Electronic Supplementary Information (ESI) for

Hierarchically Ordered Structures of Disk-Cube Triads Containing Hexa-peri-Hexabenzocoronene and Polyhedral Oligomeric Silsesquioxane

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Experimental section

Chemicals and solvents.

1-Bromo-4-iodobenzene (98%, J&K Chemical), trimethylsilylacetylene (98%, J&K Chemical), trimethyl 1,3,5-benzenetricarboxylate (98%, J&K Chemical), *N*,*N′*-dicyclohexylcarbodiimide (DCC, 99%, J&K Chemical), 4-dimethylaminopyridine (99%, J&K Chemical), dichloro-bis(triphenylphosphine)palladium(II) (TCI), 1,1′-bis(diphenylphosphino)ferrocene palladium dichloride (99%, TCI), 4-ethoxy-4-oxobutylzinc bromide (0.5 M in tetrahydrofuran, TCI), 9-borabicyclo[3,3,1]nonane (9-BBN) monomer (0.5 M in tetrahydrofuran, J&K Chemical), ethyl 10-undecenoate (97%, J&K Chemical), dicobalt octacarbonyl (stabilized with 1-5% hexane, TCI), iron(III)chloride (98%, J&K Chemical), lithium aluminum hydride (1.0 M solution in tetrahydrofuran, J&K Chemical), 1,4-dioxane (99.5%, superdry, J&K Chemical), aminopropylheptaisooctyl POSS (BPOSS-NH_2) (> 97%, Hybrid Plastics), and 3-hydroxypropylheptaisobutyl-POSS (BPOSS-OH) (> 97%, Sigma Aldrich) were used as received. Toluene (HPLC, J&K Chemical), dichloromethane (HPLC, J&K Chemical), and tetrahydrofuran (HPLC, J&K Chemical) were purified using the MBraun SPS-800 solvent purification system. Triethylamine (Et_3N) was redistilled before use. 4-dimethylamino-pyridine-p-toluenesulfonate (DPTS) was synthesized according to the corresponding literatures.[1] The rest of the chemical reagents were commercially available and used without further purification.

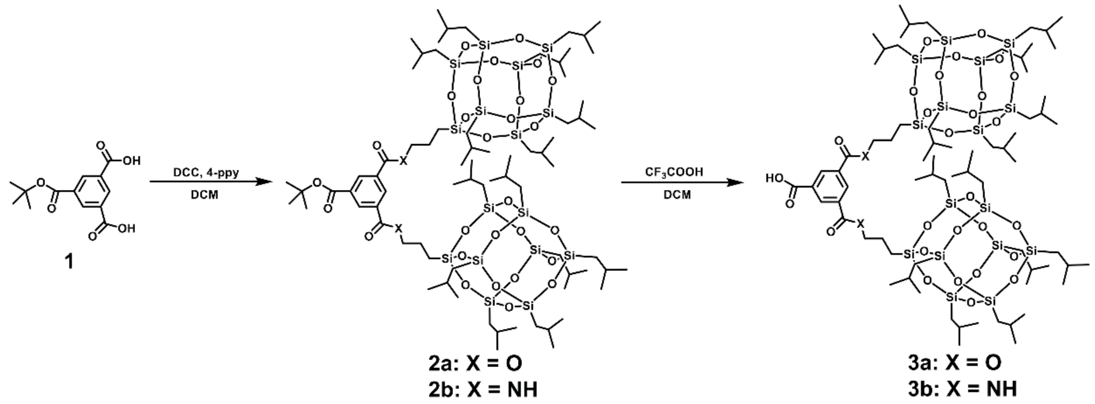
Instrumentation and characterization.

^{1}H and ^{13}C NMR spectra were acquired by a Bruker-400 (400 MHz) or Bruker-500 (500 MHz) spectrometer. The chemical shift of $CDCl_3$ was 7.27 ppm in ^{1}H NMR spectra and 77.00 ppm in ^{13}C NMR spectra. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Autoflex III MALDI-TOF spectrometer. The matrix is α-cyano-4-hydroxycinnamic acid (CCA). Thermogravimetric analysis (TGA) were conducted on a Q600 analyzer under N_2 atmosphere with a heating rate of 10 ^{o}C min^{-1}. Differential scanning calorimetry (DSC) experiments were conducted on a DSC Q100 calorimeter under N_2 gas. The scanning rate of DSC measurements is 10 ^{o}C min^{-1}

