

## Supporting information

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### Chiral induction, transfer and modulation in C3-symmetric Columnar Liquid Crystalline Assemblies

Jingang Hu, Tianyi Zhu, Chenlu He, Yan Zhang, Qijin Zhang, Gang Zou\*

CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, iChEM, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China, E-mail: [gangzou@ustc.edu.cn](mailto:gangzou@ustc.edu.cn)

## Experimental Section

### 1 Materials

Monomer 10,12-Pentacosadiynoic acid (PCDA) and Stearic acid (SA) were purchased from Tokyo Chemical Industry Co., Ltd., PCDA was purified to remove the polymerized part before use. Sodium azide (99.5%), 1,3,5-tribromobenzene, CuI (98%), (+)-sodium L-ascorbate, CuSO<sub>4</sub>·5H<sub>2</sub>O were purchased from Sigma-Aldrich Chemical Co. Anhydrous MgSO<sub>4</sub> (min. 99%), anhydrous potassium carbonate (min. 99%), potassium hydroxide (min. 85%) were purchased from Duksan Pure Chemical, Korea. 1-Bromododecane, trimethylsilylacetylene (TMS-acetylene), bis(triphenylphosphine)palladium(II)dichloride were purchased from Tokyo Chemical Industry. Dichloromethane (DCM) was dried over anhydrous magnesium sulfate and filtered before use. Trichloromethane was distilled from calcium hydride. *N,N'*-Dimethylformamide (DMF) was distilled under vacuum, and stored over a type 4 Å molecular sieve. Tetrahydrofuran (THF) was dried by distillation from sodium metal, and stored over a type 4 Å molecular sieve. Triethylamine and pyridine were distilled from calcium hydride, and stored over a type 4 Å molecular sieve. Milli-Q water (18.25 MΩ cm) was used in all cases.

### 2 Synthesis

#### Synthesis of 1-azidododecane

Compounds 1-azidododecane were synthesized as follows. 1-Bromododecane (2.56 g, 10.28 mmol) and sodium azide (2.00 g, 30.82 mmol) were dissolved in 30 mL of anhydrous DMF. The reaction mixture was heated at 100 °C for 24 h under N<sub>2</sub> atmosphere. After cooling down to room temperature, the solvent was removed in a rotary evaporator. Then the mixture was extracted with dichloromethane and deionized water three times, and then dried over anhydrous MgSO<sub>4</sub>. After removing dichloromethane in a rotary evaporator, the final mixture was purified by a silica gel column chromatography using hexane as the eluent, to yield 1.95 g (90.1%) colorless

oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 3.26 (t, *J* = 6.7 Hz, 2H, -CH<sub>2</sub>N<sub>3</sub>), 1.63-1.53 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>), 1.26 (m, 18H, (CH<sub>2</sub>)<sub>9</sub>C<sub>2</sub>H<sub>4</sub>N<sub>3</sub>), 0.88 (t, *J* = 6.6 Hz, 3H, -CH<sub>3</sub>).

#### **Synthesis of 2-Azidoethanol**

In a round-bottom flask, sodium azide (2.99 g, 46 mmol) was dissolved in water (20 mL). 2-Chloroethanol (2.4 mL, 36 mmol) was added and the mixture was then stirred at 80 °C for 24 h. The reaction mixture was cooled down to room temperature, the product was extracted with DCM and saturated brines three times. The organic layer was dried over sodium sulfate and then the solvent was removed in a rotary evaporator to obtain 2-azidoethanol as a colorless oil (1.98 g, 63%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 3.71 (q, *J* = 55.7 Hz, 2H, -CH<sub>2</sub>-OH), 3.37 (t, *J* = 55.0 Hz, 2H, -CH<sub>2</sub>-N<sub>3</sub>), 2.60 (t, *J* = 55.8 Hz, 1H, -CH<sub>2</sub>-OH).

