

Electronic Supplementary Information for

**Ordered Structure Constructed by C<sub>2</sub>-Symmetric Hexa-*peri*-Hexabenzocoronene Linked  
with Oligo(Dimethylsiloxane)**

Wei Zhang<sup>#</sup>, Weilu Yang<sup>#</sup>, Hongbing Pan, Xiaolin Lyu, Anqi Xiao, Dong Liu, Zhihao Shen<sup>\*</sup>,  
Huai Yang, and Xing-He Fan<sup>\*</sup>

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

**Table of Contents**

|   |     |
|---|-----|
| <b>Experimental Section</b>   | S2  |
| <b>Results</b>  | S6  |
| Table S1 Thermal transition data of the hybrids   | S6  |
| Figure S1 <sup>1</sup> H NMR spectrum of <i>p</i> -HBC-4Si <sub>7</sub>                               | S6  |
| Figure S2 <sup>1</sup> H NMR spectrum of <i>p</i> -HBC-6Si <sub>7</sub>                               | S7  |
| Figure S3 <sup>13</sup> C NMR spectrum of <i>p</i> -HBC-4Si <sub>7</sub>                              | S7  |
| Figure S4 <sup>13</sup> C NMR spectrum of <i>p</i> -HBC-6Si <sub>7</sub>                              | S8  |
| Figure S5 MALDI-TOF mass spectra of <i>p</i> -HBC-4Si <sub>7</sub> and <i>p</i> -HBC-6Si <sub>7</sub> | S8  |
| Figure S6 TGA thermogram of the hybrids   | S9  |
| Figure S7 PLM micrographs of <i>p</i> -HBC-4Si <sub>7</sub> at ambient temperature                    | S9  |
| Figure S8 Temperature-dependent WAXS profile of <i>p</i> -HBC-4Si <sub>7</sub>                        | S10 |
| Figure S9 Temperature-dependent WAXS profile of <i>p</i> -HBC-6Si <sub>7</sub>                        | S10 |
| Figure S10 Cross-sectional SEM images of thin films   | S10 |
| Figure S11 AFM height image and cross-sectional scan curve of <i>p</i> -HBC-4Si <sub>7</sub>          | S11 |
| Figure S12 Large-area AFM phase image of <i>p</i> -HBC-6Si <sub>7</sub>                               | S11 |
| <b>References</b>   | S12 |

