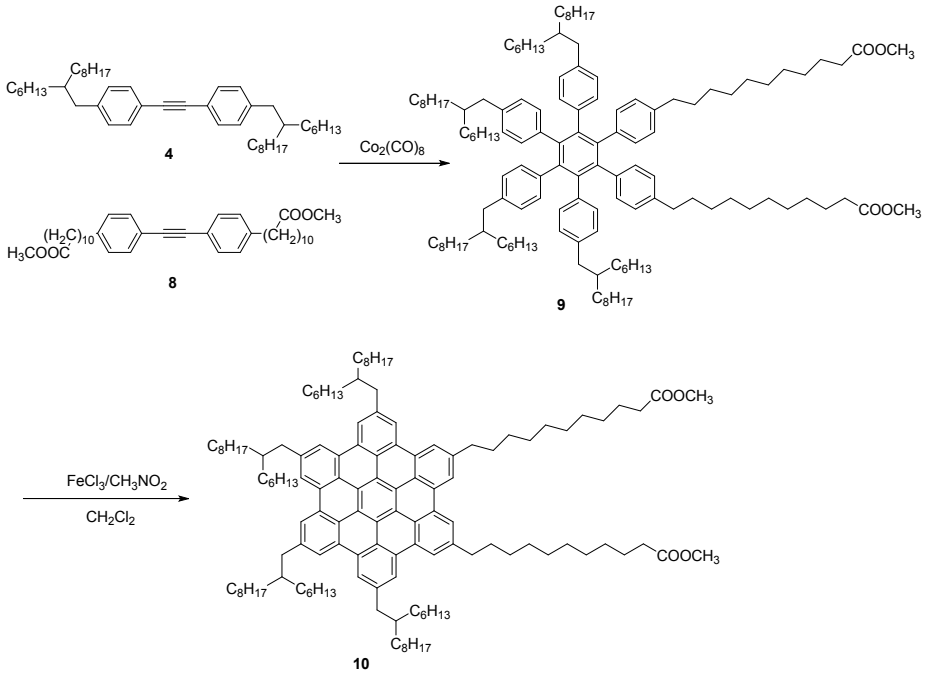
129.22, 128.44, 125.57, 120.68, 120.58, 89.00, 51.43, 40.56, 39.67, 35.93, 34.12, 33.20, 33.17, 31.96, 31.94, 31.29, 30.03, 29.71, 29.66, 29.53, 29.49, 29.46, 29.39, 29.29, 29.18, 26.57, 24.99, 22.73, 14.16.

Synthesis of compound 6. 3.41 g (5.44 mmol) of **4**, 1.23 g (2.05 mmol) of **5,** and 0.332 g (0.970 mmol) of $Co_2(CO)_8$ were dissolved in 60 mL of dry 1,4-dioxane under a nitrogen atmosphere. The resulting mixture was refluxed at 115 ^oC for 48 h. After the mixture was cooled to ambient temperature, the solvent was removed under a reduced pressure. And the residue was purified with column chromatography on silica gel with petroleum ether (PE)/CH_2Cl_2 as the eluent (4:1, v:v) to afford **6** as a white waxy solid (41%). ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.66–6.56 (m, 24H), 3.66 (s, 3H), 2.34–2.24 (m, 14H), 1.65–1.58 (m, 2H), 1.42–1.32 (m, 7H), 1.27–1.04 (m, 132H), 0.88 (t, 30H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 174.30, 140.28, 140.26, 139.04, 138.29, 138.26, 138.02, 137.97, 131.53, 131.39, 127.22, 126.38, 51.42, 40.09, 40.00, 39.46, 35.46, 34.14, 32.89, 32.00, 31.99, 31.33, 30.13, 29.78, 29.76, 29.66, 29.55, 29.43, 29.34, 29.23, 29.13, 26.46, 26.40, 25.00, 22.74, 22.73, 14.16, 14.14.

Synthesis of compound 7. 0.690 g (0.370 mmol) of **6** was dissolved in 70 mL of CH_2Cl_2. A constant stream of nitrogen was bubbled into the solution through a needle for 15 min. A solution of $FeCl_3$ (1.94 g, 11.9 mmol) in 4.2 mL of CH_3NO_2 was added dropwise with a syringe. After 1.5 h, the mixture was quenched with MeOH, and the precipitate was filtered off. Then the precipitate was purified with column

chromatography on silica gel with CH_2Cl_2 as the eluent to afford **7** as a yellow solid (81%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.51–8.45 (m, 12H), 3.66 (s, 3H), 3.09–3.01 (m, 12H), 2.30 (t, 2H), 2.00 (m, 7H), 1.65–1.22 (m, 134H), 0.88–0.79 (tt, 30H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 174.29, 139.98, 138.84, 129.84, 129.64, 129.61, 129.59, 123.34, 123.29, 121.96, 121.91, 121.08, 119.56, 51.42, 41.70, 40.08, 37.43, 34.15, 33.43, 32.61, 32.12, 32.01, 30.34, 30.22, 30.00, 29.97, 29.89, 29.73, 29.50, 29.45, 29.30, 26.84, 26.83, 26.76, 26.73, 25.04, 22.79, 22.71, 14.17, 14.10.

