

Supporting Materials for “The Origin of Self-Assembled Helical Supra-Molecular Structure in Achiral C6 Biphenyl Carboxylic Acid Model Compounds”

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Identifications of crystal and LC structures. BPCA-C6-P was chosen as an example for crystalline structure identification of this series of achiral C6 biphenyl model compounds using both 2D WAXD and SAED techniques. Figures S1a - S1c show a set of 2D WAXD patterns for mechanically sheared BPCA-C6-P along three incident X-ray beam directions (the through, the edge and the end directions as illustrated in Figure S1d) at room temperature. In Figure S1a, the X-ray beam is in the through direction, and no diffraction peaks can be found in the low 2θ -angle region. However, when the X-ray beam is along the edge and end directions, as in Figures S1b and S1c, a pair of diffraction peaks at $2\theta = 2.028^\circ$ (d-spacing of 4.356 nm) is observed on the meridian. Even higher order diffractions ($2\theta = 4.06^\circ, 6.09^\circ, 8.12^\circ, 10.16^\circ$ and 12.19°) can be clearly seen in the inset of Figures S1b and S1c. The orientation of the diffraction peaks in Figure S1b is better than those in Figure S1c, as judged by the azimuthal distribution of the diffraction spots. These observations indicate that the diffraction at $2\theta = 2.03^\circ$ is attributed to the layer structure of which the layer normal is parallel to the through direction. Namely, the layer structure normal is parallel to the z -axis in Figure S1d; therefore, the layer is parallel to the

x-y plane. The d-spacing of the layer structure is 4.36 nm. Note that one BPCA-C6-P molecule is 2.30 nm in length after energy minimization in vacuum using COMPASS force-field (Cerius² 4.6) at 0 K. Therefore, the layer structure is expected to be constructed from more than one molecule. Moreover, this compound can form a head-to-head dimer via the inter-molecular *H*-bonding formation between the carboxylic acid groups of two molecules as previously reported (also see the FT-IR results in main text). The length of this head-to-head dimer should be 4.59 nm. Since the layer spacing is 4.36 nm, the dimers in the layer must be tilted at an angle of 18.4° with respect to the layer normal direction in order to fit the layer d-spacing.