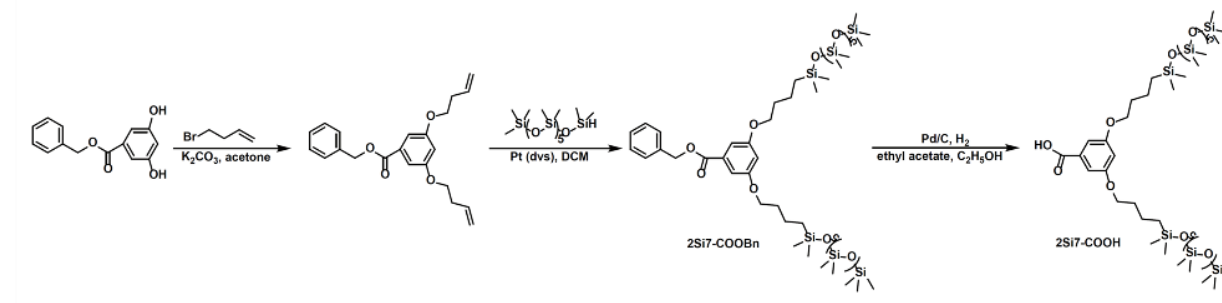
## Experimental Section

### Materials

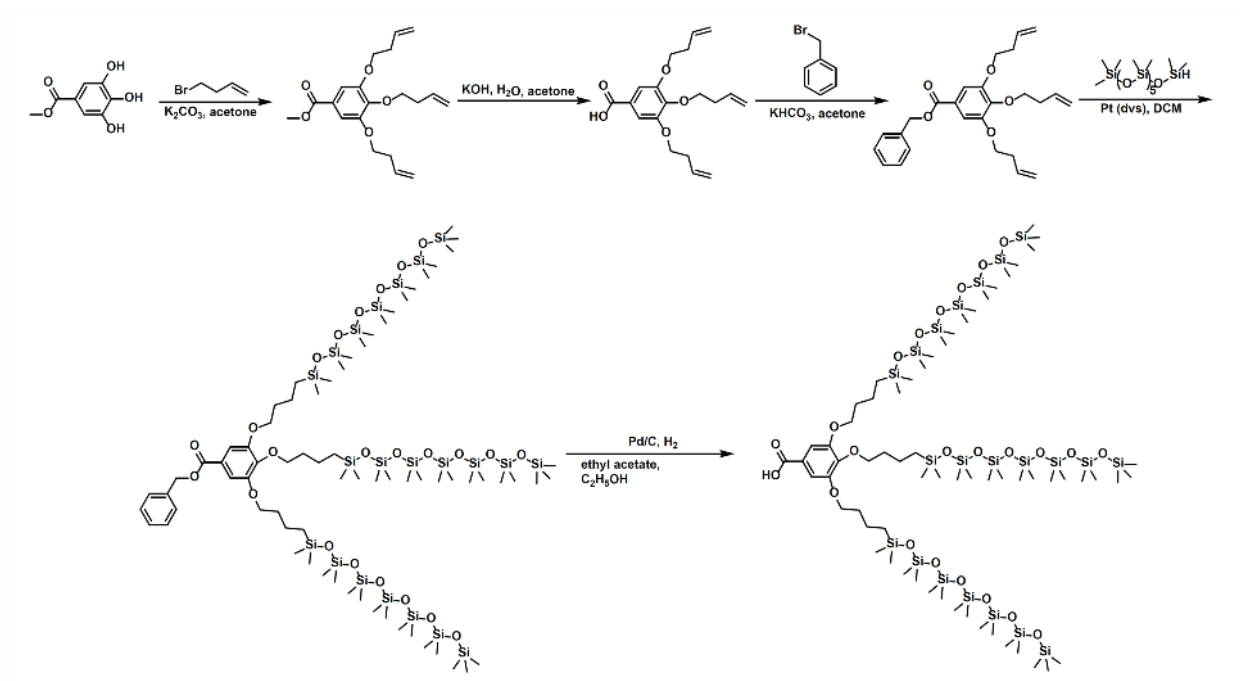
*N,N'*-dicyclohexylcarbodiimide (DCC, 99%, J&K Chemical), 4-bromobut-1-ene (97%, Aladdin), potassium carbonate (AR, Acros), Karstedt catalyst solution (Pt(dvs), Pt ~2% in Xylene, Energy Chemical), Pd/C (10% on carbon, TCI), potassium hydroxide (AR, Aladdin), benzyl bromide (97%, Amethyst), potassium bicarbonate (99%, Sigma-Aldrich), ethanol (HPLC, J&K Chemical), and ethyl acetate (HPLC, J&K Chemical) were used as received. Dichloromethane (DCM, HPLC, J&K Chemical) and acetone (HPLC, J&K Chemical) were purified using the M Braun SPS-800 solvent purification system. 4-Dimethylamino-pyridine-*p*-toluenesulfonate (DPTS) was synthesized according to the literature.<sup>1</sup> The rest of the chemical reagents were commercially available and used without further purification.

### Synthetic Procedures

The synthetic routes of **2Si<sub>7</sub>-COOH** and **3Si<sub>7</sub>-COOH** intermediates are shown in Schemes S1 and S2, respectively. The synthesis of **Si<sub>7</sub>-H** followed the procedure in Meijer's publication.<sup>2</sup>