The synthesis of the precursor of HBC-2POSS-COO (**2E**) is illustrated in Scheme S2. The experimental details are described as follows.



Scheme S2. Synthetic route of the precursor of **2E**.

Synthesis of dimethyl 11,11'-(ethyne-1,2-diylbis(4,1-phenylene))diundecanoate (8).

Compound **8** was prepared similarly to the procedure for preparing compound **5**.

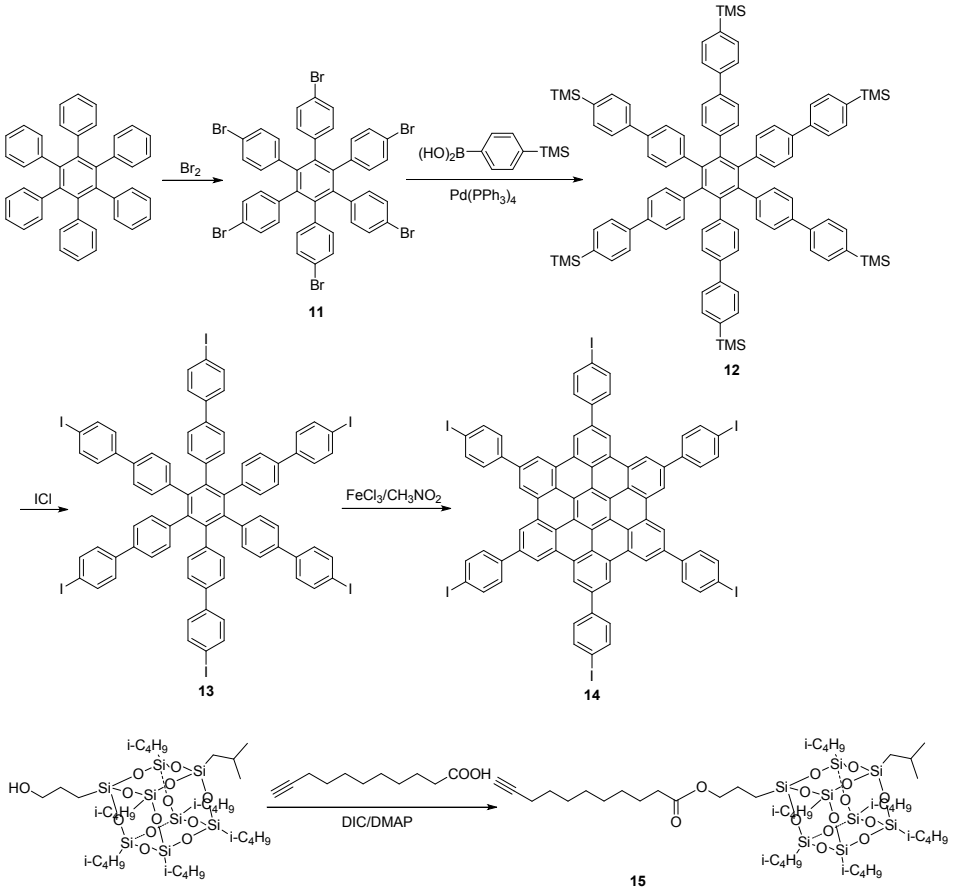
After column chromatography separation, the crude product was dissolved in 10 mL of CH_2Cl_2 and then dropped into 200 mL of MeOH. A white solid was obtained by filtration with a yield of 72%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.44 (d, 4H), 7.15 (d, 4H), 3.67 (s, 6H), 2.61 (t, 4H), 2.31 (t, 4H), 1.64–1.57 (m, 8H), 1.38–1.29 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 174.40, 143.19, 131.46, 128.44, 120.61, 88.93, 51.48, 35.91, 34.13, 31.27, 29.50, 29.46, 29.43, 29.26, 29.24, 29.15, 24.97.