#### **Synthesis of Azidodiacetylene**

DA (374.56 mg, 1 mmol), 2-Azidoethanol (113.21 mg, 1.3 mmol), DCC (247.59 mg, 1.2 mmol), and DMAP (12.2 mg, 0.1 mmol) were dissolved in 30 mL dry DCM. The reaction mixture was stirred at room temperature for 24 h under N<sub>2</sub> atmosphere. After removing the solvent, the residue was extracted with DCM and saturated brines three times, and the organic layer was dried over anhydrous MgSO<sub>4</sub>. The solvent was removed in rotary evaporator, and the crude product was purified by silica gel column chromatography (Hexane: DCM, 1: 1) to yield 0.51 g (46.72%) of a white solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 4.245 (d, *J* = 8.3 Hz, 2H, -CH<sub>2</sub>-O-C), 3.470 (d, *J* = 8.3 Hz, 2H, -CH<sub>2</sub>N<sub>3</sub>), 2.35 (s, 2H, -CH<sub>2</sub>-C=O), 2.236 (q, *J* = 6.5 Hz, 4H, -CH<sub>2</sub>-C≡C-C≡C-CH<sub>2</sub>-), 1.253 (m, 34H, -CH<sub>2</sub>-), 0.877 (m, 3H, -CH<sub>3</sub>).

#### **Synthesis of 1,3,5-triethynylbenzene.**

1,3,5-Tribromobenzene (4.06 g, 12.89 mmol), TMS-acetylene (9.00 mL, 63.5 mmol), copper(I)iodide (0.036 g, 0.18 mmol) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.071 g, 0.101 mmol) were dissolved in 35 mL of dry triethylamine and 10 mL of dry pyridine. The mixture was heated overnight at 55 °C under N<sub>2</sub> atmosphere. After cooled down to room temperature, pyridine and triethylamine were removed by rotary evaporator. The reaction mixture was extracted with dichloromethane and deionized water three times. After removing dichloromethane in rotary evaporator, the resulting compound was purified by a silica gel column chromatography using hexane as the eluent, to yield 4.50 g (96.4%) of a pale yellow solid. The product (2.00 g, 5.46 mmol) was dissolved with potassium carbonate (4.67 g, 83.15 mmol) in 30 mL of THF and 20 mL of methanol. The reaction mixture was stirred for 2 hours under N<sub>2</sub> atmosphere at 50 °C. The solvent was removed by a rotary evaporator. The resulting mixture was extracted with dichloromethane and deionized water three times, and then dried over MgSO<sub>4</sub>. After removing dichloromethane in a rotary evaporator, the resulting compound was purified by a silica gel column chromatography using hexane as the eluent, to yield 0.72 g (87.76%) of a white solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 7.57 (s, 3H, Ar-H), 3.11 (s, 3H, Ar-C≡CH).

#### **Synthesis of TDTB.**

1,3,5-Triethynylbenzene (31.54 mg, 0.21 mmol), 1-azidododecane (277.4 mg, 0.64 mmol), (+)-sodium L-ascorbate (83.2 mg, 0.42 mmol), CuSO<sub>4</sub>·5H<sub>2</sub>O (52.44 mg, 0.21 mmol) were dissolved in 20 mL of THF and 5 mL of deionized water. The reaction mixture was stirred for 12 hours at room temperature. The solvent was removed by a rotary evaporator, and the resulting mixture was extracted with dichloromethane and deionized water three times, and then dried over MgSO<sub>4</sub>. After removing dichloromethane by a rotary evaporator, and the remaining azido compound was removed by a silica gel column chromatography using dichloromethane : ethyl acetate = 1:1 as the eluent, to yield 265.31 mg (85.92%) of a faint yellow solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 8.36 (s, 3H, Ar-H), 8.06 (s, 3H, H-triazole), 4.72 (t, *J* = 7.5 Hz, 6H, -CH<sub>2</sub>-O-C), 4.55 (t, *J* = 7.5 Hz, 6H, triazole-CH<sub>2</sub>-), 2.35 (s, 6H, -CH<sub>2</sub>-C=O), 2.21 (q, *J* = 6.5 Hz, 12H, -CH<sub>2</sub>-C≡C-C≡C-CH<sub>2</sub>-), 1.72-1.15 (m, 102H, -CH<sub>2</sub>-), 0.88 (m, 9H, -CH<sub>3</sub>).