**Scheme S1.** Synthetic route of **2Si<sub>7</sub>-COOH** intermediates.



**Scheme S2.** Synthetic route of **3Si<sub>7</sub>-COOH** intermediates.

**Synthesis of Benzyl 3,5-Bis(but-3-en-1-yloxy)benzoate.** Benzyl 3,5-dihydroxybenzoate (5.50 g, 22.5 mmol), 4-bromobut-1-ene (12.2 g, 90.1 mmol), and K<sub>2</sub>CO<sub>3</sub> (12.5 g, 90.1 mmol) were dissolved in 100 mL of acetone. Then the reaction mixture was stirred at 80 °C overnight. After acetone was removed under vacuum, the residue dissolved in dichloromethane (DCM, 50 mL) was washed by 30 mL of deionized water for three times. The DCM solution was collected and dried by anhydrous Na<sub>2</sub>SO<sub>4</sub>. And DCM was evaporated under a reduced pressure. The crude product was purified by column chromatography (eluent: petroleum ether (PE)/DCM = 3:1, v:v) on silica gel to afford 3.10 g of benzyl 3,5-bis(but-3-en-1-yloxy)benzoate. Yield: 40.9%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 7.38 (m, 5H), 7.21 (d, 2H), 6.65 (t, 1H), 5.88 (m, 2H), 5.34 (s, 2H), 5.13 (m, 4H), 4.02 (t, 4H), 2.53 (m, 4H).

**Synthesis of 2Si<sub>7</sub>-COOBn.** A Schlenk flask was charged with benzyl 3,5-bis(but-3-en-1-yloxy)benzoate (1.00 g, 2.97 mmol) and Me-Si<sub>7</sub>-H (3.86 g, 7.43 mmol), and then the system was put under a Nitrogen atmosphere. 5 mL of DCM and a drop of Karstedt's

catalyst (1% in xylene) were subsequently added. The reaction solution was stirred at ambient temperature for 12 h. After the reaction was quenched by adding 0.5 mL of methanol, the organic solvent was removed under vacuum. And the crude product was purified using column chromatography (eluent: petroleum ether (PE)/DCM = 5:1, v:v) to afford 2.93 g of 2Si<sub>7</sub>-COOBn. Yield: 71.7%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 7.38 (m, 5H), 7.19 (d, 2H), 6.63 (t, 1H), 5.35 (s, 2H), 3.96 (t, 4H), 1.80 (m, 4H), 1.50 (m, 4H), 0.60 (m, 4H), 0.09 (s, 18H), 0.09–0.07 (m, 48H), 0.05 (d, 24H).

**Synthesis of 2Si<sub>7</sub>-COOH.** A round-bottomed flask was charged with 2Si<sub>7</sub>-COOBn (1.57 g, 1.14 mmol) and Pd/C (Pd content: 10%, 365 mg, 0.343 mmol). Then 2 mL of ethyl acetate (EA) and 6 mL of ethanol were added using a syringe. The reaction solution was bubbled by hydrogen for 30 min and stirred under a hydrogen atmosphere for 3 h. After the Pd/C was filtered off, 1.44 g of 2Si<sub>7</sub>-COOBn was obtained as a colorless oil liquid. Yield: 100%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 7.23 (d, 2H), 6.68 (t, 1H), 3.99 (t, 4H), 1.82 (m, 4H), 1.51 (m, 4H), 0.61 (m, 4H), 0.10–0.07 (m, 66H), 0.05 (d, 24H).

**Synthesis of Methyl 3,4,5-Tris(but-3-en-1-yloxy)benzoate.** Methyl 3,4,5-trihydroxybenzoate (5.00 g, 27.2 mmol), 4-bromobut-1-ene (18.3 g, 136 mmol), and K<sub>2</sub>CO<sub>3</sub> (18.8 g, 136 mmol) were dissolved in 150 mL of acetone. Then the reaction mixture was stirred at 80 °C overnight. After acetone was removed under vacuum, the residue dissolved in dichloromethane (DCM, 50 mL) was washed by 30 mL of deionized water for three times. DCM solution was collected and dried by anhydrous Na<sub>2</sub>SO<sub>4</sub>. And DCM was evaporated under a reduced pressure, the crude product was purified by column chromatography (eluent: petroleum ether (PE)/DCM = 2:3, v:v) on silica gel to afford 2.22 g of methyl 3,4,5-tris(but-3-en-1-yloxy)benzoate. Yield: 23.6%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 7.27 (s, 2H), 5.92 (m, 3H), 5.12 (m, 6H), 4.08 (m, 6H), 3.89 (s, 3H), 2.58 (m, 4H), 2.51 (m, 2H).

