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Supporting information

Deciphering Helix Assembly in the Heliconical Nematic Phase *via* Tender Resonant X-ray Scattering

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Material Synthesis



Scheme S1. Reagents and conditions of compound FBTBT synthesis. (i) NaSH, NMP, 180 °C, 12h; (ii) C₁₁H₂₃COCl, AlCl₃, -36 °C, 2h; (iii) KOH, NH₂-NH₂, 220 °C, 28h; (iv) Br₂, CH₂Cl₂, rt, 2h; (v) C₆F₅B(OH)₂, Pd(PPh₃)₄, P(t-Bu)₃, CsF, Ag₂O, DMF, 100 °C, 12h.

(1) Benzothieno[3,2-b]benzothiophene (BTBT)

To a 100 mL flask, 2-chlorobenzaldehyde (5 g, 35.6 mmol), N-methyl-2-pyrrolidone (NMP, 15 mL), sodium hydrosulfide hydrate (NaSH, 8 g, 0.11 mol) were added and heated at 80°C for 1 h; then heated at 180°C for 12 h with stirring. After the reaction was finished, which was monitored by thin-layer chromatography (TLC), the reaction mixture was poured into saturated aqueous NH4Cl solution. The deposit was collected by filtration and washed by ethanol. Recrystallization from toluene resulted in a yellow crystals BTBT (1.92g, 45%).

¹H NMR (CDCl₃, TMS, 400 MHz) δ: 7.86–7.92 (m, 4H, 4ArH), 7.37–7.47 (m, 4H, 4ArH).

(2) 2-Dodecanoyl-BTBT

In a 250 mL flask, BTBT (2 g, 8.32 mmol) and dichloromethane (200 mL) were added and protected under argon, and was cooled to -17° C. Then AlCl₃ (3 g, 22.5 mmol) was added and cooled to -36° C. Dodecanoyl chloride (2 g, 9.14 mmol) was added slowly and stirred at -36° C for 2 h, then room temperature for 1 h. After reaction was finished, cold water and methanol were added. The extraction by dichloromethane was further purified by column chromatography (Silica, petroleum/dichloromethane/toluene, 3:1:1, v). It was recrystallized from toluene to give white crystals 2-dodecanoyl-BTBT (3 g, 85%).

¹H NMR (CDCl₃, TMS, 400 MHz) δ: 8.31(d, J = 6.8 Hz, 1H, ArH), 7.92 (s, 1H, ArH), 7.52 (d, J = 7.2 Hz, 1H, ArH), 7.44–7.47 (m, 2H, ArH), 2.58 (d, J = 7.2 Hz, 2H, CH₂), 1.76 (t, J = 6.8 Hz, 2H, CH₂), 1.28 (s, 16H, CH₂), 0.89 (t, J = 6.8 Hz, 3H, CH₃).

(3) BTBT-C12

To a 100 mL flask, 2-dodecanoyl-BTBT (200 mg, 0.47 mmol), KOH (139.4 mg, 2.48 mmol), 2ethoxyethanol (20 mL), and hydrazine hydrate (80%, 0.7 mL) were added and heated at 120°C for 1 h, and heated at 220°C for 28 h. The reaction was monitored by TLC. Cooling the mixture resulted in solid crystals, and recrystallization from toluene yielded white solid 2-dodecyl-BTBT (189.5 mg, 98%).

¹H NMR (CDCl₃, TMS, 400 MHz) δ: 7.90 (d, J = 8.0 Hz, 1H, ArH), 7.87 (d, J = 8.0 Hz, 1H, ArH), 7.79 (d, J = 8.4 Hz, 1H, ArH), 7.72 (s, 1H, ArH), 7.45 (t, J = 7.2 Hz, 1H, ArH), 7.38 (t, J = 7.2 Hz, 1H, ArH), 7.29 (d, J = 8.0 Hz, 1H, ArH), 2.76 (t, J = 8.0 Hz, 2H, CH₂), 1.61–1.78 (m, 2H, CH₂), 1.26–1.33 (m, 18H, CH₂), 0.88 (t, J = 7.2 Hz, 3H, CH₃).