Synthesis of compound 9. Compound **9** was prepared similarly according to the procedure described above for compound **6**. Yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.66–6.56 (m, 24H), 3.66 (s, 6H), 2.35–2.25 (m, 16H), 1.63–1.56 (m, 6H), 1.40–1.05 (m, 126H), 0.88(t, 24H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 174.29, 140.27, 139.01, 138.33, 138.28, 138.26, 138.02, 137.98, 131.49, 131.37, 127.23, 126.42, 51.42, 40.09, 40.01, 39.46, 35.40, 34.13, 32.89, 32.00, 31.29, 30.13, 29.77, 29.64, 29.55, 29.53, 29.44, 29.33, 29.22, 28.98, 26.46, 26.41, 25.00, 22.74, 14.15, 14.14.

Synthesis of compound 10. Compound **10** was prepared similarly according to the procedure described above for compound **7**. Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.55–8.46 (m, 12H), 3.65 (s, 6H), 3.09 (t, 4H), 3.01 (m, 8H), 2.30 (t, 4H), 2.02–1.96 (m, 8H), 1.65–1.59 (m, 10H), 1.40–1.05 (m, 114H), 0.88–0.79(tt, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 174.32, 139.84, 138.68, 129.68, 129.66, 129.52, 129.50, 129.44, 123.19, 123.15, 121.79, 121.00, 119.42, 51.45, 41.69, 41.67, 40.07,

37.43, 34.15, 33.43, 32.69, 32.14, 32.03, 30.37, 30.24, 30.00, 29.98, 29.92, 29.74, 29.52, 29.46, 29.30, 26.84, 26.83, 26.77, 26.73, 25.04, 22.81, 22.73, 14.20, 14.12.

The synthesis of the precursor of HBC-6POSS-COO (**6E**) is illustrated in Scheme S3. The experimental details are described as follows.



Scheme S3. Synthetic route of the precursor of **6E**.

Synthesis of 4,4''-dibromo-3',4',5',6'-tetrakis(4-bromophenyl)-1,1':2',1''-terphenyl (11). Liquid Br_2 (1 mL) was added slowly to a 10 mL Schlek flask charged with 1.12 mmol (0.598 g) of hexaphenylbenzene under an ice/salt bath. After 1 h of stirring, the ice/salt bath was removed, and the solution was stirred overnight. A saturated solution of sodium sulfite (3 mL) was added to quench the reaction. And then the solution was poured into a large amount of a saturated solution of sodium sulfite. The precipitate

was filtered off. Then the precipitate was washed with water and CH_2Cl_2/acetone (1:30, v:v), each for two times. A white solid was obtained with a yield of 89%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.06 (tt, 12H), 6.62 (tt, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 139.55, 138.40, 132.55, 130.45, 120.32. Elemental analysis: Calcd.: C 50.04, H 2.40, Br 47.56; Found: C 50.01, H 2.27.

Synthesis of (3'',4'',5'',6''-tetrakis(4'-(trimethylsilyl)-[1,1'-biphenyl]-4-yl)-[1,1':4', 1'':2'',1''':4''',1''''-quinquephenyl]-4,4''''-diyl)bis(trimethylsilane) (12). 0.329 mmol (0.332 g) of **11**, 3.01 mmol (0.585 g) of (4-(trimethylsilyl)phenyl)boronic acid, 10.1 mmol (1.39 g) of K_2CO_3, and 0.0600 mmol (70.0 mg) of tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) were dissolved in 20 mL of toluene and 10 mL of water under a nitrogen atmosphere. The mixture was refluxed at 100 ^{o}C for 24 h. After being cooled to ambient temperature, the mixture was extracted with CH_2Cl_2 for three times. And then the organic phase was dried by Na_2SO_4. The solvent was removed under vacuum and purified by column chromatography with PE/CH_2Cl_2 (3:1, v:v) as the eluent to afford a white solid with a yield of 84%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.47–7.40 (q, 24H), 7.15 (d, 12H), 6.95(d, 12H), 0.23(s, 54H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 141.25, 140.53, 140.00, 138.96, 137.74, 133.82, 132.18, 126.28, 125.53, -0.89.

Synthesis of Compound 13. 0.267 mmol (0.380 g) of **12** was dissovled in 150 mL of chloroform ($CHCl_3$) under a nitrogen atmosphere. A iodinemonochloride (ICl) solution (3.5 mL, 1.0 M in CH_2Cl_2) was dropped slowly into the flask. After a two-