**Synthesis of 3,4,5-Tris(but-3-en-1-yloxy)benzoic Acid.** A round-bottomed flask was charged with methyl 3,4,5-tris(but-3-en-1-yloxy)benzoate (2.22 g, 6.41 mmol) and 30 mL of acetone. Then 3 mL of deionized water dissolved with KOH (0.720 g, 12.8 mmol) was added. The reaction solution was stirred at 60 °C overnight. Hydrochloric solution was added to make the pH of the reaction solution be 2. Afterwards, the reaction solution was extracted by 50 mL of DCM for three times. The DCM solution was dried by hydrous Na<sub>2</sub>SO<sub>4</sub>. Then DCM was removed under vacuum to afford 2.13 g of 3,4,5-tris(but-3-en-1-yloxy)benzoic acid. Yield: 100%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 7.34 (s, 2H), 5.92 (m, 3H), 5.13 (m, 6H), 4.10 (t, 6H), 2.59 (m, 4H), 2.52 (m, 2H).

**Synthesis of Benzyl 3,4,5-Tris(but-3-en-1-yloxy)benzoate.** A round-flask was charged with 3,4,5-tris(but-3-en-1-yloxy)benzoic acid (2.13 g, 6.41 mmol), (bromomethyl)benzene (2.19 g, 12.8 mmol), and KHCO<sub>3</sub> (963 mg, 9.62 mmol). Then 30 mL of *N,N*-dimethylformamide (DMF) was added. The reaction solution was stirred at 80 °C overnight. After DMF was evaporated under vacuum, the crude product was purified by column chromatography (eluent: petroleum ether (PE)/DCM = 2:3, v:v) on silica gel to afford 1.76 g of benzyl 3,4,5-tris(but-3-en-1-yloxy)benzoate. Yield: 65.0%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 7.37 (m, 5H), 7.31 (s, 2H), 5.91 (m, 3H), 5.34 (s, 2H), 5.12 (m, 6H), 4.07 (t, 6H), 2.56 (m, 4H), 2.51 (m, 2H).

**Synthesis of 3Si<sub>7</sub>-COOBn.** The synthetic procedure of 3Si<sub>7</sub>-COOBn was similar to that of 2Si<sub>7</sub>-COOBn. Yield: 62.0%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 7.38 (m, 5H), 7.29 (s, 2H), 5.35 (s, 2H), 4.00 (m, 6H), 1.80 (m, 6H), 1.49 (m, 6H), 0.60 (m, 6H), 0.10–0.03 (m, 135H).

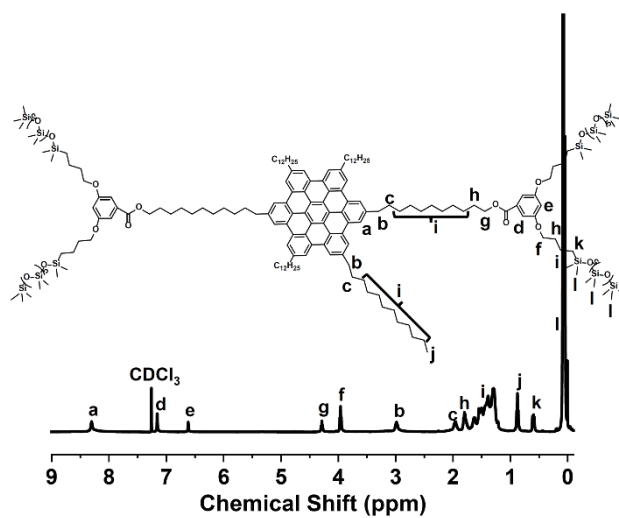
**Synthesis of 3Si<sub>7</sub>-COOH.** The synthetic procedure of 3Si<sub>7</sub>-COOH was similar to that of 2Si<sub>7</sub>-COOH. Yield: 100%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 7.32 (s, 2H), 4.02 (m, 6H), 1.81 (m, 6H), 1.51 (m, 6H), 0.60 (m, 6H), 0.10–0.03 (m, 135H).