during heating and cooling processes. The IR experiments were conducted on a Bruker FTIR TENSOR 27 with a hot stage. Polarized light microscopy (PLM) experiments were carried out on a Nikon DS-Ril microscopy with an Instec HCS302 hot stage. All samples were treated through thermal annealing on a Mettler Toledo FP82HT hot stage before density measurements, wide-angle X-ray scattering (WAXS) experiments, 2D wide-angle X-ray diffraction (WAXD) experiments, and transmission electron microscope (TEM) experiments. HBC-C4-2POSS-COO (**4-E**), HBC-C4-2POSS-NH (**4-A**), and HBC-C11-2POSS-NH (**11-A**) were heated to 200 ^{o}C and cooled at 0.1 ^{o}C min^{-1} to 30 ^{o}C. HBC-C11-2POSS-COO (**11-E**) was heated to 150 ^{o}C and cooled at 0.1 ^{o}C min^{-1} to 30 ^{o}C. And the bulk samples were quenched by liquid nitrogen during the cooling process for WAXS experiments to determine their structures at different temperatures. All samples were sheared by a mechanic force before 2D WAXD tests. WAXS profiles were acquired on Xenocs Xeuss 2.0, and 2D WAXD patterns were obtained on Bruker D8Discover diffractometer with a General Area Detector Diffraction System (GADDS) as a 2D detector. The wavelength of X-ray is 1.54 Å. Also, the WAXS experiments were carried out at Beamline 1W2A of Beijing Synchrotron Radiation Facility (BSRF).[2] The slices of all bulk samples were obtained by a Leica EM UC6 ultramicrotome. Then the slices were transferred to amorphous carbon-coated copper grids for TEM measurements. Prior to subjecting to TEM observation, ruthenium tetroxide (RuO_4) staining of the samples was performed at ambient temperature. TEM images were recorded on Tecnai G2 F20 with an accelerating voltage of 200 kV.

Synthesis procedures

The synthetic routes of 2POSS-COOH (**4a** and **4b**) intermediates are shown in Scheme S1. The synthesis of compound **2** followed the procedure in literatures.[3, 4]



Scheme S1. Synthetic route of the 2POSS-COOH intermediates.

Synthesis of compound 2a. A mixture of compound **1** (50.0 mg, 0.188 mmol), 4-pyrrolidinopyridine (4-ppy, 27.8 mg, 0.188 mmol), and BPOSS-OH (494 mg, 0.564 mmol) were dissolved in HPLC-grade dichloromethane (DCM, 20 mL). The solution was cooled to 0 ^{o}C in an ice/water bath, and DCC (116 mg, 0.564 mmol) dissolved in 2 mL of DCM was slowly added. Afterwards, the ice/water bath was removed, and the reaction solution was stirred overnight at ambient temperature. The reaction solution was washed two times by deionized water and one time by brine. The organic solution was dried by Na_2SO_4, and the organic solvent was removed under a reduced pressure. The product was purified by column chromatography (eluent: petroleum ether (PE)/DCM = 1:1, v:v) to afford 200.4 mg of compound **2a** (53.8%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.83 (t, 1H), 8.78 (d, 2H), 4.34 (t, 4H), 1.93–1.78 (m, 18H), 1.63 (s, 9H), 0.95 (q, 84H), 0.73 (m, 4H), 0.61 (q, 28H).

Synthesis of compound 2b. The synthetic procedure of compound **2b** is similar to that of compound **2a**. The raw product was purified by column chromatography (eluent: DCM/ethyl acetate (EA) = 50:1, v:v) to afford compound **2b** (75.5%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.46 (d, 2H), 8.36 (t, 1H), 6.28 (t, 2H), 3.47 (q, 4H), 1.91−1.79 (m, 14H), 1.72 (m, 4H), 1.62 (s, 9H), 0.95 (q, 84H), 0.68 (m, 4H), 0.61 (q, 28H). MALDI-TOF MS for **2b**: $[M + Na]^+/z$, Calcd., 2001.7; Found, 2001.8.

Synthesis of compound 3a. Compound **2a** (200 mg, 0.101 mmol) was dissolved in 15 mL of DCM, and 3 mL of CF_3COOH was added dropwise. The reaction solution was stirred at ambient temperature for 3 h. Afterwards, the reaction solution was washed by a hydrochloric acid solution, deionized water, and brine in sequence. The organic solution was dried by Na_2SO_4, and the organic solvent was removed under a reduced pressure to afford 194 mg of the product as a white solid (100%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.91 (t, 1H), 8.89 (d, 2H), 4.35 (t, 4H), 1.94–1.78 (m, 18H), 0.95 (q, 84H), 0.72 (m, 4H), 0.61 (q, 28H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 169.63, 164.80, 135.43, 134.96, 131.81, 130.12, 67.70, 25.71, 25.66, 23.89, 23.87, 23.85, 22.50, 22.43, 22.31, 8.31. MALDI-TOF MS for **3a**: $[M]^+/z$, Calcd., 1923.6; Found, 1923.5.