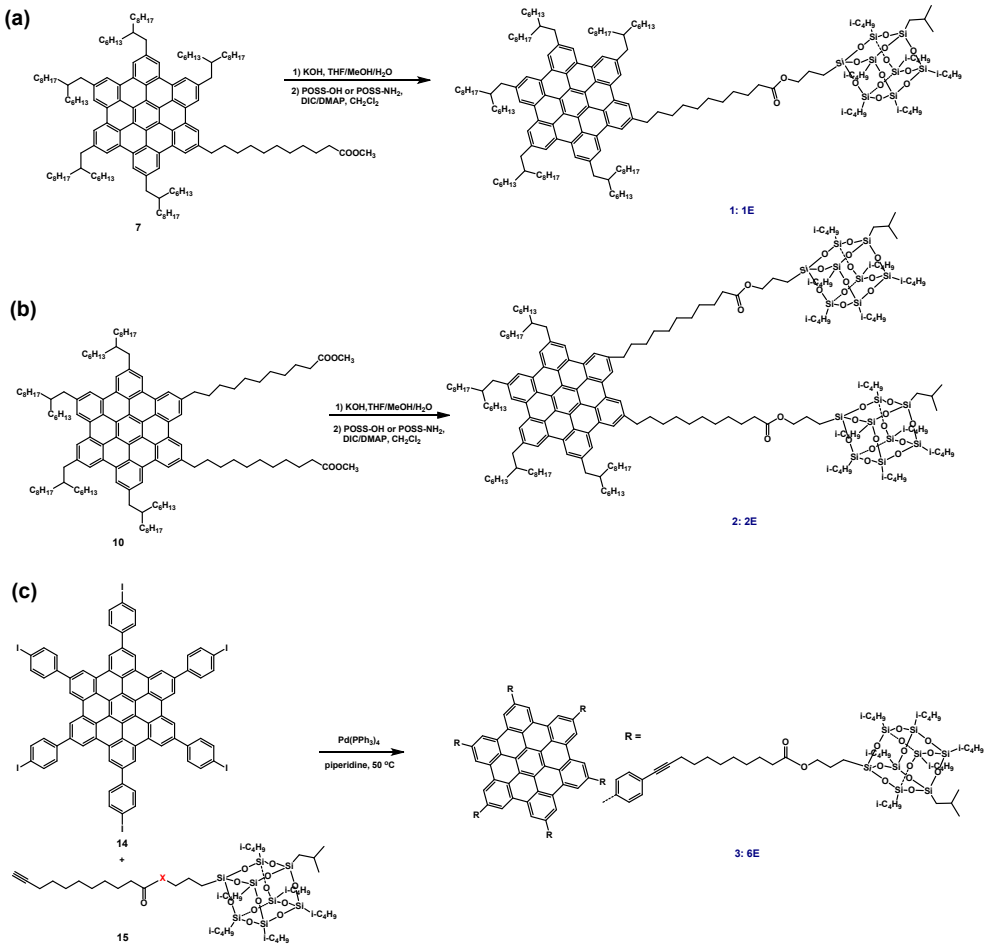
hour stirring, a 10% solution of sodium sulfite was added to quench the reaction. Then the mixture was separated, and the organic phase was washed with water for three times and then dried by Na_2SO_4. After the solvent was removed under vaccum, the solid was dissolved in 5 mL of CH_2Cl_2 and then dropped into 20 mL of MeOH. The product was obtained by fitration as a white solid with a yield of 89%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.63 (d, 12H), 7.15–7.10 (dd, 24H), 6.93 (d, 12H).

Synthesis of Compound 14. 0.229 mmol (0.400 g) of **13** was dissolved in 240 mL of CH_2Cl_2 and 120 mL of carbon disulfide (CS_2). A constant stream of nitrogen was bubbled into the solution through a needle for 15 min. A solution of $FeCl_3$ (4.10 g, 25.3 mmol) in 15 mL of CH_3NO_2 was added dropwise with a syringe. After 4 h, the mixture was poured into a large amount of MeOH, and the precipitate was filtered off. Then the precipitate was washed with MeOH until the filtrate was colorless. A dark yellow solid was obtained with a yield of 90%. MALDI-TOF MS (CCA as matrix): 1733.7 (m/z).

Synthesis of Compound 15. 0.704 mmol (0.600 g) of POSS-OH, 0.185 g undec-10-ynoic acid, and 0.409 mmol (0.0500 g) of DMAP were dissolved in 15 mL of CH_2Cl_2, and the solution was stirred at 0 ^{o}C for 10 min. Then 1.44 mmol (0.210 mL) of *N,N*'-diisopropylcarbodiimide (DIC) was added to the solution. The resulting mixture was stirred at ambient temperature for 24 h. After the solvent was removed under a reduced pressure, the residue was purified with column chromatography on silica gel

(eluent: PE/CH_2Cl_2 = 3:1, v:v). A yellow solid was obtained with a yield of 91%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.03 (m, 2H), 2.29 (m, 2H), 2.20–2.16 (dt, 2H), 1.93 (t, 1H), 1.90–1.80 (m, 7H), 1.75–1.68 (m, 2H), 1.64–1.60 (m, 2H), 1.56–1.48 (m, 2H), 1.43–1.26 (m, 8H), 0.95 (d, 42H), 0.65–0.59 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 173.87, 84.71, 68.21, 66.21, 34.34, 29.14, 29.12, 28.92, 28.68, 28.44, 25.71, 25.68, 24.98, 23.89, 23.86, 22.49, 22.42, 22.21, 18.39, 8.34.

