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# **Electronic Supplementary Information for**

### Shape effect-induced spiral superstructure in self-assembled achiral

## disc-bent core amphiphile

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#### **Experimental Section**

**Materials**. Tetrahydrofuran (THF) was purified with the M.Braun SPS-800 solvent purification system. Triethylamine was distilled over  $CaH_2$  prior to use. Aqueous poly(acrylic acid) (PAA) (25 wt% with a molecular weight of 24,000 Da) was purchased from J&K Chemical. All other chemicals were commercially available and were used as received.

Instruments. NMR spectra were obtained on a Bruker-400 (400 MHz) spectrometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a Bruker Autoflex III MALDI-TOF spectrometer. Elemental analysis (EA) was performed on a Vario EL element analyzer. Differential scanning calorimetry (DSC) examination was carried out on a TA DSC Q100 calorimeter under nitrogen. Small-angle X-ray scattering (SAXS) experiments were performed on a in-house X-ray scattering instrument (SAXSess mc2, Anton Paar, Cu-K<sub>a</sub>,  $\lambda = 0.154$  nm). SAXS measurements were also performed in the transmission mode with synchrotron radiation at Beamline BL16B1 of Shanghai Synchrotron Radiation Facility (SSRF) and at beamline 1W2A at Beijing Synchrotron Radiation Facility (BSRF) ( $\lambda = 0.124 \text{ nm}$ ).<sup>1</sup> AFM experiments are performed on a Bruker Dimension Icon atomic force microscopy. Thin sections of samples were sliced on a Leica EM UC6 ultramicrotome and observed on a JEM 2100 transmission electron microscope (TEM) with an accelerating voltage of 200 kV. Circular dichroism (CD) spectra of the thin film on carbon-coated quartz were performed on a JASCO J-810 spectrometer at 25 °C. UV-vis experiment was carried out on a Lambda 35 UV-vis spectrometer (Perkin Elmer).

**Reconstruction of Electron Density Map.** The electron density map was reconstructed based on the equation for two-dimensionally ordered structures:

$$\rho(xy) = \sum_{kk} F(hl) \exp[2\pi i(hx + ly)]$$
$$= \sum_{kk} \sqrt{I(hl)} \exp[2\pi i(hx + ly) + i\phi(hl)]$$

where *I* is the intensity of the (*hl*) reflection and  $\Phi(hl)$  is the phase of the (*hl*) reflection. The set of phases of signals is not the only possible, but it is the most reasonable one. The electron density maps were picked out by considering the number of molecules in a unit cell and the

distribution of the electron density.

**Molecular Dynamics Simulation**. Molecular dynamics simulation was performed on Materials Studio (Accelrys Inc.) using the Forcyte Module. The snapshots were obtained after 30 temperature cycles of constant volume dynamics between 300 and 700 K. Three dimensional periodic boundary conditions equal the calculated unit cell parameters *a*, *b*, *c*, and  $\gamma$ <sup>2,3</sup>.

#### Sample preparation

To prepare the spiral superstructures, a 0.5 wt% toluene solution of HBC-BC was spin-coated on highly oriented pyrolytic graphite (HOPG), giving a uniform thin film. The film was then thermally treated according to the DSC result (Figure S1) to induce the formation of the spiral superstructures.<sup>4, 5</sup> There are two endothermic peaks in the DSC heating trace and two exothermic peaks in the cooling trace. Based on the temperature-dependent SAXS results, the isotropization of the mesophase occurs at 121.5 °C (18.9 kJ/mol) during the cooling process. The transition between the mesophase and the crystalline phase occurs at 109.3 °C (80.9 kJ/mol). It was first heated to the isotropic state at 155 °C and subsequently quenched to 115 °C. After being isothermally annealed for different periods of time, the film was cooled down slowly to ambient temperature and imaged by AFM directly. Platinum (Pt) was shadowed on the sample for TEM observation.<sup>4</sup> Then one drop of aqueous poly(acrylic acid) (PAA, 25 wt%) was cast on the Pt-shadowed sample and dried in air overnight. The solidified PAA layer was carefully peeled off by tweezers and placed on water with the PAA side down to dissolve the PAA layer. The Pt-shadowed thin film was picked up by grids for TEM observation. For UV-vis and CD spectra, the thin layer of carbon was coated on quartz. The broad absorption peak from 200 to 300 nm in the UV-vis spectrum is attributed to the  $\pi$ - $\pi$ \* transition of the phenyl chromophores of the BC segment<sup>6</sup> whereas the absorption peaks centered at 360 and 410 nm are the  $\beta$  band and p band of HBC (Figure S3a), respectively.<sup>7</sup> The sample was thermally treated with the same procedure as that for the sample on HOPG. A self-assembled structure similar to that on highly oriented pyrolytic graphite (HOPG) was observed by AFM (Figure S2).