## Results

**Table S1.** Thermal transition data of *p*-HBC-4Si<sub>7</sub> and *p*-HBC-6Si<sub>7</sub><sup>a</sup>

| Sample                         | First cooling                          | Second heating                 |
|--------------------------------|--|--------------------------------|
| <i>p</i> -HBC-4Si <sub>7</sub> | I-190(2.6)-Col <sub>h</sub> -34(46.3)- | LamCol <sub>r</sub> -53(41.2)- |
|                                | LamCol <sub>r</sub>                    | Col <sub>h</sub> -212(0.6)-I   |
| <i>p</i> -HBC-6Si <sub>7</sub> | I-202(1.0)-Col <sub>h</sub> -10(33.3)- | LamCol <sub>r</sub> -27(28.0)- |
|                                | LamCol <sub>r</sub>                    | Col <sub>h</sub> -210(1.5)-I   |

<sup>a</sup> Onset phase transition temperatures (°C) with transition enthalpies (kJ mol<sup>-1</sup>, values in parentheses), Col<sub>h</sub> = hexagonal columnar phase, LamCol<sub>r</sub> = lamello-columnar phase with a 2D rectangular structure, I = isotropic.



**Figure S1.** <sup>1</sup>H NMR spectrum of *p*-HBC-4Si<sub>7</sub>.

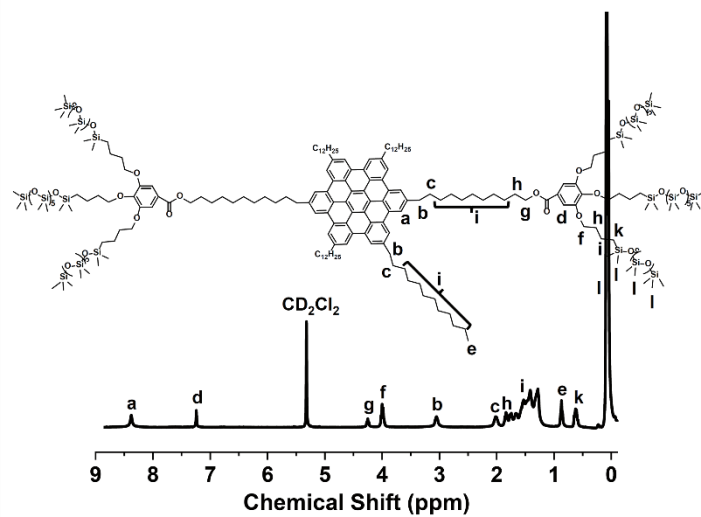


Figure S2. <sup>1</sup>H NMR spectrum of *p*-HBC-6Si<sub>7</sub>.

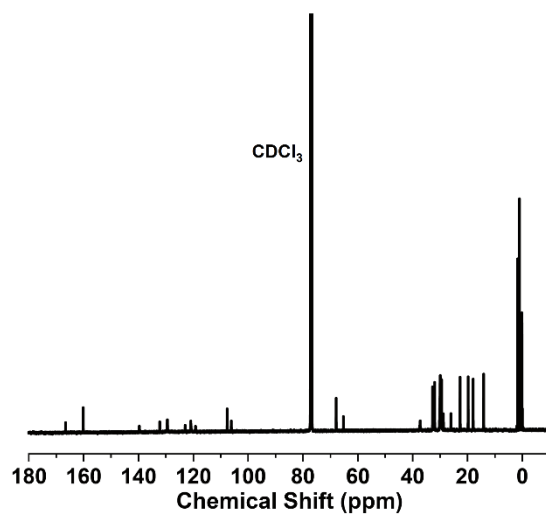


Figure S3. <sup>13</sup>C NMR spectrum of *p*-HBC-4Si<sub>7</sub>.