Synthesis of compound 3b. The synthetic procedure of compound **3b** is the same as that of compound **3a**. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.59 (d, 2H), 8.47 (t, 1H), 6.34 (t, 2H), 3.49 (q, 4H), 1.91–1.79 (m, 14H), 1.74 (m, 4H), 0.95 (q, 84H), 0.69 (m, 4H), 0.61 (q, 28H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 168.64, 165.56, 135.58, 130.96, 130.57, 130.45, 42.86, 25.71, 25.69, 23.90, 23.87, 23.85, 23.04, 22.50, 22.45, 9.62. MALDI-TOF MS for **3b**: $[M]^+/z$, Calcd., 1921.6; Found, 1921.4.

^{1}H NMR, ^{13}C NMR, and MALDI-TOF MS data of 4-A, 11-E, and 11-A:

^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm) for **4-A**: 8.58 (d, 2H), 8.40 (t, 1H), 8.37–8.07 (m, 12H), 6.36 (t, 2H), 4.52 (t, 2H), 3.46 (q, 4H), 2.96 (m, 12H), 2.14–1.90 (m, 12H), 1.85 (m, 14H), 1.72 (m, 4H), 1.75–1.20 (m, 92H), 0.95 (q, 84H), 0.87 (t, 15H), 0.67 (m, 4H), 0.61 (q, 28H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm) for **4-A**: 165.53, 165.46, 139.74, 139.59, 138.60, 135.49, 131.41, 130.43, 129.66, 129.52, 129.37, 129.33, 129.29, 123.22, 123.00, 122.88, 122.79, 121.03, 120.98, 120.93, 120.87, 120.79, 120.73, 119.23, 119.17, 119.06, 119.10, 65.97, 42.80, 37.35, 37.28, 37.18, 36.75, 32.64, 32.54, 32.45, 31.99, 30.23, 30.16, 30.11, 30.05, 30.02, 29.99, 29.96, 29.89, 29.88, 29.79, 29.72, 29.46, 28.86, 28.52, 25.71, 25.69, 23.90, 23.87, 23.85, 23.05, 22.72, 22.50, 22.45, 14.13, 9.63. MALDI-TOF MS for **4-A**: $[M + H]^+/z$, Calcd., 3340.8; Found, 3340.7.

^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm) for **11-E**: 8.84 (s, 3H), 8.24–7.96 (m, 12H), 4.35 (m, 6H), 2.87 (m, 12H), 1.98–1.78 (m, 32H), 1.68–1.22 (m, 104H), 0.95 (q, 84H), 0.88 (t, 15H), 0.72 (m, 4H), 0.61 (q, 28H). ^{13}C NMR (125 MHz, CDCl$_3$, δ, ppm) for **11-E**: 165.15, 165.03, 139.30, 139.25, 134.41, 131.50, 129.31, 129.26, 129.17, 129.12, 122.84, 122.80, 122.69, 122.65, 120.65, 120.54, 118.92, 67.60, 65.89, 37.28, 37.24, 32.73, 32.58, 32.54, 32.51, 32.00, 30.35, 30.23, 30.16, 30.13, 30.06, 30.04, 29.99, 29.91, 29.85, 29.82, 29.72, 29.52, 29.48, 28.78, 26.02, 25.71, 25.69, 25.66, 23.89, 23.87, 23.85, 22.74, 22.50, 22.43, 22.29, 14.14, 8.29. MALDI-TOF MS for **11-E**: [M]$^+$/z, Calcd., 3439.8; Found, 3439.5.

^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm) for **11-A**: 8.52 (d, 2H), 8.39 (t, 3H), 8.23–7.93 (m, 12H), 6.32 (t, 2H), 4.35 (t, 2H), 3.47 (q, 4H), 2.87 (m, 12H), 2.01–1.77 (m, 28H), 1.73 (m, 4H), 1.68–1.18 (m, 104H), 0.95 (q, 84H), 0.89 (t, 15H), 0.68 (m, 4H), 0.61 (q, 28H). ^{13}C NMR (125 MHz, CDCl$_3$, δ, ppm) for **11-A**: 165.48, 165.46, 139.31, 139.26, 135.47, 131.47, 130.31, 129.51, 129.31, 129.25, 129.16, 129.11, 122.83, 122.78, 122.68, 122.64, 120.65, 120.54, 118.92, 66.02, 42.75, 37.40, 37.28, 37.24, 32.74, 32.58, 32.54, 32.51, 32.00, 30.35, 30.23, 30.16, 30.13, 30.06, 30.04, 29.99, 29.91, 29.82, 29.71, 29.53, 29.48, 28.78, 26.04, 25.71, 25.69, 25.66, 23.90, 23.86, 23.85, 23.06, 22.74, 22.50, 22.47, 14.14, 9.61. MALDI-TOF MS for **11-A**: [M]$^+$/z, Calcd., 3437.9; Found, 3437.5.

Results

Table S1. TGA and DSC data of the triads.