(4) 7-Bromo-BTBT-C12

To a 50 mL flask was added 2-dodecyl-BTBT (800 mg, 1.96 mmol) and dichloromethane (16 mL). The solution of Br₂ (313.6 mg) in CH₂Cl₂ (5mL) was added and stirred at room temperature for 3 h. The reaction was monitored by thin-layer chromatography. The solid was filtered out and recrystallized from toluene and yielded a white solid, 7-bromo-2-dodecyl-BTBT (181.3 mg, 76%). ¹H NMR (CDCl₃, TMS, 400 MHz) δ : 8.04 (s, 1H, ArH), 7.78 (d, J = 8.0 Hz, 1H, ArH), 7.71 (t, J = 6.0 Hz, 2H, ArH), 7.53–7.56 (m, 1H, ArH), 7.28 (d, J = 8.4 Hz, 1H, ArH), 2.76 (t, J = 7.6 Hz, 2H, CH₂), 1.65–1.73 (m, 2H, CH₂), 1.25–1.34 (m, 18H, CH₂), 0.88 (t, J = 6.4 Hz, 3H, CH₃).

(5) FBTBT

To an argon protected 25 mL reaction tube, 7-bromo-2-dodecyl-BTBT (147 mg, 0.3 mmol), $C_6F_5B(OH)_2$ (70mg, 0.33mmol), CsF (91.2 mg, 0.6 mmol), Ag₂O (45 mg, 0.36 mmol), and Pd(PPh₃)₄ (41.2 mg, 0.036 mmol) were added. Then the solution of P(t-Bu)₃ (9.1 mg, 0.045 mmol) in DMF (3 mL) was injected, and stirred at 100 °C for 12 h. Silica gel TLC was used to monitor the reaction (eluted by petroleum ether: $CH_2Cl_2 = 2: 1, v$). It was cooled, the solid deposit collected, washed by water (5 mL x 2) and CH_2Cl_2 (5 mL x 2), purified by silica gel column chromatography with elution of toluene and recrystallization in toluene-petroleum ether to get the target molecule (88.1mg, 51%).

¹H NMR (CDCl₃, TMS, 400MHz) δ: 7.97 (d, J = 8.0 Hz, 2H, ArH), 7.83 (d, J = 8.0 Hz, 1H, ArH), 7.74 (s, 1H, ArH), 7.43-7.50 (m, 1, ArH), 7.24-7.32 (m, 1H, ArH), 2.71 (t, J = 7.6 Hz, 2H, CH₂), 1.69-1.83 (m, 2H, CH₂), 1.26-1.35 (m, 18H, CH₂), 0.88 (t, J = 7.2 Hz, 3H, CH₃). HRMS (m/z) Calcd. for C₃₂H₃₁F₅S₂: 574.18; Found: 574.1785.



Figure S1. Energy scan of the N_{TB} phase in asymmetric dimers (a) CBSC5OCB and (b) CBSC7OCB. All N_{TB} peaks show strong energy dependence near S K-edge. Red thick lines correspond to the scattering at E = 2741 eV, slightly below S K edge.



Figure S2. (a) SAXS diffractogram of CBSC7OCB at crystal phase. To avoid resonant effect, the beam energy was tuned to 3keV. The two scattering peaks are in a ratio of 1:2 indicating a smectic-like phase; (b) TReXS energy scan of crystal phase of CBSC7OCB at room temperature. The resonant signal represents double-layer distance which exhibits a feature of anticlinic packing; (c) TReXS energy scan of crystal phase of FBTBT at room temperature. Low and high angle regions were shown separately so that distinct features can be observed clearly. Peaks at low angle region were visible even far away from the S K-edge with significant intensity dip as partially resonant SmA peak. The peak at q = 3.25 nm⁻¹ is visible only in the vicinity of S K-edge and considered as pure resonant peak. The peak at q = 2.17 nm⁻¹ exhibited combined features of both partially resonant and pure resonant peaks. Red thick lines correspond to the scattering at E = 2741eV, slightly below S K edge.