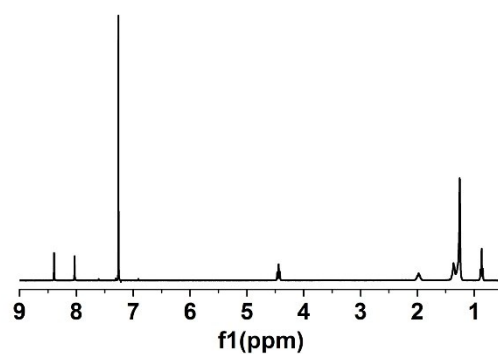
**TATB** were prepared in a similar manner. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 8.39 (s, 3H, Ar-H), 8.03 (s, 3H, H-triazole), 4.44 (t, *J* = 7.5 Hz, 6H, triazole-CH<sub>2</sub>-), 1.98 (m, 6H, triazole-CH<sub>2</sub>CH<sub>2</sub>-), 1.45-1.20 (m, 54H, -CH<sub>2</sub>-), 0.87 (m, 9H, -CH<sub>3</sub>).

### 3 Sample preparation

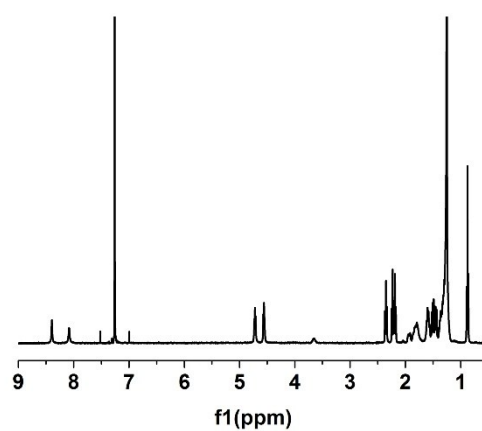
The HB complex sample was firstly dissolved in CHCl<sub>3</sub> with a concentration of 10 mg mL<sup>-1</sup>. Then films of HB complexes were prepared by spin-coating method. Before polymerization, the films were heated to LC phase and maintained for 20 minutes. Then, the samples were irradiated with CPUL (7.3 mW cm<sup>-2</sup>) for 2 minutes. For TEM samples, A few drops of the solution were added to 3 mm copper grids covered with a carbon substrate. The polymerization process is the same as above mentioned methods.