Compounds	T_{d} (°C)[a]	Phase Transition Temperature (°C)	ΔH (kJ/mol)
		First Cooling[b]/Second Heating[c]	First Cooling[b]/Second Heating[c]
4-E	371	94/105; 176	20.8/16.4;3.60
4-A	392	140/163	47.0/41.6
11-E	375	75/110	21.7/22.7
11-A	405	117/156	40.0/53.8

[a] 5% weight loss temperature evaluated by TGA at a rate of 10 °C min^{-1} under nitrogen;

[b] Evaluated by DSC during the first cooling cycle at a rate of 10 °C min^{-1} under nitrogen;

[c] Evaluated by DSC during the second heating cycle at a rate of 10 °C min^{-1} under nitrogen.

Table S2. WAXS data of **4-E** at ambient temperature.

(*hk*)	q (nm^{-1})		d (nm)	
	Exptl.	Calc.	Exptl.	Calc.
(10)	0.80	0.80	7.85	7.85
(20)	1.61	1.59	3.90	3.94
(01)	2.02	2.02	3.11	3.11
(30)/(11)	2.45	2.39/2.45	2.56	2.62/2.56
(21)	2.95	3.03	2.13	2.07
(31)	3.73	3.69	1.68	1.70
(50)	3.99	4.00	1.57	1.57
(60)	4.84	4.79	1.30	1.31
(70)	5.55	5.61	1.13	1.12

Table S3. WAXS data of **11-E** at ambient temperature.

(hk)	q (nm^{-1})		d (nm)	
	Exptl.	Calc.	Exptl.	Calc.
(10)	0.71	0.71	8.85	8.85
(02)	1.81	1.81	3.47	3.47
(22)	2.30	2.30	2.73	2.73
$(2\bar{3})$	3.07	3.08	2.05	2.04

Table S4. WAXS data of **4-A** at ambient temperature.

(hk)	q (nm^{-1})		d (nm)	
	Exptl.	Calc.	Exptl.	Calc.
(10)	0.97	0.97	6.47	6.49
(20)	1.91	1.93	3.29	3.25
(01)	2.23	2.23	2.82	2.82
$(2\bar{1})$	2.79	2.78	2.25	2.25
(30)	2.91	2.93	2.16	2.16
$(3\bar{1})$	3.52	3.46	1.78	1.81
(40)	3.81	3.87	1.65	1.62
(02)	4.49	4.45	1.40	1.41
$(\bar{2}2)$	4.75	4.67	1.32	1.35

Table S5. WAXS data of **11-A** at ambient temperature.

(*hkl*)	*q* (nm^{-1})		*d* (nm)	
	Exptl.	Calc.	Exptl.	Calc.
(100)	1.50	1.50	4.19	4.18
(010)	2.48	2.48	2.53	2.53
(1$\bar{1}$0)	2.70	2.70	2.33	2.33
(200)	3.00	3.00	2.09	2.09
(2$\bar{1}$0)	3.64	3.60	1.73	1.75
(210)	4.12	4.17	1.52	1.51
(300)	4.51	4.50	1.39	1.39
(020)	4.95	4.96	1.27	1.27
(120)/($\bar{2}$20)	5.34	5.41/5.41	1.18	1.16/1.16
(400)	6.02	6.00	1.04	1.05
(001)	6.51	6.51	0.96	0.96
(1$\bar{1}$1)	7.05	7.05	0.89	0.89
(3$\bar{2}$0)	7.16	7.18	0.88	0.87
(030)	7.34	7.44	0.86	0.84
(3$\bar{3}$0)	8.16	8.10	0.77	0.78
(401)	8.90	8.85	0.71	0.71
(002)	12.99	13.02	0.48	0.48
(3$\bar{1}$2)	13.82	13.89	0.45	0.45
(402)	14.32	14.34	0.44	0.44
(412)	14.63	14.71	0.43	0.43
(060)	14.86	14.88	0.42	0.42
(3$\bar{3}$2)	15.30	15.34	0.41	0.41
(332)	16.01	15.98	0.39	0.39
(370)	17.18	17.28	0.37	0.36
(6$\bar{6}$1)	17.56	17.46	0.36	0.36
(7$\bar{7}$0)	18.95	18.90	0.33	0.33
(023)	20.21	20.16	0.31	0.31

Table S6. WAXS data of the four triads at high temperatures.