The synthesis of ***n*E** (*n* = 1, 2, 6) is illustrated in Scheme S4. The experimental details are described as follows.



Scheme S4. Synthetic Route of ***n*E** (*n* = 1, 2, 6)

Synthesis of 1E. 0.130 mmol of **7** was dissolved in 100 mL of THF, and the solution of 5.30 mmol (0.299 g) of KOH in 5 mL of MeOH/H_2O (4:1, v:v) was added under a nitrogen atmosphere. The resulting mixture was refluxed at 75 ^oC overnight. After being cooled to ambient temperature, the solution was acidified with 10% aqueous hydrochloric acid. Then the organic phase was extracted with CH_2Cl_2, washed by water, and dried by Na_2SO_4. The solvent was removed under vacuum and purified by column chromatography with CH_2Cl_2 as the eluent to afford a yellow solid. Then the resulting solid, 0.400 mmol (0.341 g) of POSS-OH, and 0.260 mmol (0.0320 g) of DMAP were dissolved in 20 mL of CH_2Cl_2, and the solution was stirred at 0 ^oC for 10 min. Then 0.100 mL (0.640 g) of DIC was added to the solution. The resulting mixture was stirred at ambient temperature for 24 h. After the solvent was removed under a reduced pressure, the residue was purified with column chromatography on silica gel (eluent: PE/CH_2Cl_2 = 6:1, v:v). A yellow solid was obtained with a yield of 64%. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.66–8.57 (m, 12H), 4.03 (t, 2H), 3.16–3.05 (m, 12H), 2.31 (t, 2H), 2.07–1.96 (m, 7H), 1.90–1.80 (m, 7H), 1.75–1.70 (m, 2H),1.65–1.22 (m, 134H), 0.96–0.94 (dd, 42H), 0.88–0.79 (tt, 30H), 0.65–0.59 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 172.79, 137.82, 128.83, 128.58, 122.24, 120.88, 120.09, 118.52, 65.16, 40.65, 39.04, 36.43, 33.37, 32.37, 31.63, 31.07, 30.96, 29.29, 29.03, 28.93, 28.84, 28.79, 28.52, 28.45, 28.37, 25.79, 25.71, 25.69, 24.66, 24.64, 24.06, 22.86, 22.83, 21.74, 21.66, 21.47, 21.41, 21.19, 13.13, 13.05, 7.31. MALDI-TOF MS (CCA as matrix): 2685.6 ($[M]^+$/z), calcd. 2685.8. Elemental analysis: Calcd.: C 73.32, H 9.98, O 8.34, Si 8.36; Found: C 72.87, H 9.83.

Synthesis of 2E. The synthetic procedure was similar to that of **1E**. Yield: 53%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.68–8.52 (m, 12H), 4.03 (t, 4H), 3.16–3.05 (m, 12H), 3.14 (t, 4H), 3.03 (m, 8H), 2.31 (t, 4H), 2.06–1.96 (m, 8H), 1.92–1.78 (m, 14H), 1.75–1.60 (m, 13H), 1.48–1.22 (m, 103H), 0.96–0.94 (dd, 84H), 0.88–0.79 (tt, 24H), 0.65–0.59 (m, 32H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 172.78, 138.93, 137.70, 128.78, 128.51, 128.48, 122.31, 122.20, 122.15, 120.87, 120.81, 120.77, 120.07, 118.48, 65.16, 40.63, 39.03, 36.45, 33.36, 32.37, 31.71, 31.08, 30.96, 29.29, 29.03, 28.93, 28.85, 28.78, 28.52, 28.45, 28.45, 28.36, 25.80, 25.78, 25.73, 25.69, 24.67, 24.64, 24.06, 22.86, 22.83, 21.75, 21.67, 21.47, 21.41, 21.19, 13.13, 13.06, 7.31. MALDI-TOF MS (CCA as matrix): 3501.7 ($[M]^{+}$/z), calcd. 3502.0. Elemental analysis: Calcd.: C 65.13, H 9.26, O 12.79, Si 12.82; Found: C 65.14, H 9.34.