### 4 Characterization

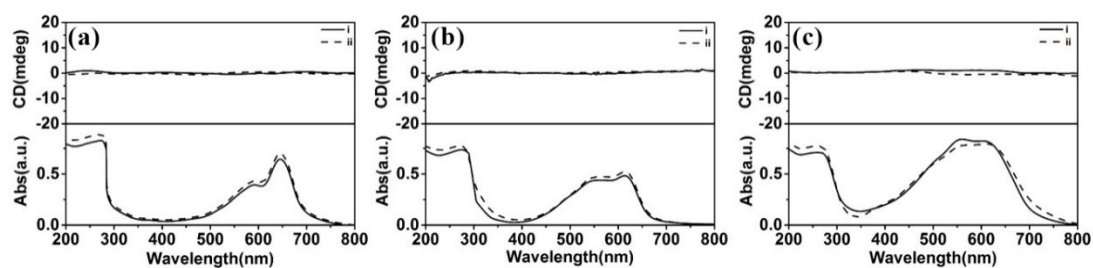
FTIR experiments were performed on a MAGNA 750 FT-IR spectrometer. The ultraviolet-visible (UV-Vis) spectra were recorded using a SHIMADZU UV-2550 PC spectrophotometer, using a 1 mm width quartz plate. <sup>1</sup>H-NMR spectra experiments were carried out with a JEOL FX-90Q NMR 300 spectrometer. A Hamamatsu LC6 Hg/Xe lamp were used as the CPUL irradiation source and the UV irradiation source, respectively. Polarized optical microscopy (POM) images were obtained in an Olympus BX-51 fluorescence microscope equipped a heating stage with an INSTRON mK1000 high precision temperature controller. Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments Q2000DSC at a heating and cooling rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere. XRD measurements were performed with a Rigaku AX-G by using a CuKα (λ=0.154 nm) beam. The circular dichroism (CD) spectra were measured by using JASCO CD spectrometer J-810. Transmission electron microscopy (TEM) images were obtained in a JEOL-2000 microscope (operated at 200kV). AFM measurements were performed with a Bruker Dimension Icon type scanning probe microscope (SPM). TGA experiment were performed under nitrogen atmosphere on a SDT Q600 instrument.



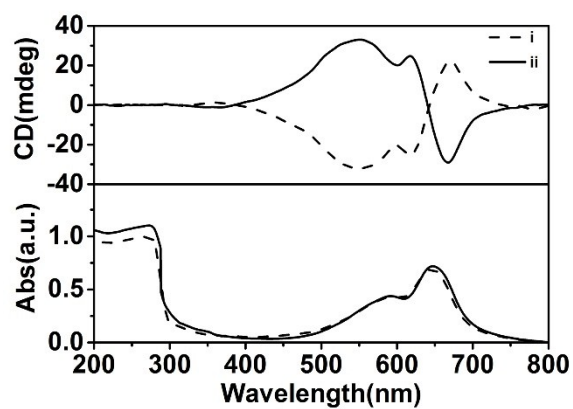
FigureS1:  $^1\text{H}$ -NMR spectra of TATB.



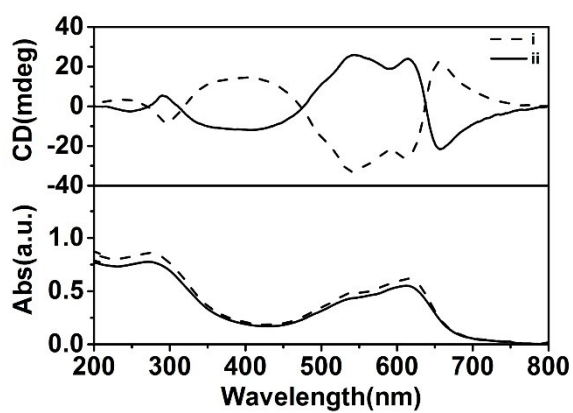
FigureS2:  $^1\text{H}$ -NMR spectra of TDTB.



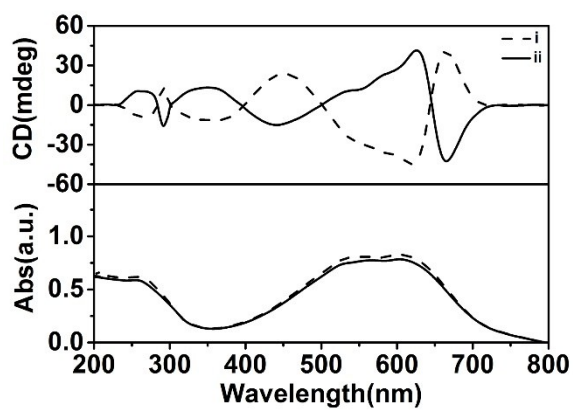
FigureS3: CD and UV spectra of the HB complexes after CPUL irradiation in crystal state (i: R-CPUL, ii: L-CPUL)  
(a) HB1, (b) HB2, (c) HB3.