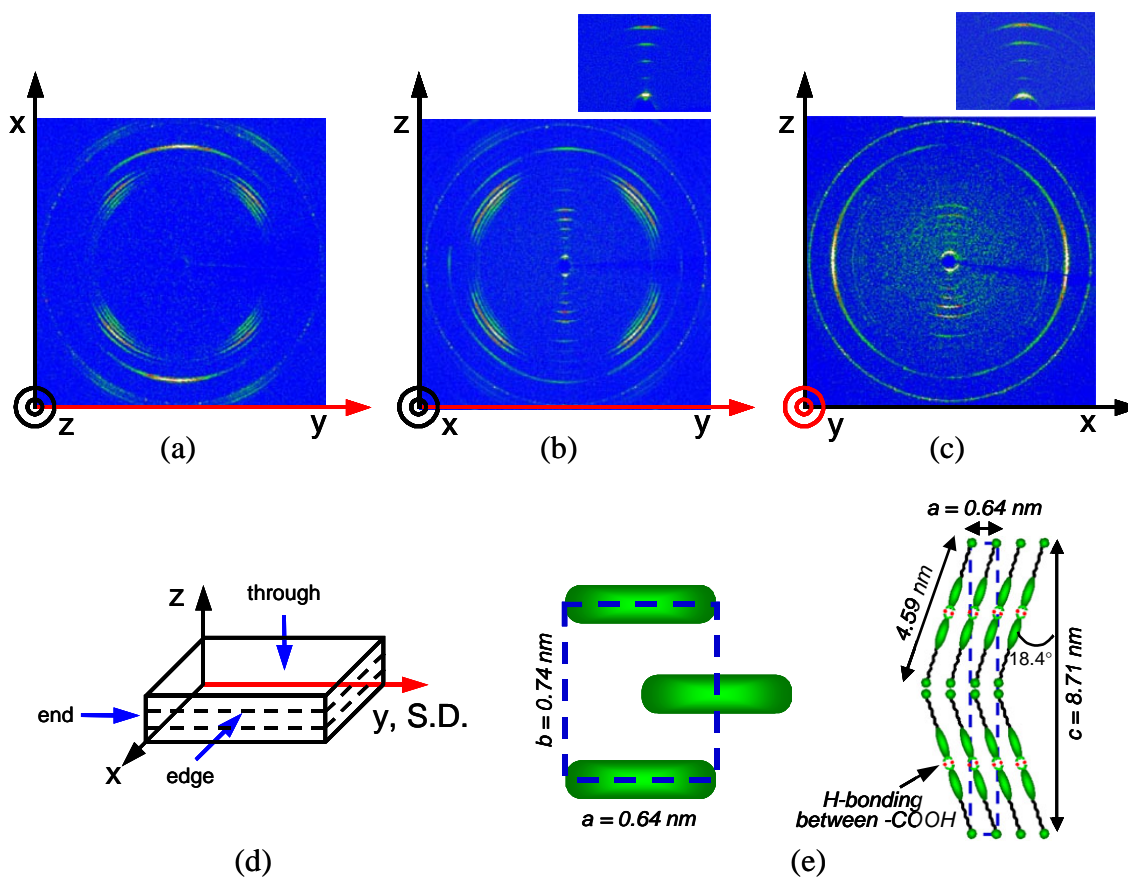


Figure S1 A set of 2D WAXD patterns of a mechanically sheared BPCA-C6-P sample along three directions: (a) the X-ray beam is along the through direction, (b) along the edge direction, (c) along the end direction, (d) the sheared sample geometry and (e) a schematic illustration of molecular arrangement in the crystal. In Figures S1b and S1c, the inserts are the enlarged 2D WAXD patterns in the low 2θ -angle region.

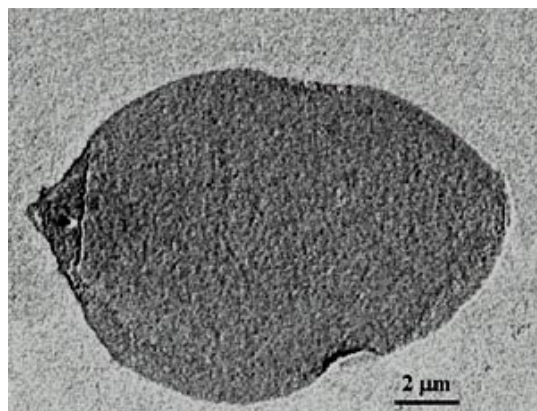
Figures S1a - S1c show symmetric 2D WAXD patterns for the oriented BPCA-C6-P sample, i.e., the diffractions in the wide angle region appear in all the four quadrants of the 2D WAXD pattern. Therefore, dimeric building blocks in the layers must be tilted anticlinically layer-by-layer. If c is assigned along the z direction which is the layer normal, a and b are along the y and x axes, respectively, as shown in Figure S1d. Detailed structural analysis based on these three 2D WAXD patterns of the oriented BPCA-C6-P sample indicates that this crystal possesses an orthorhombic lattice (K_O) with $a = 0.64$ nm, $b = 0.74$ nm, $c = 8.71$ nm, and $\alpha = \beta = \gamma = 90^\circ$. From the crystallographic point of view, the c axis is twice the layer thickness which further supports the anticlinic dimer tilting layer-by-layer. Table S1 lists the experimentally observed d-spacings and the calculated d-spacings based on this unit cell lattice. With four dimers (eight molecules) in one unit cell, its calculated crystallographic density is 1.27 g/cm³. The experimentally observed density is 1.26 g/cm³, which fits well with the calculated data.

The structure determination and the dimer-packing model of BPCA-C6-P (Figure S1e) proposed from 2D WAXD patterns are also supported by SAED results obtained from lamellar single crystals. The TEM morphology in Figure S2a shows a single crystal of BPCA-C6-P, which was grown from the melt. The SAED pattern from the [001] zone shown in Figure S2b can be observed from the lamellar single crystal without sample tilting, which means the c axis of the orthorhombic lattice (K_O) is parallel to the lamellar single crystal normal. The symmetry and d-spacing from this SAED pattern from the [001] zone fully agrees with the dimer-packing model presented in Figure S1e.

