

Macroscopically anisotropic supramolecular materials prepared from an undercooled liquid-crystalline phase of a cholesterol-based low-molecular-weight compound

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Table of Contents

S1. Supplementary methods.....	2
S1a. General methods	2
S1b. Melt-moulding method	2
S1c. Filament extrusion method	3
S2. Materials and synthesis	4
S2a. Materials	4
S2b. Synthesis of Chol-C₆	4
S2c. Synthesis of Chol-C₁₂	5
S2d. Synthesis of Chol-C₁₂ without using column chromatography	5
S2e. Synthesis of Chol-C₁₈	6
S3. Supplementary figures	10
S3a. Thermogravimetric analysis (TGA).....	10
S3b. Characteristic texture observed via polarized optical microscopy (POM).....	11
S3c. Temperature-dependent FT-IR spectra of methylene stretching	12
S3d. Temperature-dependent XRD profiles and FT-IR spectra	13
S3e. Quenching temperature effect.....	15
S3f. Isothermal crystallization of Chol-C₁₂	17
S3g. Viscosity of Chol-C₁₂	20
S3h. Selective reflection by the chiral smectic phase of Chol-C₁₂	21
S3i. Temporal variation in hue degree of pressed Chol-C₁₂ (sheet-0)	22
S3j. Comparison with another cholesteryl compound	23
S3k. Appearance of sheet-0 and sheet-4	24
S3l. Molecular alignment with different t_{inc}	25
S3m. Polarized photographs of the obtained sheets with different t_{inc}	26
S3n. Relaxation of molecular alignment via shallow quenching.....	27
S3o. Order parameter (S) for various sheets (sheet-0 to sheet-4).	28
S3p. Macroscopic view of the molecular alignment in sheet-4	29
S3q. Tensile testing results of sheet-0 and sheet-4	30
S3r. Tensile testing results after environmental moisture exposure	31
S3s. Recyclability of Chol-C₁₂	32
S3t. Hibernation of metastable LC Chol-C₁₂	33
S3u. Tensile testing results of Chol-C₁₂ filaments	34
S4. Reference	35

S1. Supplementary methods

S1a. General methods

Nuclear magnetic resonance (NMR) spectra were recorded on a JNM-ECZ400S spectrometer (400 MHz). All chemical shifts are reported in parts per million (ppm) from tetramethylsilane (0 ppm for ^1H), residual CHCl_3 (77 ppm for ^{13}C) as internal standards. Electrospray ionization mass spectra (ESI-MS) were obtained using a Thermo Fisher Scientific Exactive Plus instrument. Samples were dissolved in a 1:1 (v/v) mixture of CHCl_3 and MeOH prior to measurement. Thermal analyses were conducted on a Netzsch STA 2500 Regulus and a Netzsch DSC 300 Caliris equipped with a cooling accessory under a nitrogen atmosphere. Characteristic textures of the LC phases were examined using an Olympus BX53-P polarizing microscope equipped with a Linkam 10083L heating stage. X-ray diffraction (XRD) patterns of samples were measured using a Rigaku NANOPIX equipped with a HyPix-6000 detector. For temperature-dependent measurements, a Linkam HSF350-GI heating stage was used. The scattering vector ($q = 4\pi\sin\theta/\lambda$), scattering angle θ , and the position of the incident X-ray beam on the detector were calibrated using several orders of layer reflections from silver behenate ($d = 58.380 \text{ \AA}$), where λ refers to the wavelength of the X-ray beam (Cu $K\alpha$, $1.54 \text{ \AA}$). The sample-to-detector distance was approximately 300 mm. Using the Rigaku 2DP software, the obtained diffraction patterns were integrated along the Debye–Scherrer rings to afford 1D intensity data. Temperature-dependent Fourier-transform infrared (FT-IR) spectra were collected using a PerkinElmer Spectrum Two FT-IR spectrometer equipped with an Instec mK1000 controller attached to a HCS402 heating stage. Polarized FT-IR spectra were acquired on a Thermo Fisher Scientific Nicolet iS50 FT-IR spectrometer. Alignment of molecules in supramolecular bulk materials was examined under crossed Nicols by polarizing films (Narika Co., Ltd.) on an LED light tracing board (Figure 3f,k in the main text). Viscosities were measured using an Anton Paar MCR 302e rheometer with a measuring cone CP25-2. Pressing process was performed using an Imoto Machinery Co., Ltd. IMC-11FD hydraulic press machine. Evolution of selective reflection was monitored using a JASCO J-820 spectropolarimeter. Colour information in the real-time video was analyzed by ImageJ (Fiji). Extrusion process was performed using a Shimadzu CFT-500EX flow tester. Tensile, compression, and three-point flexural tests were performed using a Shimadzu AGS-X universal testing machine. Fractured morphology was examined using a Leica Ivesta 3 Greenough stereo microscope.