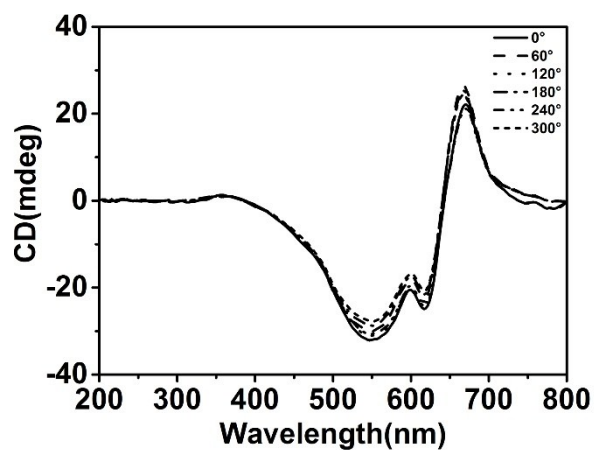
FigureS4: CD and UV spectra of HB1 after CPUL irradiation in liquid crystal phase (i: R-CPUL, ii: L-CPUL).



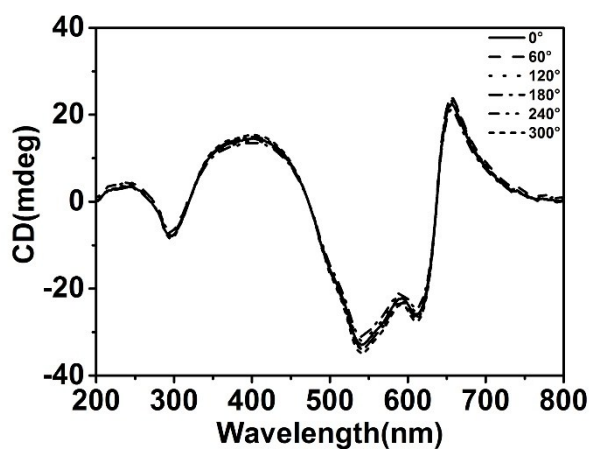
FigureS5: CD and UV spectra of HB2 after CPUL irradiation in liquid crystal phase (i: R-CPUL, ii: L-CPUL).



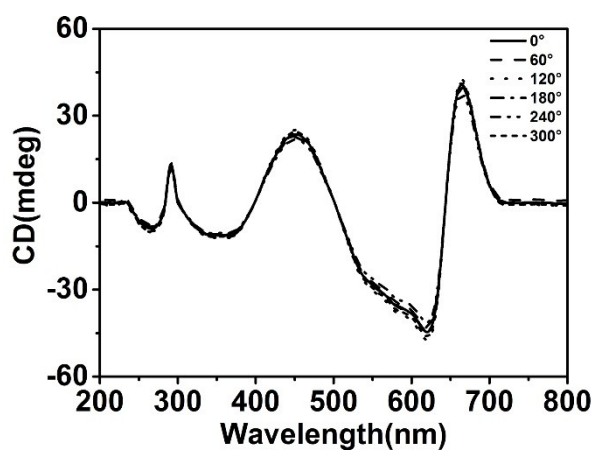
FigureS6: CD and UV spectra of HB3 after CPUL irradiation in liquid crystal phase (i: R-CPUL, ii: L-CPUL).