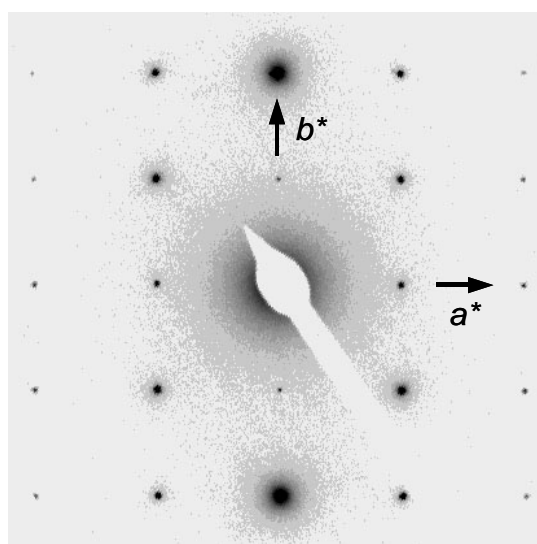
Table S1 Experimental and Calculated Crystallographic Parameters of the K_0 Orthorhombic Phase of BPCA-C6-P

<i>hkl</i>	2 θ (deg)		<i>d</i> -spacing (nm)	
	expt	calc ^a	expt	calc ^a
010	12.0	12.0	0.74	0.74
020	24.2	24.2	0.37	0.37
030	36.5	36.6	0.25	0.25
100	14.0	13.9	0.63	0.64
110	18.4	18.4	0.48	0.48
$\bar{1}$ 10	18.4	18.4	0.48	0.48
120	28.0	28.0	0.32	0.32
$\bar{1}$ 20	28.0	28.0	0.32	0.32
130	39.2	39.3	0.23	0.23
$\bar{1}$ 30	39.2	39.3	0.23	0.23
200	28.2	28.1	0.32	0.32
210	30.6	30.7	0.29	0.29
$\bar{2}$ 10	30.6	30.7	0.29	0.29
220	37.3	37.4	0.24	0.24
$\bar{2}$ 20	37.3	37.4	0.24	0.24
300	42.6	42.7	0.21	0.21
002	2.03	2.03	4.36	4.36
004	4.06	4.06	2.18	2.18
006	6.09	6.09	1.45	1.45
116	19.3	19.4	0.46	0.46
$\bar{1}$ 16	19.3	19.4	0.46	0.46
118	19.8	19.8	0.45	0.45

^aThe calculated data listed are based on the K_0 orthorhombic unit cell with $a = 0.64$ nm, $b = 0.74$ nm, $c = 8.71$ nm, and $\alpha = \beta = \gamma = 90.0^\circ$.



(a)



(b)

Figure S2 (a) TEM micrograph of the BPCA-C6-P sample and (b) the SAED pattern of the [001] zone. The [001] zone SAED pattern was obtained without sample tilting.

The crystalline structures of BPCA-C6-*Pm*OH, BPCA-C6-*Pp*OH and BPCA-C6-*Pm*OCH₃ are also identified utilizing 2D WAXD and SAED, as shown in Figures S3 and S4, respectively. Monoclinic unit lattices have been determined for BPCA-C6-*Pm*OH and BPCA-C6-*Pp*OH, as listed in Table 2 in the text, which are identical with those even-numbered compounds of BPCA-

C_n - $PmOH$ ($n = 8$ and 10).¹ This indicates that when the dimers are synclinically tilted layer-by-layer in the crystals, their lattices are always monoclinic. The synclinal tilting results from the formation of H -bonding between the hydroxyl groups at the end of dimers.