(*hkl*)	$q_{\mathbf{4\text{-}E}}$ (nm^{-1})	$q_{\mathbf{4\text{-}A}}$ (nm^{-1})	$q_{\mathbf{11\text{-}E}}$ (nm^{-1})	$q_{\mathbf{11\text{-}A}}$ (nm^{-1})
(100)	1.67	1.84	1.51	1.70
(110)	2.89	3.21	2.60	2.95
(200)	3.33	3.73	2.96	–

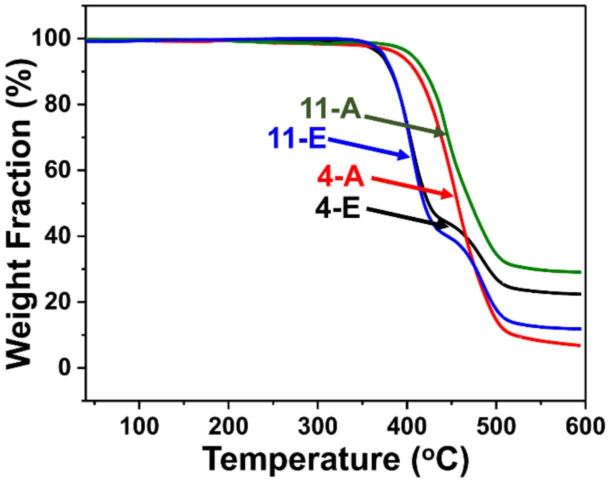


Figure S1. TGA curves of the four triads at a rate of 10 °C min^{-1} under nitrogen atmosphere.

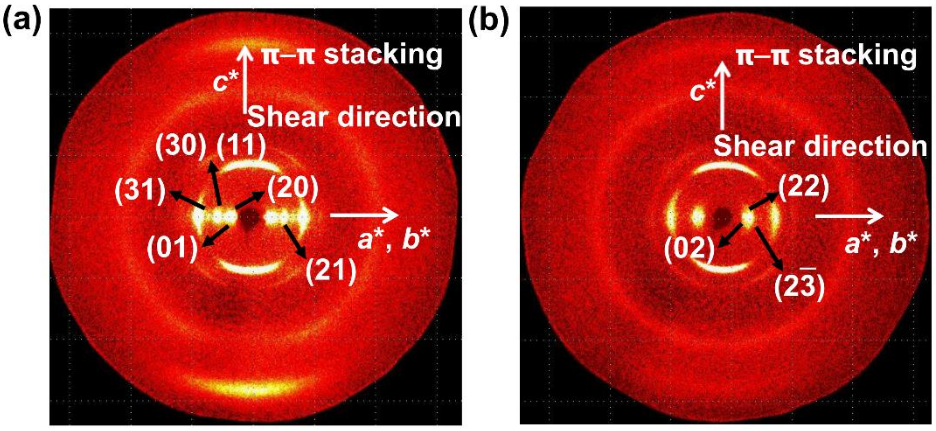


Figure S2. 2D WAXD patterns of a sheared **4-E** sample (a) and a sheared **11-E** sample (b) at ambient temperature.

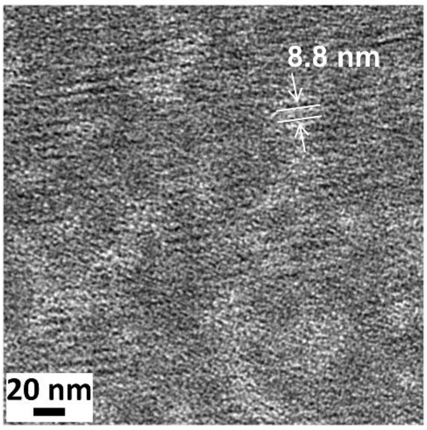


Figure S3. TEM bright-field micrograph along the <001> direction of **11-E**.

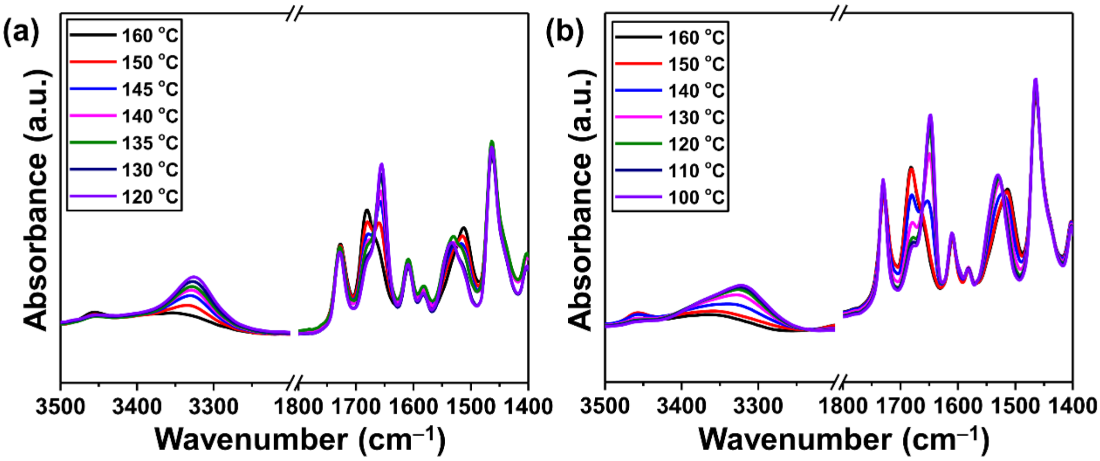


Figure S4. FTIR spectra of the samples **4-A** (a) and **11-A** (b) during the cooling processes. Curves are offset for clarity.