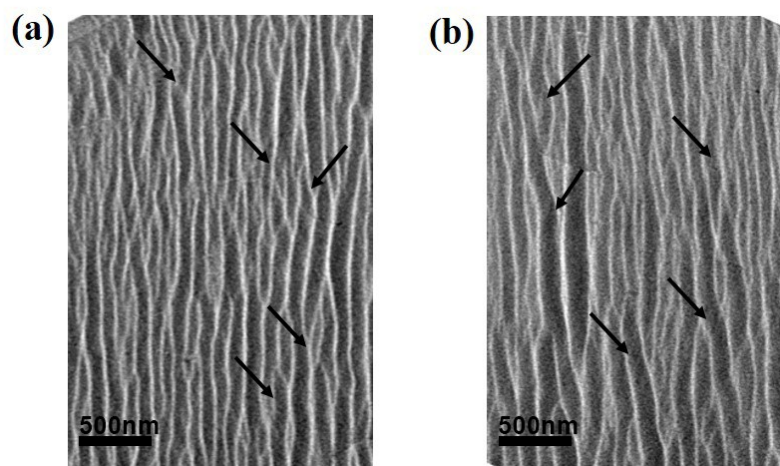
FigureS7: CD spectra of HB1 at various rotation angles about surface normal for the samples polymerized by R-CPUL.



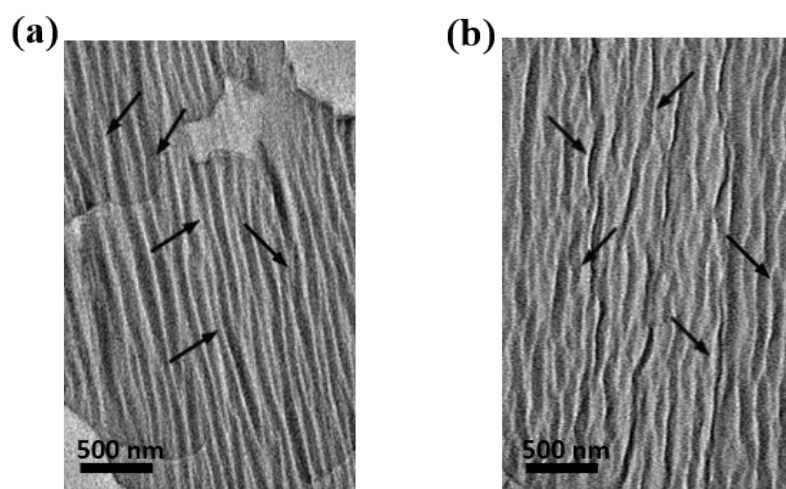
FigureS8: CD spectra of HB2 at various rotation angles about surface normal for the samples polymerized by R-CPUL.



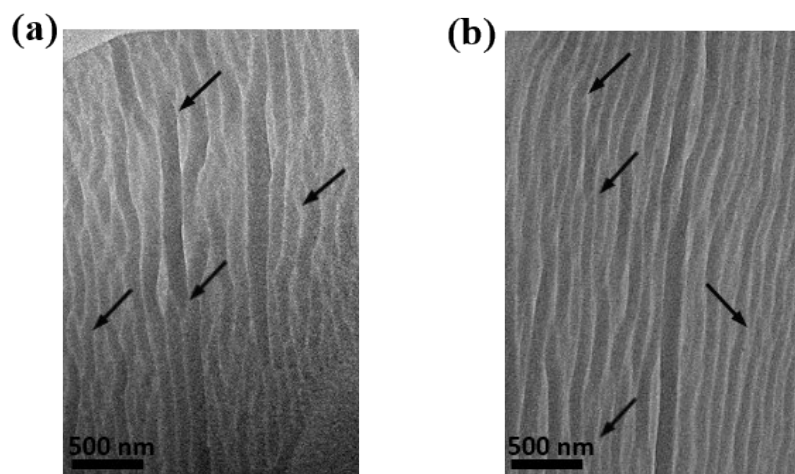
FigureS9: CD spectra of HB3 at various rotation angles about surface normal for the samples polymerized by R-CPUL.