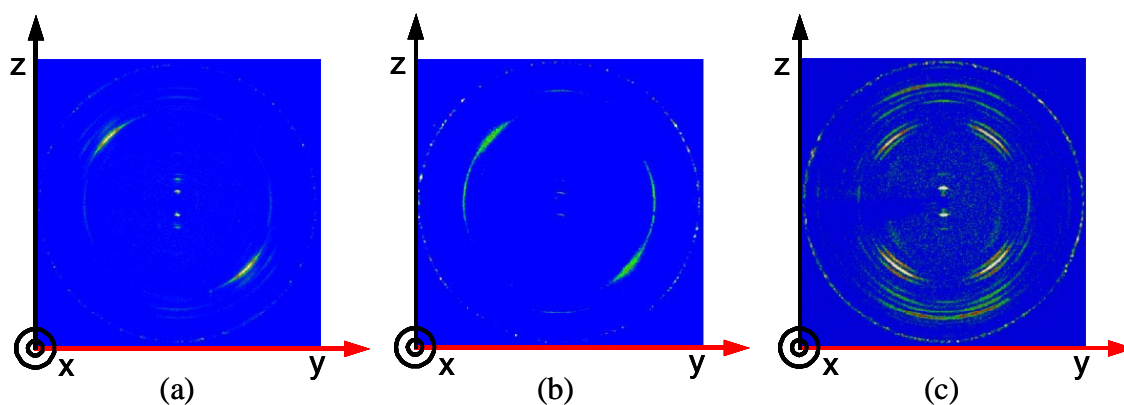


Figure S3 2D WAXD patterns when the X-ray beam is along the edge direction of mechanically sheared (a) BPCA-C6- $PmOH$, (b) BPCA-C6- $PpOH$ and (c) BPCA-C6- $PmOCH_3$ samples. The sheared sample geometry for 2D WAXD is identical with Figure S1d.

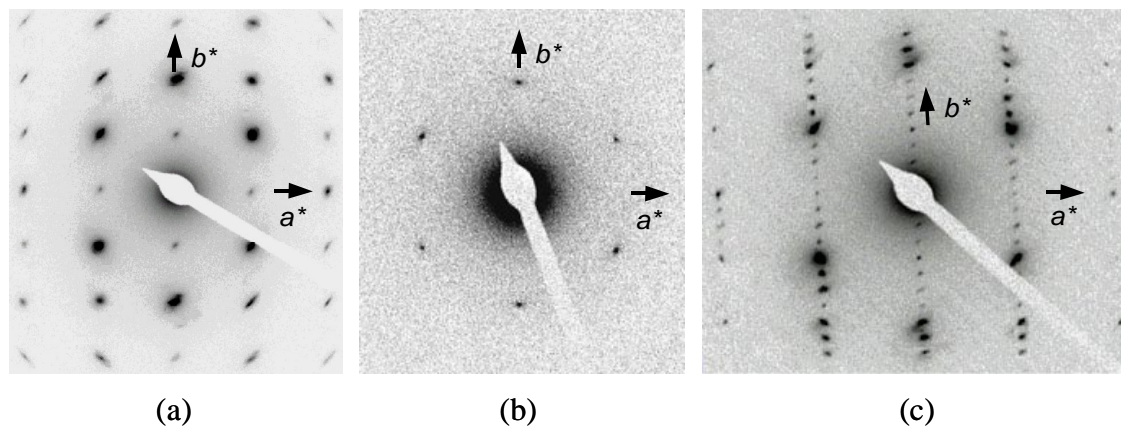


Figure S4 The $[001]$ zone SAED patterns for (a) BPCA-C6- $PmOH$, (b) BPCA-C6- $PpOH$ and (c) BPCA-C6- $PmOCH_3$ samples.

On the other hand, BPCA-C6-*Pm*OCH₃ (Figures S3c and S4c), which cannot form the *H*-bonding between the layers, exhibits the anticlinically tilted dimer packing layer-by-layer similar to the case of BPCA-C6-P (Figure S1). Even though the packing symmetry is similar to that of BPCA-C6-P and the *c* axis of BPCA-C6-*Pm*OCH₃ is twice of the layer thickness, BPCA-C6-*Pm*OCH₃ contains 8 dimers in a triclinic unit cell rather than orthorhombic, and the *b* axis in this system is about four times bigger than that of BPCA-C6-P. Detailed structural parameters of this triclinic structure are also listed in Table 2 of the text. The formation of this triclinic lattice may result from the arrangement of bulky -OCH₃ groups in the crystal. Furthermore, it is evident that without the *H*-bonding between hydroxyl groups between the layers leads to a stable packing scheme of anticlinic dimer tilting between the neighboring layers in BPCA-C6-P and BPCA-C6-*Pm*OCH₃ compounds.