### Synthesis of HBC-BC

The **HBC-BC** dyad was synthesized according to Scheme S1 following the reported procedures. Steglich esterification was then used to link the two intermediates to give the disc-bent core amphiphile **HBC-BC**. **HBC-C4OH** and **V5-COOH** were synthesized following the synthesis of the V-shaped molecule according to our previous work and the reported procedure.<sup>8,9</sup> The detailed synthetic route of the hydroxyl HBC has been described previously.<sup>2, 10, 11</sup> NMR, MALDI-TOF MS, and EA experiments were performed to confirm the chemical structure.





**HBC-C4OH**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm) 8.40 – 8.05 (m, 12H), 3.83 (t, *J* = 6.4 Hz, 2H), 2.92 (s, 12H), 2.06 – 1.17 (m, 104H), 0.88 (t, *J* = 6.7 Hz, 15H). MS (MALDI-TOF, CCA):  $m/z = 1435.4 \text{ [M]}^+$  (calc. 1435.1).

**V5-COOH**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm) 8.29 (d, J = 8.7 Hz, 4H), 8.16 (d, J = 8.8 Hz, 4H), 7.93 (d, J = 2.1 Hz, 2H), 7.51 (t, J = 2.1 Hz, 1H), 7.40 (d, J = 8.7 Hz, 4H), 6.99 (d, J = 8.8 Hz, 4H), 4.06 (t, J = 6.5 Hz, 4H), 1.89 – 1.77 (m, 4H), 1.54 – 1.41 (m, 4H), 1.40 – 1.20 (m, 32H), 0.89 (t, J = 6.7 Hz, 6H). MS (MALDI-TOF, CAA): m/z = 993.4 [M+Na]<sup>+</sup> (calc. 993.5).

A mixture of HBC-C4OH (100 mg, 70.0 µmol), V5-VOOH (202 mg, 0.209 mmol), and

4-dimethylaminopyridine (0.86 mg, 7.0  $\mu$ mol) were dissolved in 20 mL of dry CH<sub>2</sub>Cl<sub>2</sub> under nitrogen. Then 0.1 mL of *N*,*N*-diisopropylcarbodiimide was added dropwise via a syringe. The mixture solution was stirred at ambient temperature for 24 h. After the solvent was removed under a reduced pressure, the crude product was purified by silica gel column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/THF to afford **HBC-BC** (72 mg, 0.030 mmol) in a yield of 60% as a yellow solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm) 8.41 – 8.25 (m, 12H), 8.05 (d, J = 8.6 Hz, 4H), 7.93–7.90 (m, 6H), 7.35 (t, J = 2.1 Hz, 1H), 7.09 (d, J = 8.6 Hz, 4H), 6.84 (d, J = 8.9 Hz, 4H), 4.58 (t, J = 6.1 Hz, 2H), 3.98 (t, J = 6.5 Hz, 4H), 3.09 (b, 2H), 2.99 (t, J = 7.6 Hz, 10H), 2.13–1.18 (m, 144H), 0.96–0.80 (m, 21H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm):  $\delta$ 165.00, 164.00, 163.70, 163.65, 155.36, 151.28, 139.54, 139.41, 132.68, 132.24, 131.63, 129.45, 129.28, 129.18, 125.92, 122.98, 122.79, 121.86, 120.79, 120.69, 120.49, 119.05, 114.24, 68.31, 65.67, 37.28, 32.55, 32.00, 31.94, 30.27, 30.25, 30.05, 30.03, 29.98, 29.90, 29.82, 29.68, 29.66, 29.62, 29.58, 29.47, 29.39, 29.37, 29.11, 28.99, 26.00, 22.73, 22.70, 14.14. MS (MALDI-TOF, CCA): m/z = 2387.59 [M]<sup>+</sup> (calc. 2387.61). EA: Calcd. for C<sub>165</sub>H<sub>214</sub>O<sub>12</sub>: C, 82.94; H, 9.03; O, 8.03. Found: C, 82.74; H, 8.94.

**Table S1**. Indices, experimental and calculated *d*-spacings, intensities, and phases used in electron density reconstruction for the (*hkl*) reflections of the crystalline phase of **HBC-BC** at 25  $^{\circ}$ C.