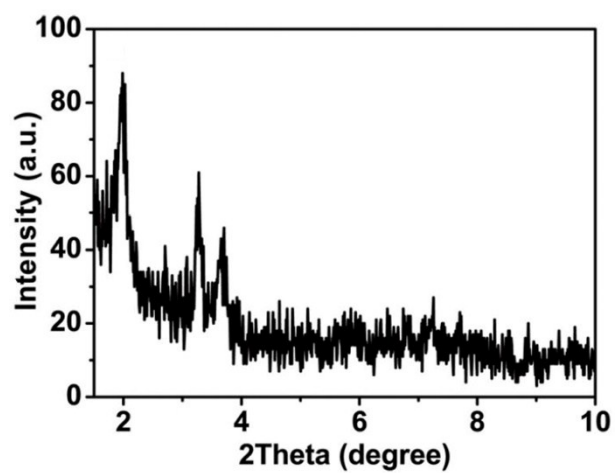
FigureS10: TEM image of HB1 polymerized in liquid crystal phase ( $7.3 \text{ mW} \cdot \text{cm}^{-2}$ ). (a) Left-handed nanofibers by application of L-CPUL irradiation, (b) Right-handed nanofibers by application of R-CPUL irradiation.



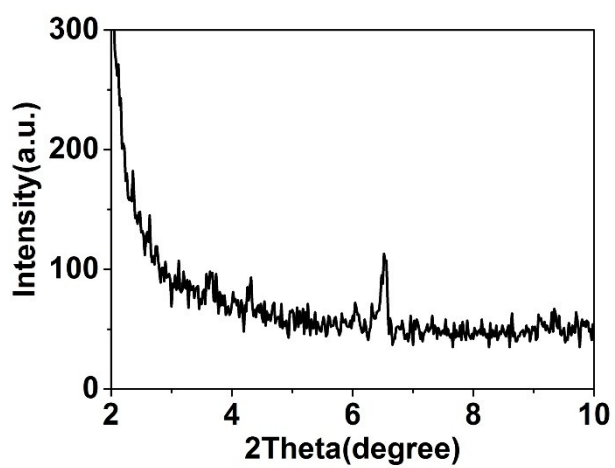
FigureS11: TEM image of HB2 polymerized in liquid crystal phase ( $7.3 \text{ mW} \cdot \text{cm}^{-2}$ ). (a) Left-handed nanofibers by application of L-CPUL irradiation, (b) Right-handed nanofibers by application of R-CPUL irradiation.



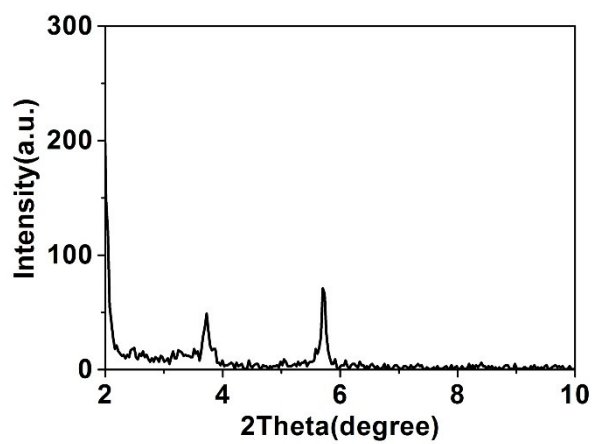
FigureS12: TEM image of HB3 polymerized in liquid crystal phase ( $7.3 \text{ mW} \cdot \text{cm}^{-2}$ ). (a) Left-handed nanofibers by application of L-CPUL irradiation, (b) Right-handed nanofibers by application of R-CPUL irradiation.



FigureS13: Small angle X-ray diffraction profile of HB1 in crystal state before polymerization.