Above the crystal melting temperatures, these compounds undergo multiple LC phases with increasing temperatures as identified by 2D WAXD results. For example, in BPCA-C6-*Pm*OH, there are four LC phases between the crystal and I phase. A highly ordered LC phase can be found between 162 °C and 192 °C. Then, another LC phase appears between 192 °C and 224 °C. A low ordered SmA LC phase is in the temperature region between 224 °C and 227 °C, and followed by a N phase between 227 °C and 229 °C. These phase transitions are also supported by morphological texture changes in PLM, similar to the case of BPCA-C8-*Pm*OH previously reported.¹

When the temperature reaches 192 °C, which corresponds to the weak exothermic process at 192 °C in DSC result, the scattering halo in the high 2θ-angle region becomes significantly sharpened. Its correlation length is about 4.5 nm, estimated by the Scherrer equation. Figure S5a – S5c exhibit a set of 2D WAXD patterns at 185 °C along the three different directions.

Figure S5a shows three pairs of scattering halos centered at $2\theta = 19.9^\circ$ ($d = 0.446$ nm). One pair is on the meridian and the other two pairs are located at $\pm 49^\circ$ away from the meridian. They can also be identified by an azimuthal scan of the 2θ -angle diffraction pairs can be observed in Figure S5d. In Figure S5b and S5c, the low 2θ -angle diffraction at 2.44° ($d = 3.62$) on the meridian can be identified with a second-order diffraction at 1.22° . A pair of scattering halos is located at 40° -counterclockwise to the meridian in the second and fourth quadrants in the Figure S5b. Therefore, the orthogonal head-to-head dimer packing in the layers can thus be identified as a synclinically tilted smectic I (SmI_S) phase.^{1,2} Figure S5e schematically illustrates the dimer packing in this phase.

The highly ordered LC phases of BPCA-C6-PpOH, BPCA-C6-PmOCH₃ and BPCA-C6-P are also identified utilizing 2D WAXD, as shown in Figures S6a – S6c, respectively. For BPCA-C6-PpOH in the highly ordered SmI phase, the building blocks are also synclinically tilted layer-by-layer (Figure S6a). The structure of BPCA-C6-PpOH is thus also identified as a SmI_S phase. In both cases, the *H*-bonding can be formed between hydroxy functions at the ends of dimers. On the other hand, the BPCA-C6-PmOCH₃ (Figure S6b) and BPCA-C6-P (Figure S6c), which cannot form the *H*-bonding between the layers, exhibit 2D WAXD patterns with two pairs of symmetric scattering halos with the identical *d*-spacing (0.446 nm) and intensity in the four quadrants. The tilting angles for both compounds are $\pm 45^\circ$ and $\pm 43^\circ$, respectively. If the dimer packing in these highly ordered LC phases retains the similar types of crystalline phases, they should possess an anticlinic dimer tilting layer-by-layer and they should be identified as a anticlinically tilted SmI (SmI_A) phases.