( <i>hkl</i> ) –	$q ({\rm nm}^{-1})$		d-spacing (nm)		- Intonsity	Dhaga
	Exptl.	Calc.	Exptl.	Calc.	- Intensity	1 1188
(100)	1.51	1.51	4.16	4.15	73	0
(001)	1.93	1.93	3.26	3.26	100	π
$(10\overline{1})$	2.17	2.17	2.90	2.90	51.5	π
(101)	2.70	2.71	2.33	2.32	47	0
(201)	3.20	3.20	1.96	1.96	31	π
$(10\overline{2})/(002)$	3.80	3.81/3.86	1.66	1.65/1.63	11.6	π
(301)/(300)	4.55	4.52/4.54	1.38	1.38/1.39		
(202)	5.40	5.41	1.16	1.16		
(003)	5.78	5.79	1.09	1.08		
(103)	6.30	6.30	1.00	1.00		
(203)	7.13	7.11	0.88	0.88		
(104)/(501)	8.20	8.19/8.22	0.77	0.77/0.76		
$(60\overline{2})/(600)$	9.02	9.03/9.08	0.70	0.70/0.69		
(304)	9.72	9.61	0.65	0.65		
(700)(503)	10.4	10.6/10.5	0.6	0.59/0.6		
(010)/(011)	12.88	12.75/12.90	0.49	0.49		
(012)/(310)	13.76	13.33/13.54	0.46	0.47/0.46		
(013)/(410)	14.18	14.01/14.12	0.44	0.45/0.44		
(014)/(510)	14.77	14.91/14.83	0.42	0.42		
(610)	15.43	15.66	0.41	0.40		
(710)	16.47	16.58	0.38	0.38		
(810)	17.68	17.59	0.36	0.36		
(017)	18.77	18.57	0.34	0.34		



Figure S1. First-cooling and second-heating DSC traces of **HBC-BC** at a rate of 10  $^{\circ}$ C/min under nitrogen. Transition temperatures ( $^{\circ}$ C), enthalpic changes in parentheses (kJ/mol), and phases are indicated. Cr = crystalline phase, Iso = isotropic phase.



Figure S2. AFM amplitude error image of spiral aggregates on carbon-coated quartz.



Figure S3. TEM micrographs of Pt-shadowed left-handed (a) and right-handed (b) spiral superstructures.



Figure S4. UV-vis (a) and CD (b) spectra of the thin film of **HBC-BC** on carbon-coated quartz.



Figure S5. Reconstructed electron density map of the bulk sample at 25  $^{\circ}$ C



Figure S6. Simulated (red) and experimental (black) SAXS profiles of HBC-BC.



Figure S7. TEM micrograph of the spiral crystal (a) and the corresponding SAED pattern (b).

### References

- 1. Z. Li, Z. Wu, G. Mo, X. Xing and P. Li, Instrum Sci. Technol. , 2014, 42, 128-141.
- 2. E. M. Sánchez-Carnerero, A. R. Agarrabeitia, F. Moreno, B. L. Maroto, G. Muller, M. J. Ortiz and S. de la Moya, *Chem. Eur. J.*, 2015, **21**, 13488-13500.
- M. Prehm, F. Liu, U. Baumeister, X. B. Zeng, G. Ungar and C. Tschierske, *Angew. Chem. Int. Ed.*, 2007, 46, 7972-7975.
- 4. C. Y. Li, D. H. Yan, S. Z. D. Cheng, F. Bai, T. B. He, L. C. Chien, F. W. Harris and B. Lotz, *Macromolecules*, 1999, **32**, 524-527.
- C. Y. Li, S. Z. D. Cheng, X. Weng, J. J. Ge, F. Bai, J. Z. Zhang, B. H. Calhoun, F. W. Harris, L. C. Chien and B. Lotz, *J. Am. Chem. Soc.*, 2001, **123**, 2462-2463.
- 6. S.-C. Lin, R.-M. Ho, C.-Y. Chang and C.-S. Hsu, *Chem. Eur. J.*, 2012, 18, 9091-9098.
- X. Feng, W. Pisula, T. Kudernac, D. Wu, L. Zhi, S. De Feyter and K. Müllen, J. Am. Chem. Soc., 2009, 131, 4439-4448.
- X. F. Chen, K. K. Tenneti, C. Y. Li, Y. W. Bai, R. Zhou, X. H. Wan, X. H. Fan and Q. F. Zhou, *Macromolecules*, 2006, **39**, 517-527.
- 9. J. Barbera, L. Puig, P. Romero, J. L. Serrano and T. Sierra, J. Am. Chem. Soc., 2006, **128**, 4487-4492.
- 10. 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.
- 11. M. Y. Zhang, K. H. Gu, Y. Zhou, S. Zhou, X. H. Fan and Z. Shen, *Chem. Commun.*, 2016, **52**, 3923-3926.