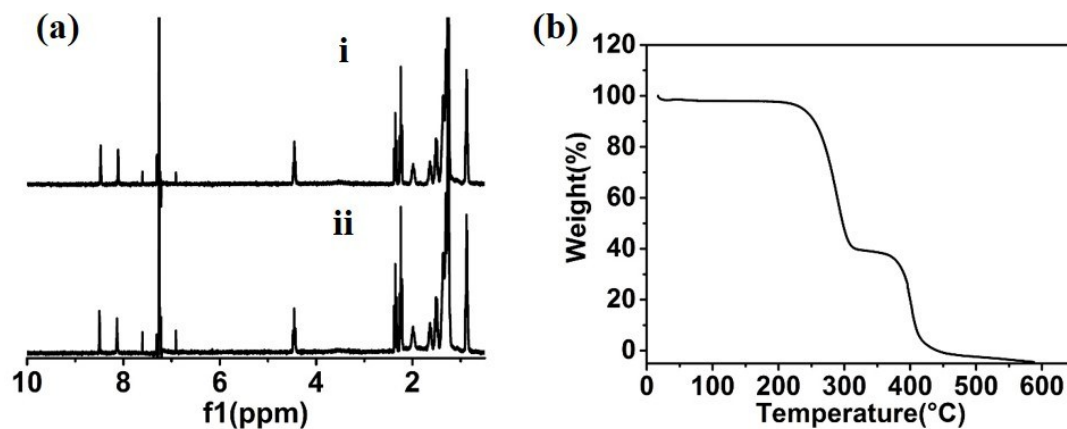


FigureS14: Small angle X-ray diffraction profile of HB2 in crystal state before polymerization.

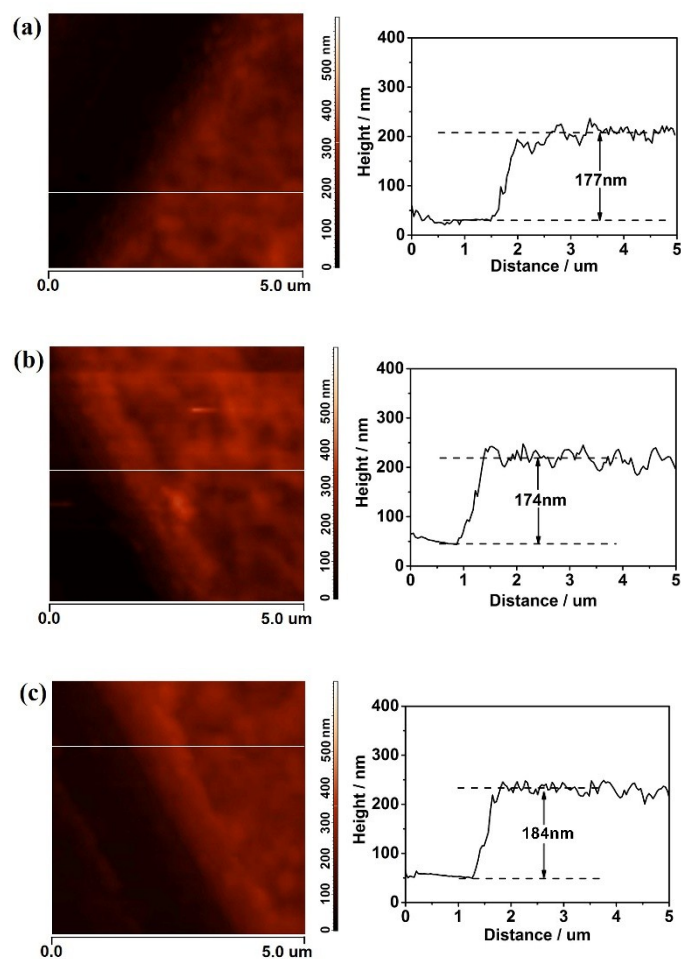


FigureS15: Small angle X-ray diffraction profile of HB3 in crystal state before polymerization.





FigureS16: (a)  $^1\text{H}$ -NMR spectra of HB1 before (i) and after (ii) heating. (b) TGA data of HB1.



FigureS17: AFM images of (a) HB1, (b) HB2 and (c) HB3 after polymerization in liquid crystalline state deposited onto silicon substrate. The step height is obtained by subtracting the lower cursor position from the upper, giving films thickness of 177 nm for HB1 and 174 nm for HB2 and 184 nm for HB3.