S1b. Melt-moulding method

Chol-C₁₂, candle wax, soap, and low-density polyethylene (LDPE) samples were placed in rectangular silicone moulds (L40 mm $\times$ W20 mm). The moulds were heated at 100 °C to melt the materials (LDPE was processed at 160 °C due to its higher melting point). After melting, the materials were cooled and solidified in an incubator (25°C) for 24 h, yielding bulk samples with a thickness of $6.6 \pm 0.65 \text{ mm}$.

S1c. Filament extrusion method

1.0 g of **Chol-C₁₂** was melted in a silicone mould at 100 °C and subsequently quenched on an aluminum block cooled in a liquid nitrogen bath for 50 s. The resulting sample was then loaded into flow tester and incubated for 4 min at 25 °C prior to extrusion. The sample was first compacted pneumatically, followed by pre-extrusion using a 0.5 kg load for 15 s to form a leading filament. Subsequently, a 30 kg load was applied to extrude the remaining **Chol-C₁₂**, yielding an anisotropic filament.

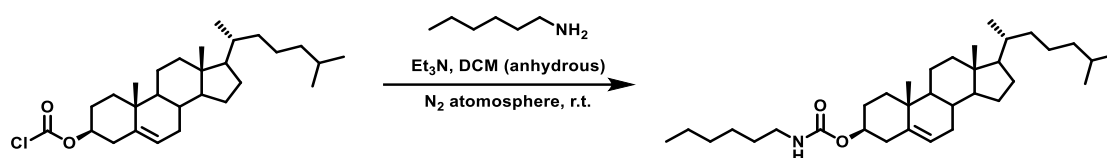
S2. Materials and synthesis

S2a. Materials

(3 β)-cholest-5-en-3-yl chloroformate (TCI Chemicals, 98%), hexan-1-amine (TCI Chemicals, 99%), dodecan-1-amine (TCI Chemicals, 97%), octadecan-1-amine (TCI Chemicals, 85%), *N,N*-diethylethanamine (Et₃N, TCI Chemicals, 99%), anhydrous dichloromethane (CH₂Cl₂, Kanto Chemicals, 99.5%), and anhydrous sodium sulfate (Na₂SO₄, Wako Chemicals, 99%) were used as received without further purification.

For the pressing process, poly(ethylene terephthalate) (PET) films (PET75X1-K-ASI5, 75 μ m thickness; NiPPA Co., Ltd.), silicon mould (Daiso) were used as received. Water-sensitive reactions were conducted under a nitrogen atmosphere using anhydrous solvents.