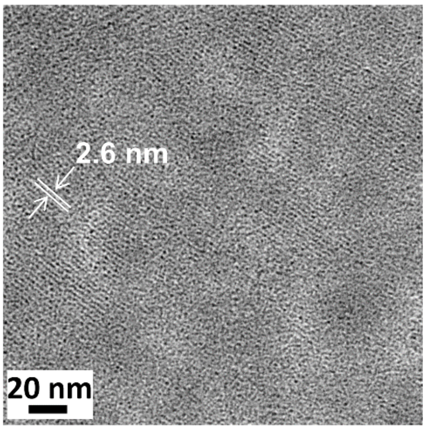


Figure S5. TEM bright-field micrograph along the <001> direction of **11-A**.

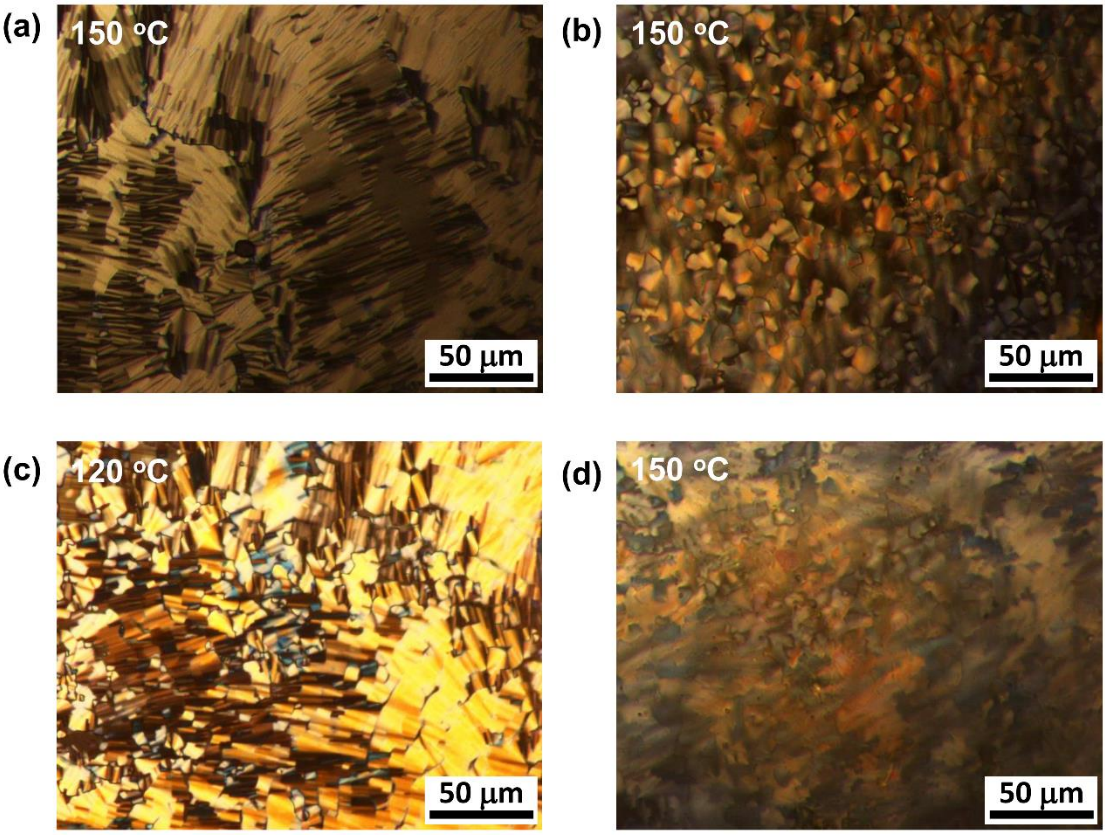


Figure S6. PLM micrographs of the textures exhibited by the Col$_h$ phase of **4-E** (a), **4-A** (b), **11-E** (c), and **11-A** (d) during the cooling process.