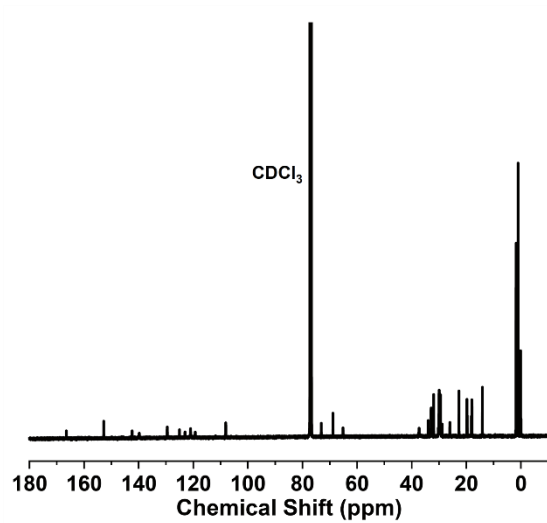


Figure S4.  $^{13}\text{C}$  NMR spectrum of *p*-HBC-6Si<sub>7</sub>.

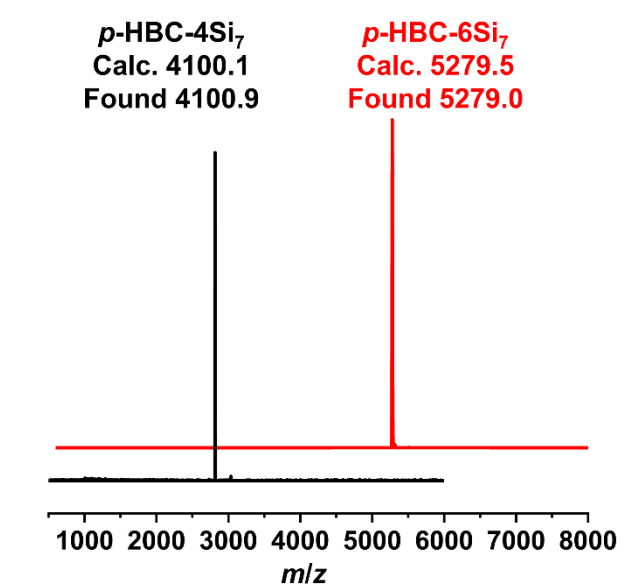


Fig. S5 MALDI-TOF mass spectra of *p*-HBC-4Si<sub>7</sub> and *p*-HBC-6Si<sub>7</sub>.



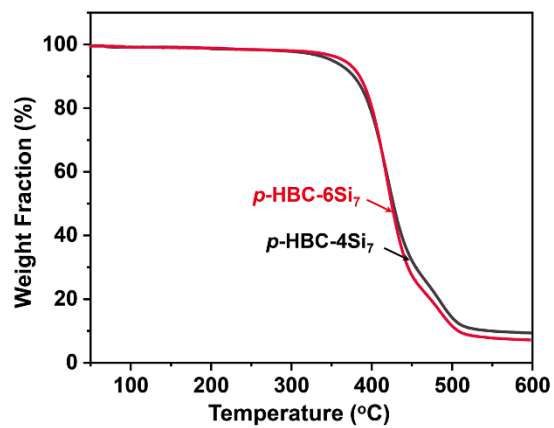


Figure S6. TGA curves of *p*-HBC-4Si<sub>7</sub> and *p*-HBC-6Si<sub>7</sub> at a rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere.