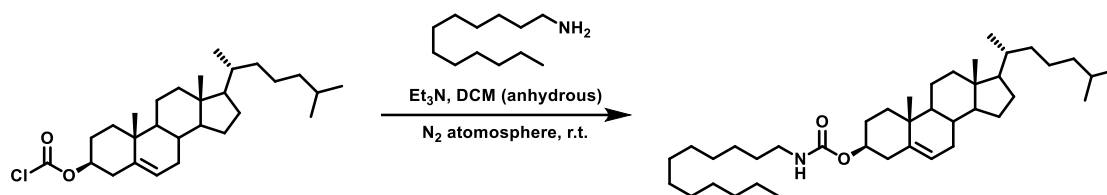
S2b. Synthesis of Chol-C₆



A solution of (3 β)-cholest-5-en-3-yl chloroformate (8.8 g, 19.6 mmol, 1.0 eq.) in anhydrous CH₂Cl₂ (70 mL) was dropwise added to a stirred solution of hexan-1-amine (2.2 g, 21.5 mmol, 1.1 eq) and Et₃N (4.4 g, 43.1 mmol, 2.2 eq.) in anhydrous CH₂Cl₂ (105 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred at room temperature for 4 h. The mixture was then washed with brine (100 mL) twice and dried over anhydrous Na₂SO₄. The filtrate was evaporated, and the solid residue was purified through column chromatography (silica gel, hexane/EtOAc = 20:1 v/v, R_f = 0.30) to yield compound **Chol-C₆** as a white solid (9.6 g, yield = 95%).

¹H NMR (400 MHz, CDCl₃, 298 K): δ (ppm) = 5.37-5.35 (m, 1H_a), 4.55-4.45 (m, 1H_b & 1H_c), 3.14 (q, *J* = 6.4 Hz, 2H_d), 2.37-0.74 (m, 51H_e), 0.68 (s, 3H_f) as shown in **Supplementary Fig. 1.**; ¹³C NMR (100 MHz, CDCl₃, 298K): δ (ppm) = 156.2, 140.0, 122.5, 77.4, 77.1, 76.8, 74.2, 56.8, 56.2, 50.1, 42.4, 41.0, 39.8, 39.6, 38.7, 37.1, 36.6, 36.3, 35.9, 32.0, 32.0, 31.6, 30.1, 28.3, 28.3, 28.1, 26.5, 24.4, 23.9, 22.9, 22.6, 21.1, 19.4, 18.8, 14.1, 11.9 as shown in **Supplementary Fig. 2.**; m.p. 87 °C; HRMS (ESI, MeOH/CHCl₃ = 1/1): *m/z* [M+Na]⁺ calcd. for C₃₄H₅₉NO₂ 536.4438, observed 536.4431.

S2c. Synthesis of Chol-C₁₂



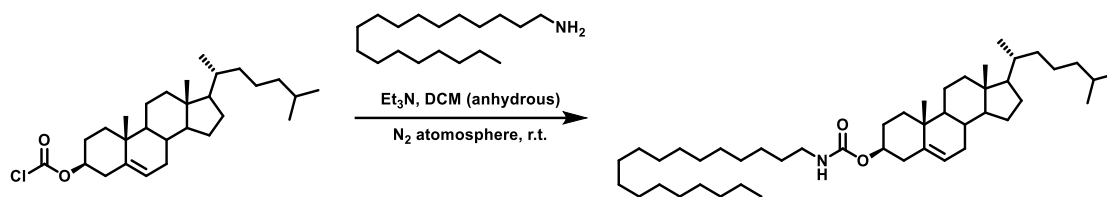
A solution of (3β)-cholest-5-en-3-yl chloroformate (7.5 g, 16.7 mmol, 1 eq.) in anhydrous CH₂Cl₂ (70 mL) was dropwise added to a stirred solution of dodecan-1-amine (3.4 g, 18.4 mmol, 1.1 eq) and Et₃N (3.7 g, 36.7 mmol, 2.2 eq.) in anhydrous CH₂Cl₂ (105 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred at room temperature for 4 h. The mixture was then washed with brine (100 mL) twice and dried over anhydrous Na₂SO₄. The filtrate was evaporated, and the solid residue was purified through column chromatography (silica gel, hexane/EtOAc = 20:1 v/v, R_f = 0.33) to yield compound **Chol-C₁₂** as a white solid (9.4 g, yield = 94%).

