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Supporting Information for:

Novel Optical Anisotropy of a Liquid Crystalline "Cubic" Phase in a Discotic Crown Ether Derivative

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Experimental Data and Calculations

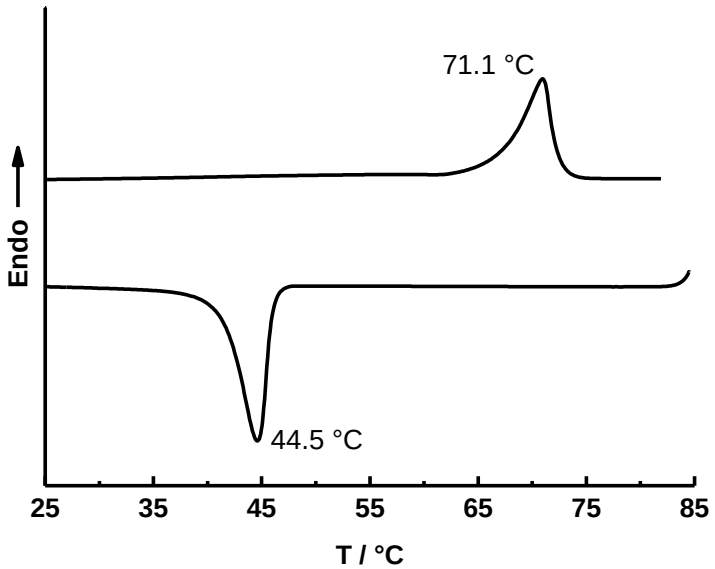

Fig. S1 DSC traces of **2** recorded upon cooling and subsequent heating at a rate of 10 ℃ min^{-1}.

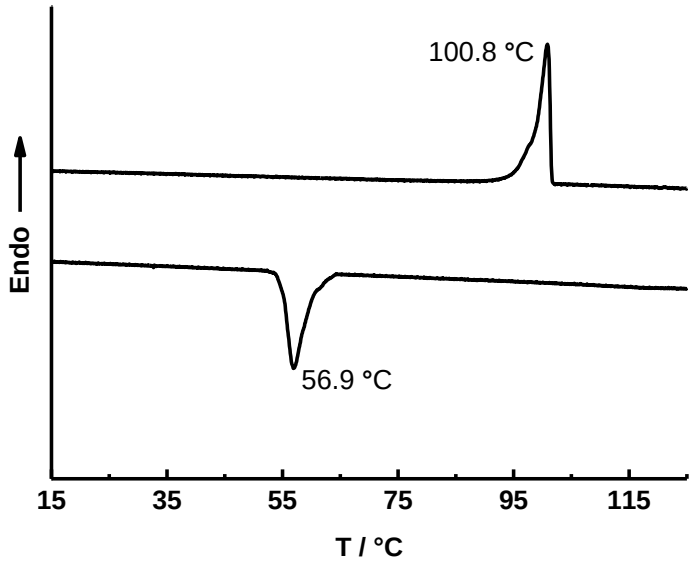

Fig. S2 DSC traces of **3** recorded upon cooling and subsequent heating at a rate of 10 ℃ min^{-1}.

Table S1 Characterization of 3 by 1D-XRD experiment

hkl	100	$1\bar{1}0$	010	$2\bar{1}0$	200	110	$1\bar{2}0$	300	020	$4\bar{2}0$	120	001
d_{exp} /nm	2.82	1.92	1.70	1.49	1.41	1.22	0.96	0.94	0.85	0.74	0.73	0.46
d_{cal} /nm	2.82	1.92	1.70	1.49	1.41	1.22	0.96	0.94	0.85	0.74	0.73	0.46

Table S2 Characterization of 2 by 1D-XRD experiment

hkl	100	010	110	200	020	120	220	300	030	001
d_{exp} /nm	3.50	3.28	2.39	1.74	1.64	1.49	1.19	1.16	1.09	0.46
d_{cal} /nm	3.50	3.28	2.39	1.75	1.64	1.49	1.19	1.16	1.09	0.46

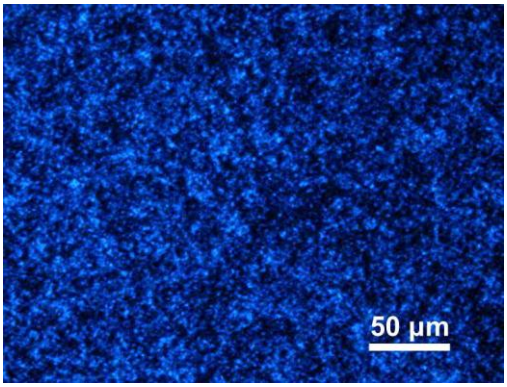

Fig. S3. POM of **1** with the sample cooled from melt to 103 ℃.

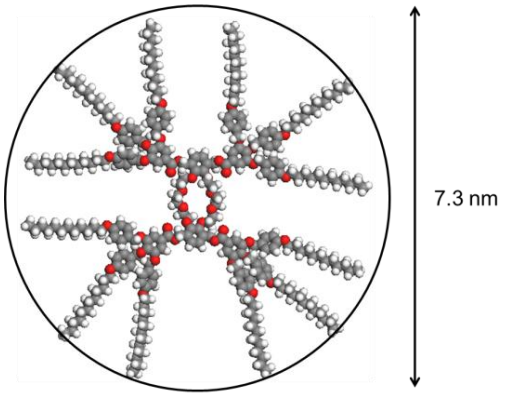

Fig. S4. CPK model of **1** with an extended conformation.