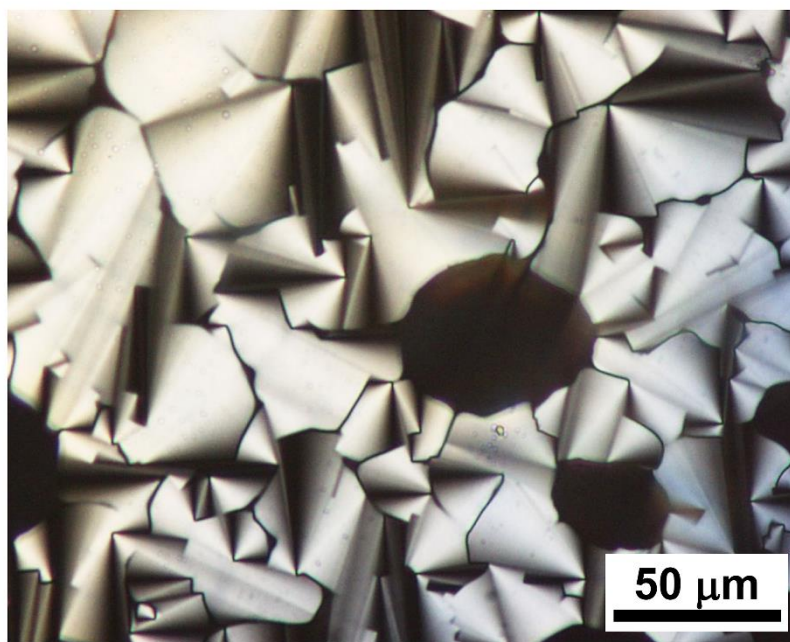


Figure S7. PLM micrographs of *p*-HBC-4Si<sub>7</sub> at ambient temperature under cross polarizers.

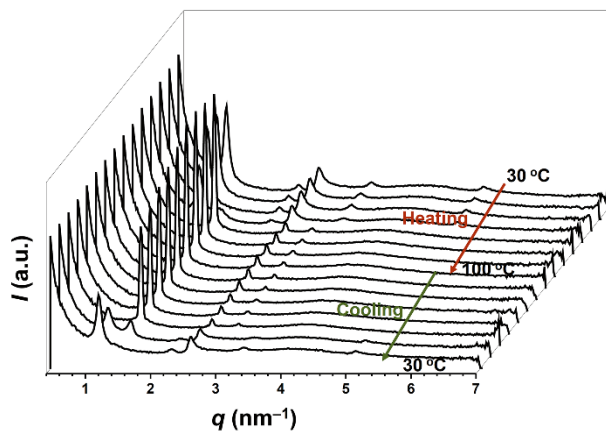


Figure S8. Temperature-dependent WAXS profile of *p*-HBC-4Si<sub>7</sub>.

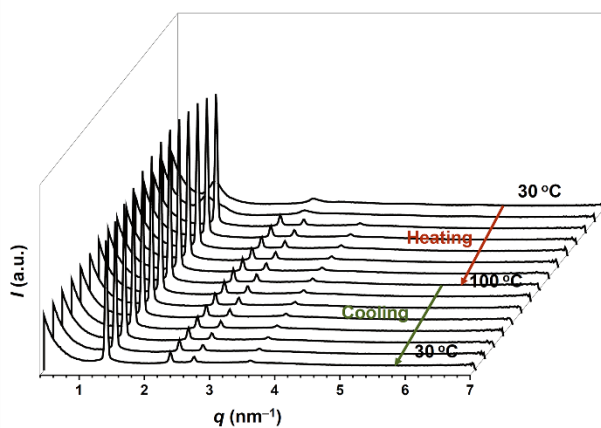


Figure S9. Temperature-dependent WAXS profile of *p*-HBC-6Si<sub>7</sub>.