S2d. Synthesis of Chol-C₁₂ without using column chromatography

The procedure is analogous to the synthesis of **Chol-C₁₂** (see above) but in a 14-gram scale. The solid residue was dissolved in hexane/EtOAc (20:1 v/v, 200 mL) and mixed with silica powder, and the resulting suspension was stirred for 30 min. The mixture was filtered to remove the silica, and the silica cake was washed with EtOAc (200 mL) twice. The combined filtrates were concentrated to yield compound **Chol-C₁₂** as a white solid (13.7 g, yield = 97%).

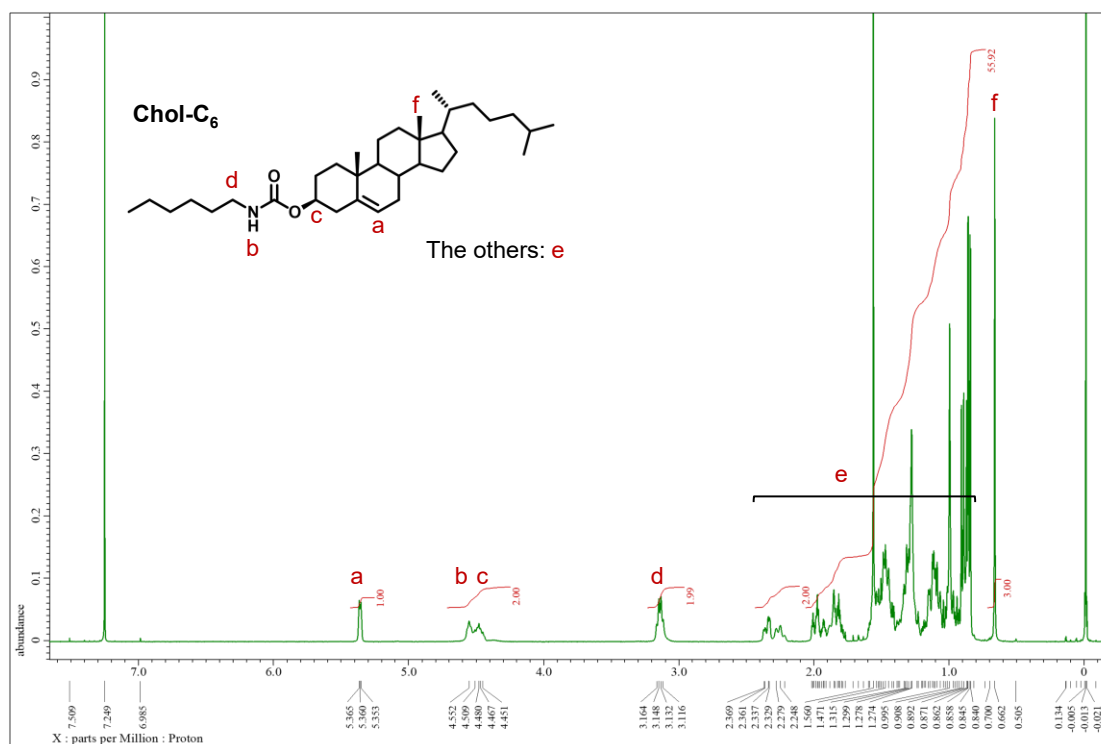
¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) = 5.36-5.35 (m, 1H_a), 4.55-4.45 (m, 1H_b & 1H_c), 3.14 (q, *J* = 6.4 Hz, 2H_d), 2.37-0.81 (m, 63H_e), 0.66 (s, 3H_f) as shown in **Supplementary Fig. 3.**; ¹³C NMR (100 MHz, CDCl₃, 298K): δ (ppm) = 156.2, 140.0, 122.5, 77.4, 77.1, 76.8, 74.2, 56.8, 56.2, 50.1, 42.4, 41.0, 39.8, 39.6, 38.7, 37.1, 36.6, 36.3, 35.9, 32.0, 32.0, 30.1, 29.7, 29.7, 29.6, 29.4, 29.4, 28.3, 28.3, 28.1, 26.8, 24.4, 23.9, 22.9, 22.8, 22.6, 21.1, 19.4, 18.8, 14.2, 11.9 as shown in **Supplementary Fig. 4.**; m.p. 78 °C.; HRMS (ESI, MeOH/CHCl₃ = 1/1): *m/z* [M+Na]⁺ calcd. for C₄₀H₇₁NO₂ 620.5377, observed 620.5371.