Synthesis of 6E. 0.0519 mmol (0.0900 g) of **14**, 0.577 mmol (0.600 g) of **15**, 0.0224 mmol (0.0260 g) of $Pd(PPh_3)_4$, and 0.0262 mmol (5.00 mg) of copper iodide (CuI) was dissolved in 10 mL of piperidine in a 25 mL Schlek flask under a nitrogen atmosphere. The mixture was stirred at 50 ^{o}C for 48 h. Then the solution was dropped into a large amount of MeOH, and the precipitate was filtered off. The precipitate was purified with column chromatography on silica gel with CH_2Cl_2 as the eluent to afford **3** as a yellow solid with a yield of 56%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.88 (m, 6H), 8.38–8.14 (m, 6H), 7.88 (d, 6H), 7.76–7.58 (m, 16H), 7.42 (d, 2H), 4.05 (t, 12H), 2.74–2.65 (m, 12H), 2.36 (t, 12H), 1.86–1.84 (m, 53H), 1.77–1.64 (m, 40H), 1.50–1.40 (m, 33H), 0.95 (t, 252H), 0.66–0.58 (m, 96H). ^{13}C NMR (100 MHz, $CDCl_3$,

δ, ppm): 173.77, 140.16, 139.31, 137.42, 137.08, 135.39, 133.37, 132.76, 132.58, 131.46, 129.92, 129.34, 128.71, 127.45, 126.80, 123.92, 123.65, 123.10, 120.20, 119.75, 119.60, 118.96, 118.01, 91.74, 80.84, 66.22, 34.39, 29.71, 29.62, 29.51, 29.41, 29.31, 29.21, 29.12, 25.83, 25.70, 25.68, 25.56, 25.11, 23.89, 23.85, 22.93, 22.87, 22.50, 22.44, 22.24, 22.07, 22.02, 20.05, 19.94, 8.35. MALDI-TOF MS (CCA as matrix): 7201.2 ($[M + H]^+/z$), calcd. 7200.8. Elemental analysis: Calcd.: C 55.00, H 7.64, O 18.65, Si 18.71; Found: C 54.88, H 7.66.

Results

Table S1. Thermal Transition Data of ***n*E** (n = 1, 2, 6) [a]

Sample	First cooling	Second heating
1E	--	**Cr**-50(10.7)-**I**
2E	**I**-92(3.37)-**Cr_1**-44(14.9)-**Cr_2**	**Cr_1**-90(5.34)-**Cr_2**-100(21.4)-**I**
6E	**BCC**-146(2.88)-**Col_h**-116(77.1)-**$Col_h + Cr_{POSS}$**	**$Col_h + Cr_{POSS}$**-148(56.9)-**Col_h**-157(2.16)-**BCC**

[a] Onset phase transition temperatures (°C) and heats of transition (kJ/mol, values in parentheses), Cr = crystal, I = isotropic, Col_h = hexagonal columnar phase, BCC = body-centered cubic phase.

Table S2. Crystallographic parameters of the supramolecular lattice of **2E**.

		q **(nm^{-1})**		***d*-spacing (nm)**	
No.	(*hkl*)	Exptl. [a]	Calc. [b]	Exptl. [a]	Calc. [b]
1	(100)	0.751	0.751	8.36	8.36
2	(200)	1.516	1.502	4.14	4.17
3	(300)	2.239	2.253	2.80	2.79
4	(010)	2.527	2.527	2.48	2.48
5	(110)	2.633	2.633	2.38	2.38
6	(210)	2.935	2.934	2.14	2.14
7	(30)	3.400	3.393	1.85	1.85
8	(500)	3.774	3.755	1.68	1.67
9	(600)/(510)	4.523	4.506/4.517	1.39	1.39
10	(700)/(220)	5.218	5.258/5.266	1.20	1.19
11	(320)	5.468	5.531	1.15	1.13
12	(620)	6.556	6.757	0.96	0.93
13	(002)	13.65	13.65	0.46	0.46

[a] Experimental values observed in X-ray scattering data. [b] Calculated based on a monoclinic crystalline unit cell of a = 8.36 nm, b = 2.48 nm, c = 0.92 nm, and γ = 89.8 °.

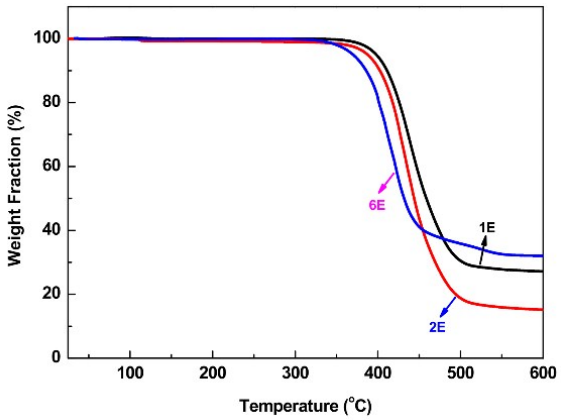


Figure S1. TGA curves of the ***n*E** (*n* = 1, 2, 6) at 10 °C/min under a nitrogen atmosphere.