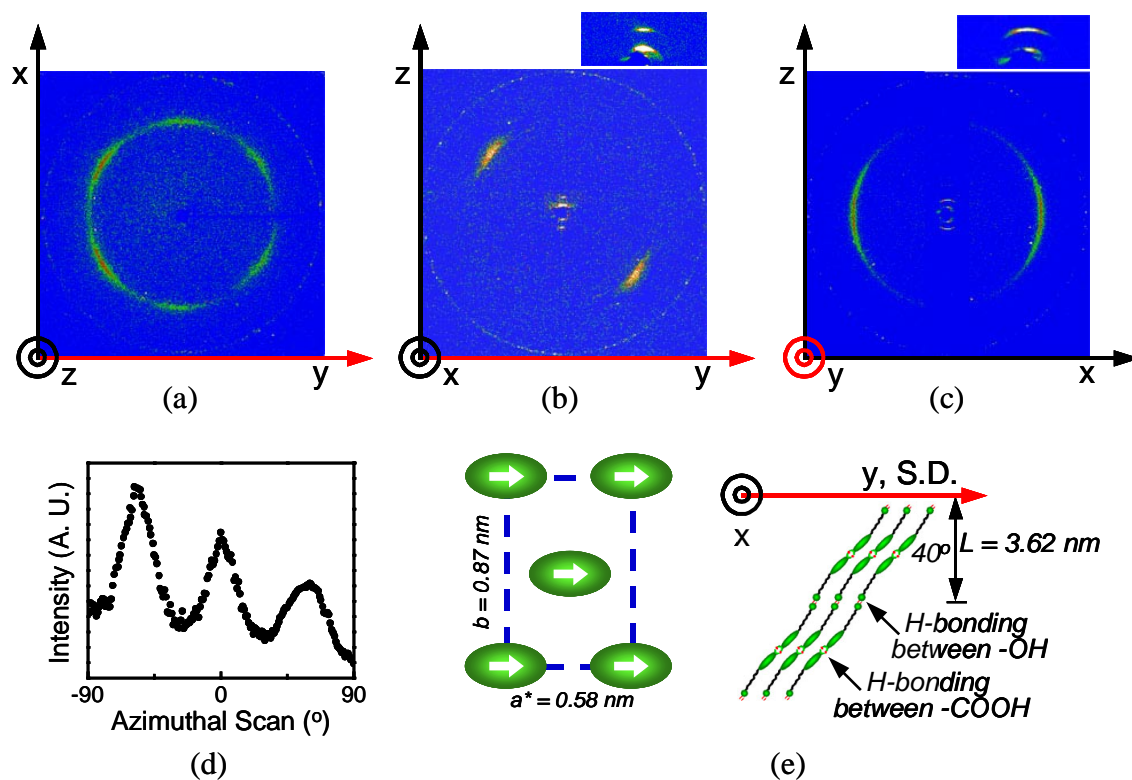


Figure S5 A set of 2D WAXD patterns of a mechanically sheared BPCA-C6-PmOH sample in the SmI LC phase at 185 °C along three directions: (a) the X-ray beam is along the through direction, (b) along the edge direction, (c) along the end direction, (d) azimuthal scan of 2θ -angle between 19° and 22° in the through direction 2D WAXD pattern, and (e) a schematic illustration of the molecular arrangement in the layer. In Figures S5b and S5c, the inserts are the enlarged 2D WAXD patterns in the low 2θ -angle region. The shear geometry is identical to that shown in Figure S1d.

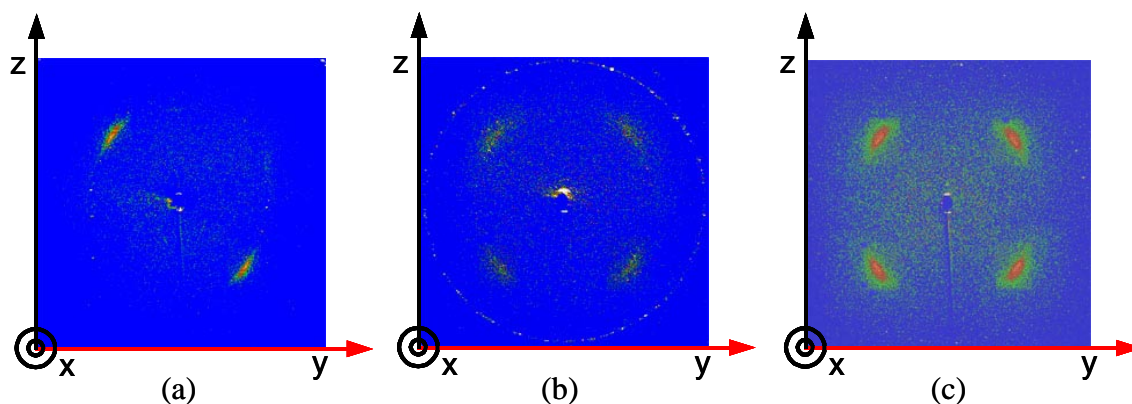


Figure S6 2D WAXD patterns when the X-ray beam is along the edge direction of mechanically sheared (a) BPCA-C6-PpOH, (b) BPCA-C6-PmOCH₃ and (c) BPCA-C6-P samples in the SmI LC phases. The sheared sample geometry for 2D WAXD is identical with Figure S1d.

References:

1. Jeong, K.-U.; Jin, S.; Ge, J. J.; Knapp, B. S.; Graham, M. J.; Ruan, J.; Guo, M.; Xiong, H.; Harris, F. W.; Cheng, S. Z. D. *Chem. Mater.* **2005**, *17*, 2852.
2. Seddon, J. M. *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 1, pp. 635-679.