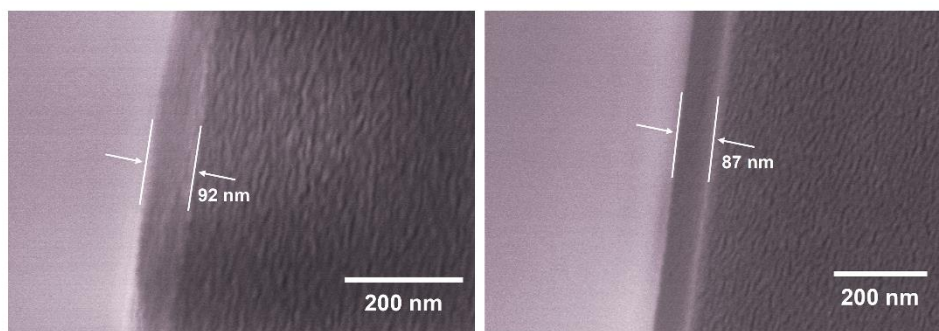
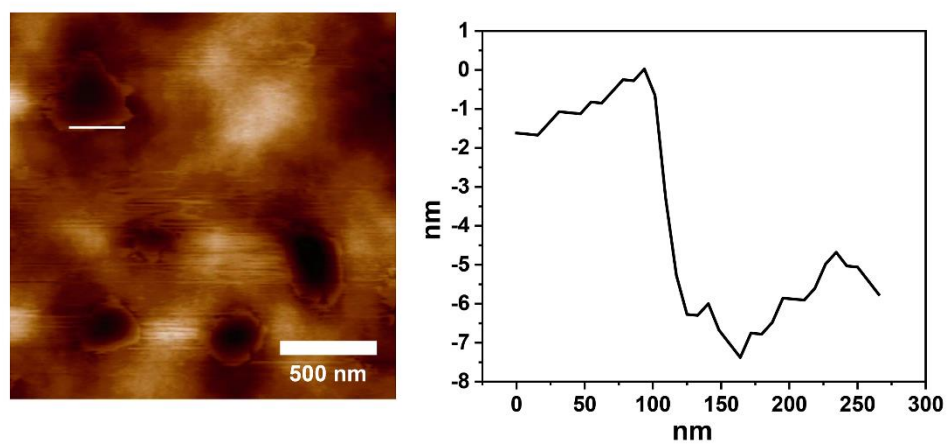
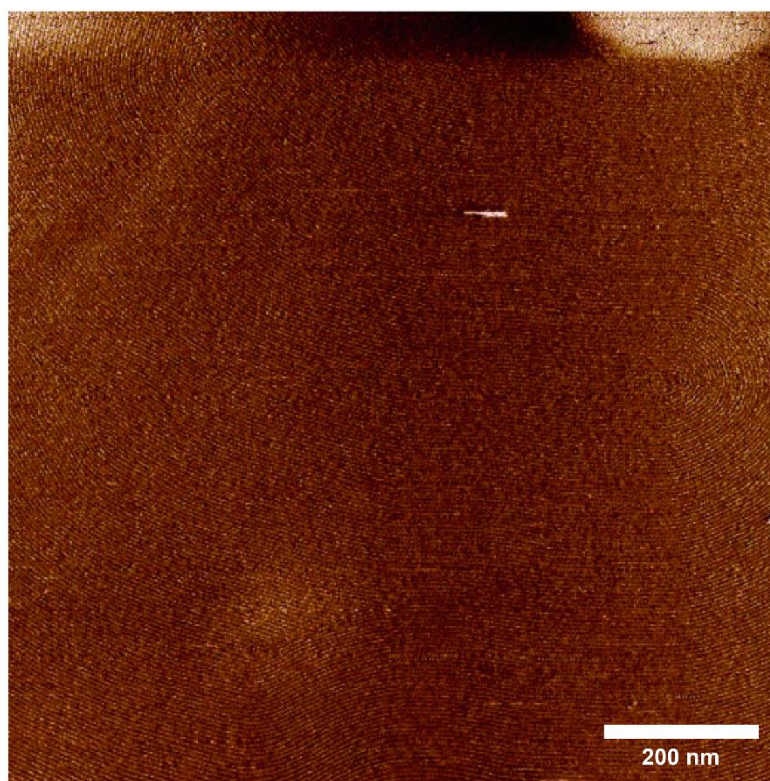


Figure S10. Cross-sectional SEM images of *p*-HBC-4Si<sub>7</sub> (left) and *p*-HBC-6Si<sub>7</sub> (right) thin films.



**Figure S11.** AFM height image (left) and cross-sectional curve (right) of *p*-HBC-4Si<sub>7</sub>.



**Figure S12.** Large-area AFM phase image of *p*-HBC-6Si<sub>7</sub>.

## References:

1. J. S. Moore and S. I. Stupp, *Macromolecules*, 1990, **23**, 65-70.
2. B. van Genabeek, B. F. M. de Waal, M. M. J. Gosens, L. M. Pitet, A. R. A. Palmans and E. W. Meijer, *J. Am. Chem. Soc.*, 2016, **138**, 4210-4218.