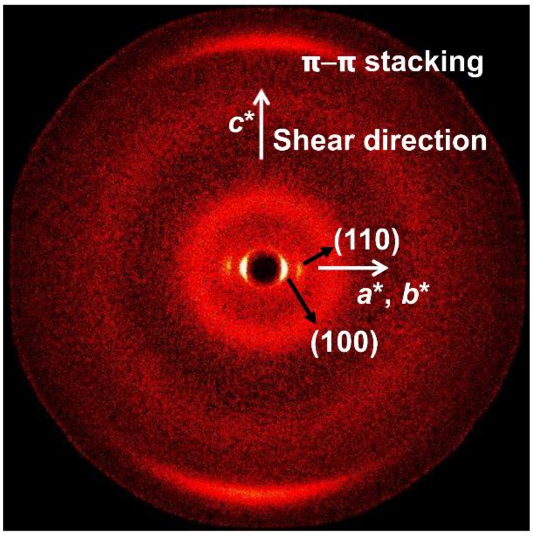


Figure S7. 2D WAXD pattern of the Col$_h$ structure of **4-A** at 150 ^{o}C during the cooling process.

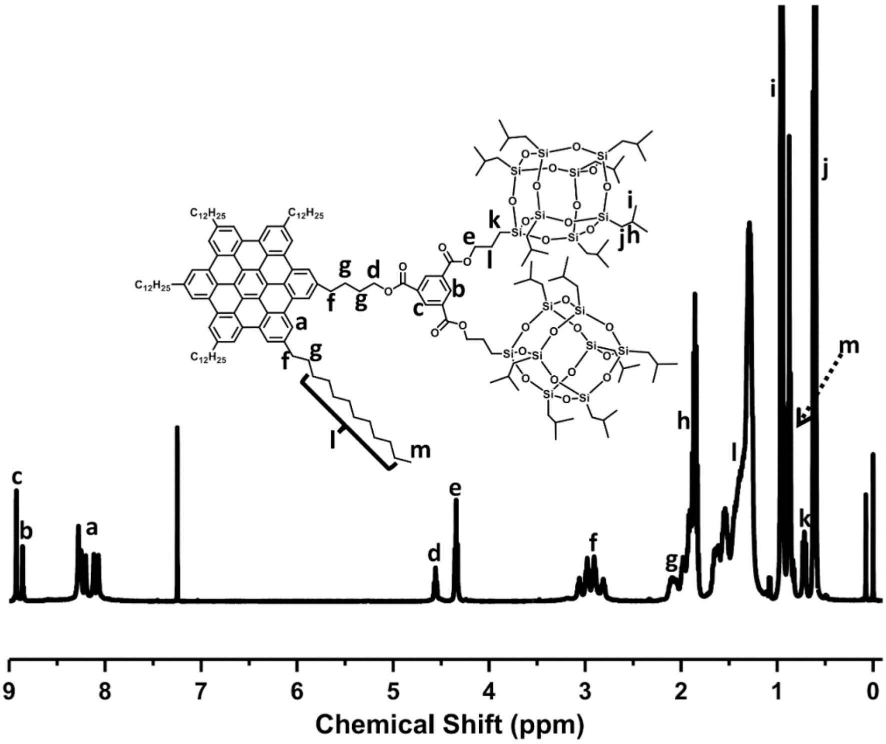


Figure S8. ^{1}H NMR spectrum of **4-E**.

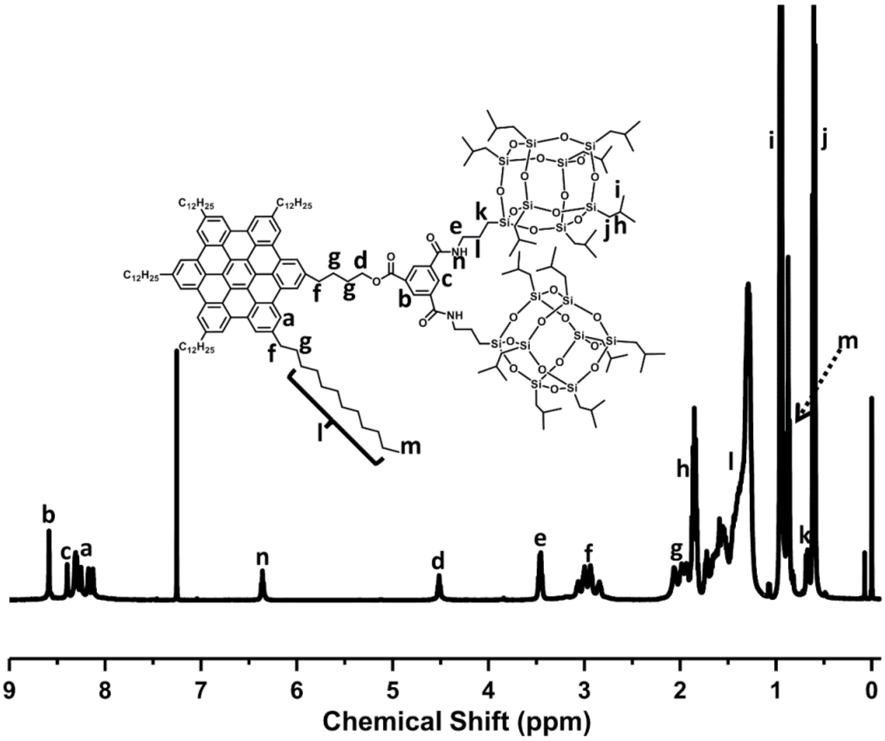


Figure S9. ^{1}H NMR spectrum of **4-A**.