Figure S3. (a) The integrated intensity of three non-resonant peaks and the measured absorption spectra *vs* X-ray energy. The non-resonant peaks and absorption spectra exhibit similar trends; (b) Plot comparing the integrated intensities of partially resonant peak (blue), pure resonant peak (purple) and resonant enhanced peak (orange). Note that for the pure resonant peak (purple), the intensity is set to be zero before 2464eV and after 2474eV because it was nearly visible experimentally.



Figure S4. Real (*f*') and imaginary (*f*'') part of dispersion correction of sulfur atom from theoretical approximation developed by Cromer and Liberman^{S1, S2}.



Figure S5. (a) SmA phase of FBTBT, 8CB and amorphous Si₃N₄ (reference). Absorption at S K edge (2472 eV) is prominent and the presence of another dip at 2481 eV is likely to be arising from beamline optics, i.e. the crystal glitches as reported by Gerrit Van Der Laan and Bernard T. Thole^{S3}; (b) N_{TB} phase of CBSC7SCB, CBSC7OCB, CBSC5OCB and amorphous Si₃N₄ (reference); (c) Absorption spectra of SmA and crystalline phases of FBTBT. The spectra are different for different phases indicating that absorption spectral can reflect structural information; (d) Absorption spectra of CBSC7SCB at different temperatures exhibiting N_{TB}, N and isotropic phases. Significant differences on absorption effect can be observed.

Sample name	CBSC7SCB	CBSC7OCB	CBSC5OCB	FBTBT	8CB
Film thickness /µm	95.7	41.4	49.6	27.4	23.5

Table S1. Liquid crystal sample thickness calculated from absorption spectroscopy

Liquid crystal samples were sandwiched between two pieces of Si₃N₄ membranes (Norcada) and the absorption spectroscopy data were collected in transmission mode with a pin diode. To compute absorption coefficient, the film thickness is needed to acquire attenuation length μ from Beer-Lambert Law $I(x) = I_0 e^{-\mu x}$, where I_0 is the incoming X-ray intensity before the sample, μ is attenuation length and x is sample thickness. In our case, we assumed that the attenuation length at 2455eV (before S K-edge) is close to that from the Center for X-ray Optics, which is based on Henke atomic scattering factors database^{S2}. The calculated sample thicknesses are listed in Table S1. The absorption coefficient (Fig. S7) and dispersion correction (Fig. S8) as a function of X-ray energy were then computed and plotted.



Figure S6. Imaginary part of dispersion correction f'' vs X-ray energy computed from experimental absorption spectra and Henke atomic scattering factors database for (a) CBSC5OCB, (b) CBSC7SCB and (c) 8CB. The minor fluctuation around 2481 eV is visible even in empty samples, and is attributed to the background from beamline optics.



Figure S7. Real part of dispersion correction f' vs X-ray energy calculated from f'' by Kramers-Kronig relation^{S4}.



Figure S8. Integrated intensity of N_{TB} peaks and computed scattering contrast $(f'^2+f''^2)$ vs X-ray energy of different dimers (a) CBSC7SCB and (b) CBSC5OCB. Both the plots suggest that the experimental peak intensity as a function of X-ray energy followed the same trend as the computed scattering contrast, which is essentially determined by the complex molecular scattering factor. This emphasizes the fact that N_{TB} peak is purely resonant.



Figure S9. 2D CCD images of three dimers 1 to 2 °C below $T_{\text{N-NTB}}$. All resonant signals are sharp without splitting, indicating well-probed orientation order.



Figure S10. (a) Helical pitch *p*, (b) correlation length λ and (c) helical stacks calculated from TReXS temperature scan at 2471 eV. Correlation length λ is calculated by $\lambda = 2\pi$ /FWHM while number for the helical stacks is obtained by λ/p .



Figure S11. Energy dependence of (a) rotation angle ϕ , (b) reduced bond angle θ and (c) dihedral angle ω from DFT calculation. Both rotation and dihedral angles appear distinct energy dependence for symmetric and asymmetric dimers.