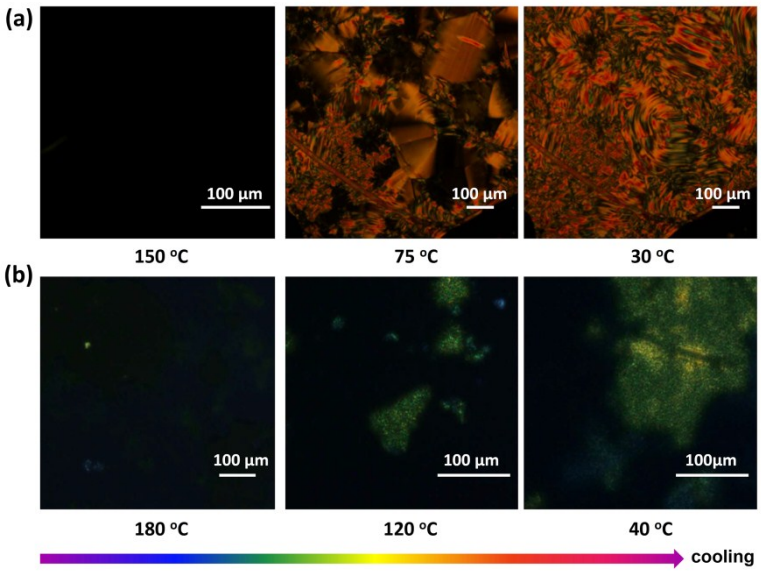


Figure S2. PLM micrographs of **2E** (a) and **6E** (b) during the cooling process.

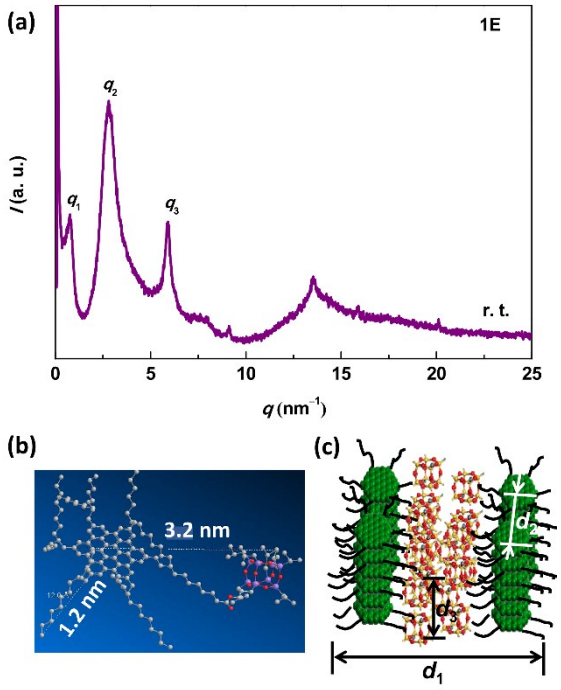


Figure S3. SAXS profile (a), simulated size using ChemOffice 3D (b), and packing scheme (c) of **1E**.

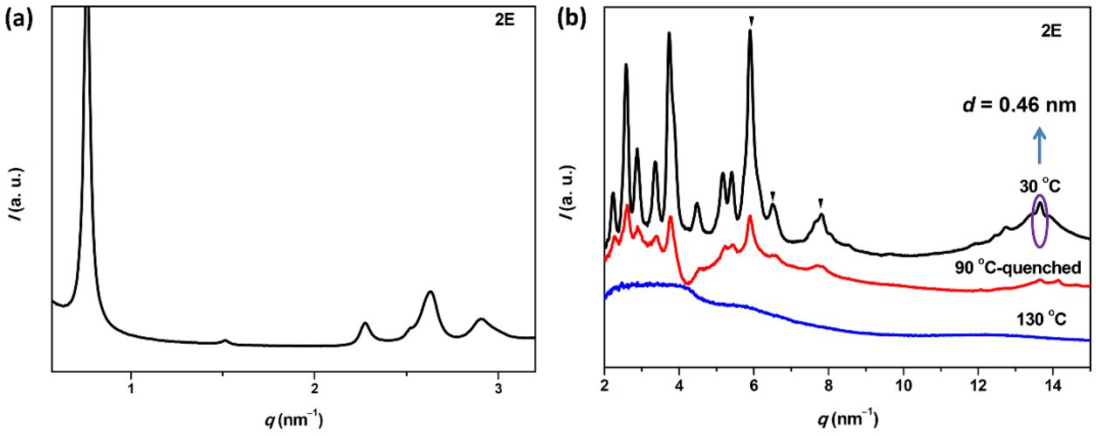


Figure S4. Synchrotron-radiation SAXS profile at 30 °C (a) and WAXD profiles at 30 °C, 90 °C, and 130 °C (b) of **2E**.