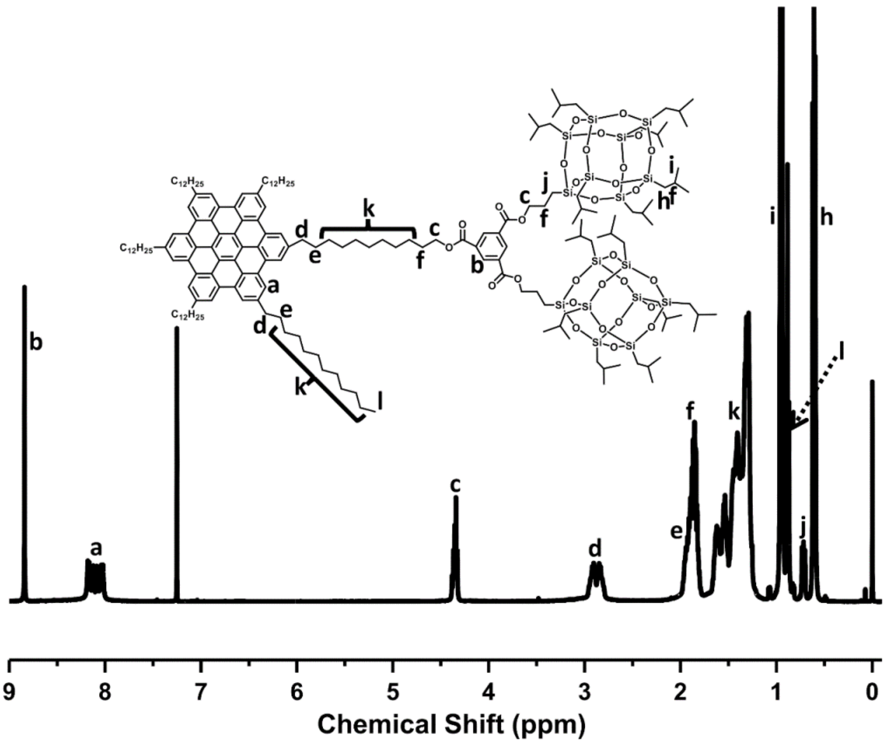


Figure S10. ^{1}H NMR spectrum of **11-E**.

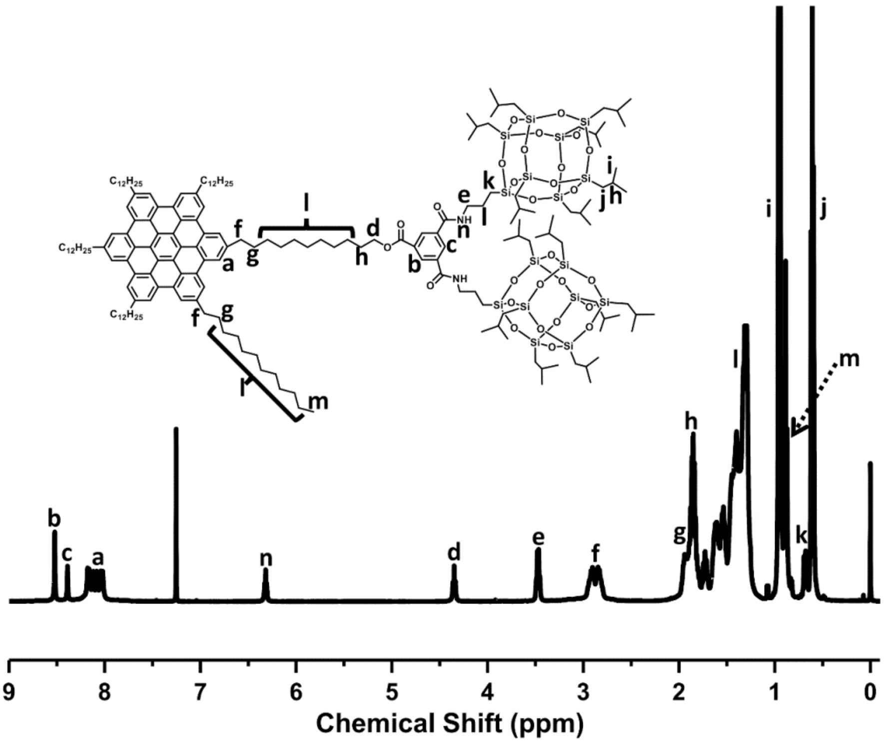


Figure S11. ^{1}H NMR spectrum of **11-A**.

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