Calculation of XRD Intensity Based on Anisotropic Ellipsoid Placed on a BCC Lattice

We found that at moderate temperatures molecule **1** could render a diffraction pattern featuring a body-centred cubic (BCC) structure, while it was optically anisotropic with strong birefringence. We consider that it can arise from the density fluctuation of columns formed by parallel stacking of discotic molecules of **1**, which leads to anisotropic beads sitting on the BCC lattice. We further assume that the anisotropic beads in the BCC lattice, of which the electron density different from the surrounding matrix, are symmetrical ellipsoids, and their long axis is along the [111] direction (i.e., the column axis of Col_h phase). We approximately set the electron densities inside and outside the ellipsoid uniform distributed. The size of ellipsoid is characterized by its lengths of long axis $2a_1$ and short axis $2a_2$. For the lattice, the structure factor F(hkl) is given by

$$F(hkl) = \int_{cell} dV\rho(\mathbf{r})\exp[-i\mathbf{G}\cdot\mathbf{r}] \qquad \text{(S-1)}$$

where $\boldsymbol{G}$(hkl) represents the reciprocal lattice vector, and $\rho(\mathbf{r})$ is electron density distribution. The intensity of (hkl) diffraction is related to the structure factor by

$$I_c(q) = \sum_{|\mathbf{G}(hkl)|=q} \left|F(hkl)\right|^2 \qquad \text{(S-2)}$$

Based our present assumption, the electron density satisfies

$$\rho(\mathbf{r}) = \begin{cases} 1.0 & \textit{when } \mathbf{r} \textit{ is inside the ellipsoid} \\ 0 & \textit{other case} \end{cases} \qquad \text{(S-3)}$$

When doing the calculations, we varied the size of ellipsoid, while keeping its long axis direction fixed (i.e., [111] direction of BCC lattice). For each specific size, the amount of absolute deviation σ between the calculated value and the experimental data is then evaluated as

$$\sigma = \sum_i \left|I_c(q) - I_e(q)\right| \qquad \text{(S-4)}$$

The sum of index i runs over all diffractions. Note that the contribution from amorphous part has been subtracted from the experimental data. All the diffraction intensities are normalized with respect to the first one. Namely, the diffraction intensity of the first diffraction from both experiment and calculation is set to be the unit. Then the size dependence of σ on two parameters space (a_1 and a_2) was constructed, as shown in Fig. S5. For simplicity, we adopt the cubic lattice parameter a as the unit and only consider the first four diffractions observed experimentally. The best fitting occurs at $a_1 = 0.38$ and $a_2 = 0.27$, with a minimum deviation of $\sigma = 0.005$. Taking $a = 5.56$ nm of the BCC lattice, a_1 and a_2 are of 2.11 and 1.50 nm, respectively.

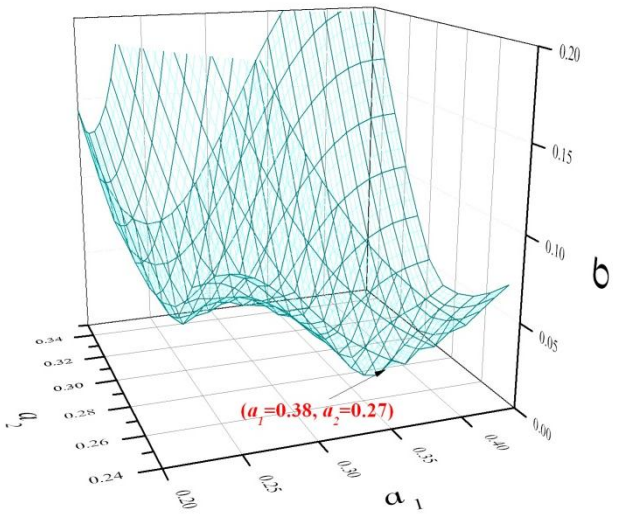

Fig. S5. The absolute deviation σ between calculated value and experimental data as a function of ellipsoid size (a_1, a_2). The arrow points the special size with the best fitting.

We also considered that the optically anisotropic "BCC" lattice may be composed of segmented column (or short cylinder) with its column axis along the [111] direction. To calculate the structure factor, we assume the cylinder has the length of L_0 and the radius of R_0, and the densities inside and outside the cylinder are uniform but different from each other. With the cubic lattice parameter a as the unit, the best fitting occurs at $L_0 = 0.78$ and $R_0 = 0.24$, and the deviation σ is of 0.043. The corresponding calculated and experimental intensities for the first four diffractions are listed below:

Diffraction	1st	2nd	3rd	4th
Experiments	1.000	0.036	0.022	0.021
Calculation	1.000	0.007	0.031	0.026

Note that for the "BCC" lattice of segmented column the best fitting possesses the deviation σ of 0.043, much larger than that of 0.005 for the ellipsoid model. Some other minor modification to the cylinder was also tried. We changed the flat surface on both sides of cylinder to be convex shaped, or let the cylinder body as convex. However, all of these modifications led to a tiny correction for the calculated diffraction intensities.