Figure S12. The relationships between (a) reduced bond angle and induced dihedral angle; (b) reduced bond angle and induced rotation angle difference; (c) dihedral angle and induced bond angle difference and (d) rotation angle and induced bond angle difference. Dihedral angle and bond angle are closely related while rotation angle and bond angle are not much related.



Figure S13. Energy scan of (a) reduced bond angle and (b) dihedral angle in step of 2° and 5° , respectively. Horizontal dashed line indicates energy barrier of 3.1 kJ/mol. Symmetric dimer can rotate freely while asymmetric one is relatively fixed. Induced (c) dihedral angle difference by reduced bond angle and (d) bond angle difference by dihedral angle. Considering the energy barrier in (b), induced bond angle difference of asymmetric dimer is less than 1° while for the symmetric dimer it is ~ 4°.

		S7S	S7O
correlation coefficient	bond angle/energy	0.964	0.967
	dihedral angle/energy	0.724	0.973
	bond angle/dihedral angle	-0.975	0.965
	dihedral angle/bond angle	-0.976	-0.987
	induced bond angle/energy	-0.586	-0.643
	induced dihedral angle/energy	-0.997	0.913

Table S2. Correlation coefficiant among bond angle, dihedral angle and energy

The calculation of Pearson correlation coefficient is based on the well accept equation

$$r = \frac{n \sum x_i y_i - \sum x_i \sum y_i}{\sqrt{[n \sum x_i^2 - (\sum x_i)^2][n \sum y_i^2 - (\sum y_i)^2]}}$$

Based on the minimized energies for bond scan, we could plot the $\delta\theta$ - δE plot and the exponential fitting of the curve fits will with θ^2 , indicating an elastic model, the calculated elastic constant is then derived as 151 J/mol/deg² for CBSC7SCB and 192 J/mol/deg² for CBSC7OCB. It evidence that asymmetric dimer CBSC7OCB requires more energy to bend.



Figure S14. Full scale energy plot of symmetric dimer CBSC7SCB. Each color plate represents one related data point in Fig S15. The color plate exhibits energy dependence of diheral angle. White solid line defines the acceptance region considering all influencial parameters while dark region stands for configurations with energy exceeding 50 kJ/mol. Appearantly, symmetric dimer exhibits relatively lower energy and larger acceptance region.



Figure S15. Full scale energy plot of asymmetric dimer CBSC7OCB. Each color plate represents one related data point in Fig S15. The color plate exhibits energy dependence of diheral angle. White solid line defines the acceptance region considering all influencial parameters while dark region stands for configurations with energy exceeding 50 kJ/mol.



Figure S16. Schematic representation of dataset chosen for simplified 2D energy plot in Fig. 5. The concentric circles represent different bond angles and angular ticks are rotation angles.



Figure S17. Schematic representation of rotation angle influence on helical pitch. With larger rotation angle, the projection of director along helical axis would decrease, which leads to the decrement of helical pitch.



Figure S18. Upon cooling, the rotation angle acceptance region of symmetric dimer would shrink faster than asymmetric dimer. Dark region stands for configurations with energy exceeding 3.1 kJ/mol.

	S		С	
	percentage	hybridization	percentage	hybridization
C42-S45	48.68%	sp ^{5.47}	51.32%	sp ^{4.03}
S45-C46	46.27%	$sp^{4.60}$	53.73%	sp ^{2.99}

 Table S3. NBO results of symmetric dimer CBSC7SCB



	0		С		
	percentage	hybridization	percentage	hybridization	
C42-O45	68.68%	sp ^{2.46}	31.32%	sp ^{3.83}	
O45-C46	67.71%	sp ^{1.96}	32.29%	sp ^{3.00}	

Table S4. NBO results of symmetric dimer CBSC7OCB



Figure S19. (a) Electron density distribution of CBSC7OCB, a dimer is shown to match the electron density map; (b) Reconstructed electron density map with superimposed molecular model of CBSC7OCB. The ED map is reconstructed by SAXS scattering intensities in Fig. S2(a)^{S5}. The molecular size is in line with calculated ED layer distance.

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