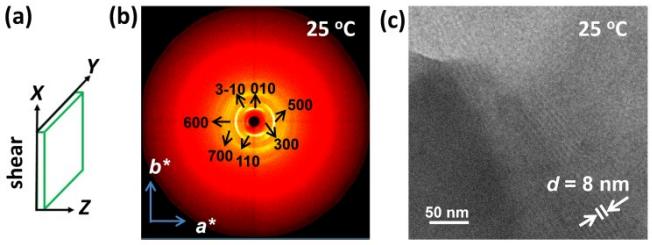


Figure S5. Shearing geometry (a) and 2D WAXD pattern of a sheared sample with the X-ray beam along the *X* direction (b) and bright-field TEM image (c) of **2E**.

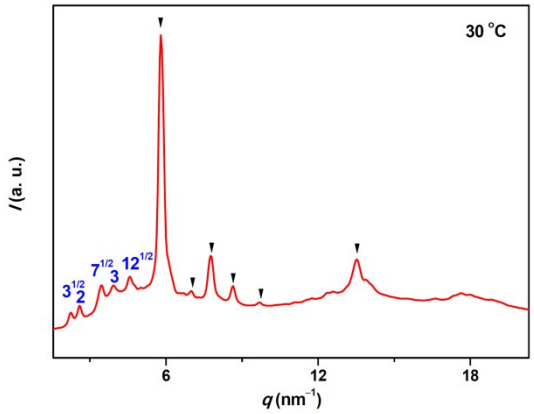


Figure S6. Synchrotron-radiation WAXD profile of **6E** at 30 °C.

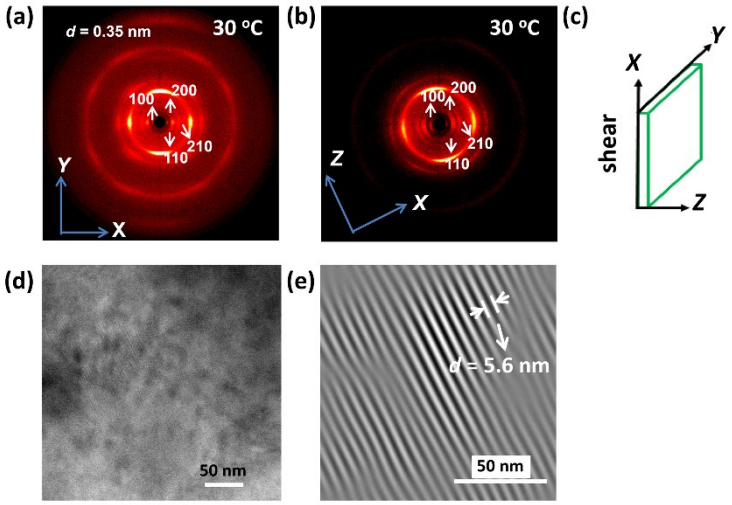


Figure S7. 2D WAXD patterns of a sheared sample with the X-ray beam along the *Z* (a) and *Y* (b) directions, the shearing geometry (c), bright-field TEM image (d), and I-FFT image (e) generated from (d) of **6E** at 30 °C.

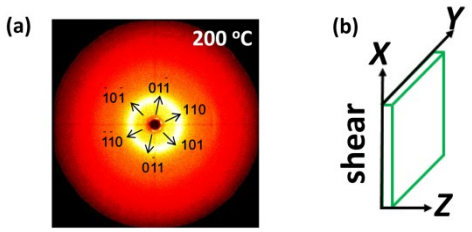


Figure S8. 2D WAXD patterns of a sheared sample of **6E** at 200 °C with the X-ray beam along the Z direction (a) and the shearing geometry (b).

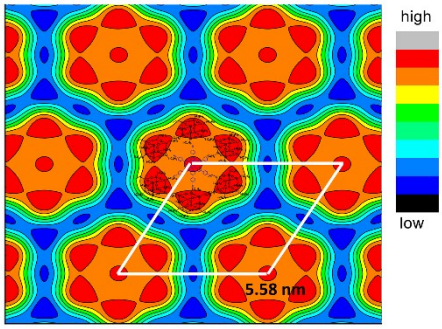


Figure S9. Reconstructed electron density map of **6E** at 150 °C.

References:

1. Z. Li, Z. Wu, G. Mo, X. Xing and P. Liu, *Instrum Sci Technol*, 2014, **42**, 128-141.

2. Y. Zhou, M.-Y. Zhang, K.-H. Gu, Y.-F. Zhu, X.-H. Fan and Z. Shen, *Asian J Org Chem*, 2015, 4, 746-755.