S2e. Synthesis of Chol-C₁₈



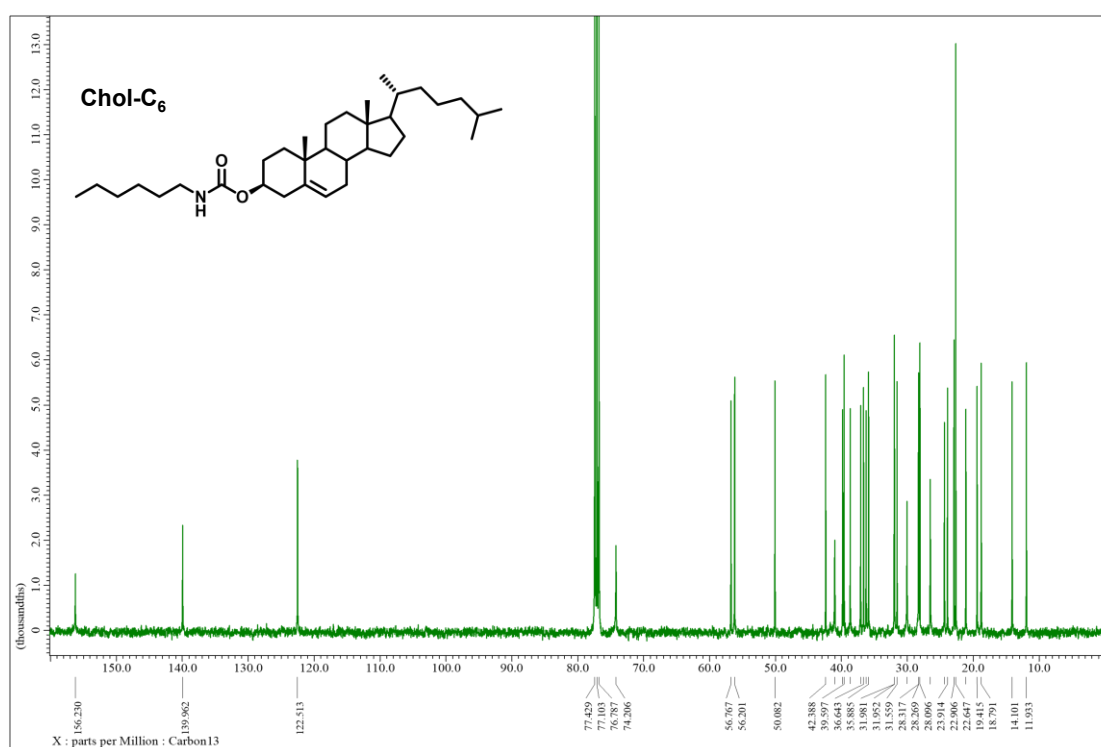
A solution of (3β)-cholest-5-en-3-yl chloroformate (7.0 g, 15.6 mmol, 1.0 eq.) in anhydrous CH₂Cl₂ (70 mL) was dropwise added to a stirred solution of octadecan-1-amine (4.6 g, 17.1 mmol, 1.1 eq) and Et₃N (3.5 g, 34.2 mmol, 2.2 eq.) in anhydrous CH₂Cl₂ (105 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred at room temperature for 4 h. The mixture was then washed with brine (100 mL) twice and dried over anhydrous Na₂SO₄. The filtrate was evaporated, and the solid residue was purified through column chromatography (silica gel, hexane/EtOAc = 20:1 v/v, R_f = 0.35) to yield compound **Chol-C₁₈** as a white solid (9.7 g, yield = 91%).

¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) = 5.36-5.35 (m, 1H_a), 4.54-4.48 (m, 1H_b & 1H_c), 3.14 (q, *J* = 6.6 Hz, 2H_d), 2.37-0.84 (m, 77H_e), 0.66 (s, 3H_f) as shown in **Supplementary Fig. 5.**; ¹³C NMR (100 MHz, CDCl₃, 298K): δ (ppm) = 156.2, 140.0, 122.5, 77.4, 77.1, 76.8, 74.2, 56.8, 56.2, 50.1, 42.4, 41.0, 39.8, 39.6, 38.7, 37.1, 36.6, 36.3, 35.9, 32.0, 32.0, 32.0, 30.1, 29.8, 29.7, 29.6, 29.5, 29.4, 28.3, 28.3, 28.1, 26.8, 24.4, 23.9, 22.9, 22.8, 22.6, 21.1, 19.4, 18.8, 14.2, 11.9 as shown in **Supplementary Fig. 6.**; m.p. 81 °C; HRMS (ESI, MeOH/CHCl₃ = 1/1): *m/z* [M+Na]⁺ calcd. for C₄₆H₈₃NO₂ 704.6316, observed 704.6310.



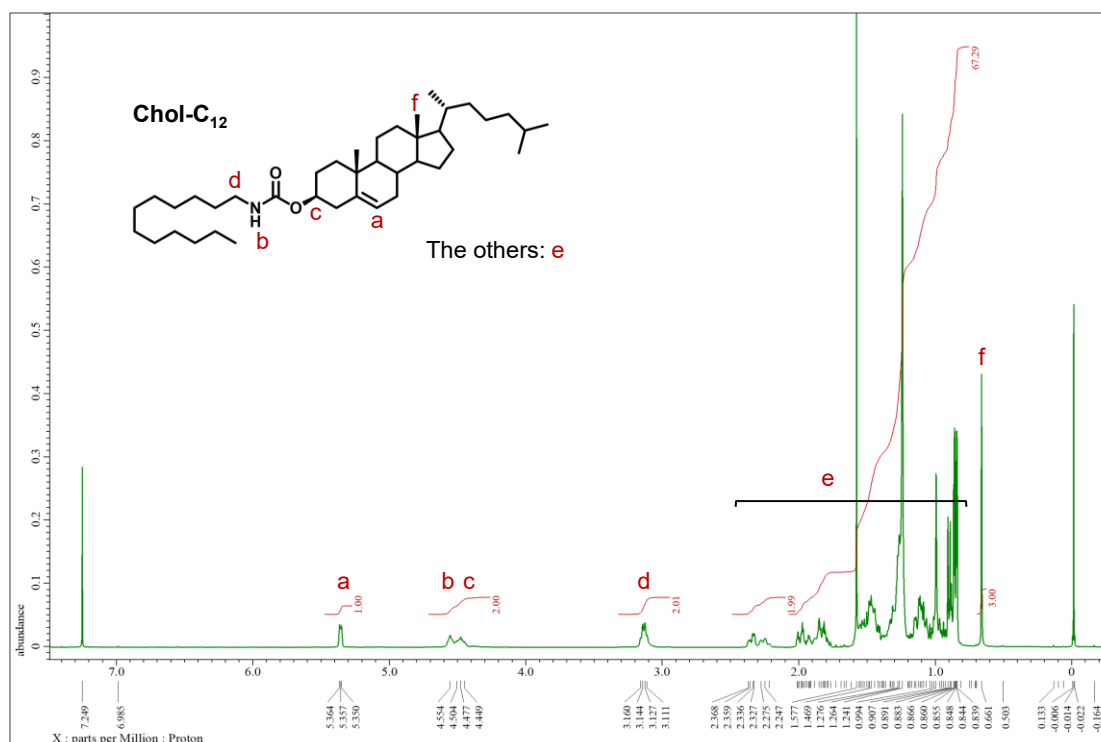
Supplementary Fig. 1.

¹H NMR (400 MHz) spectrum of **Chol-C₆** in CDCl₃ at 298 K.



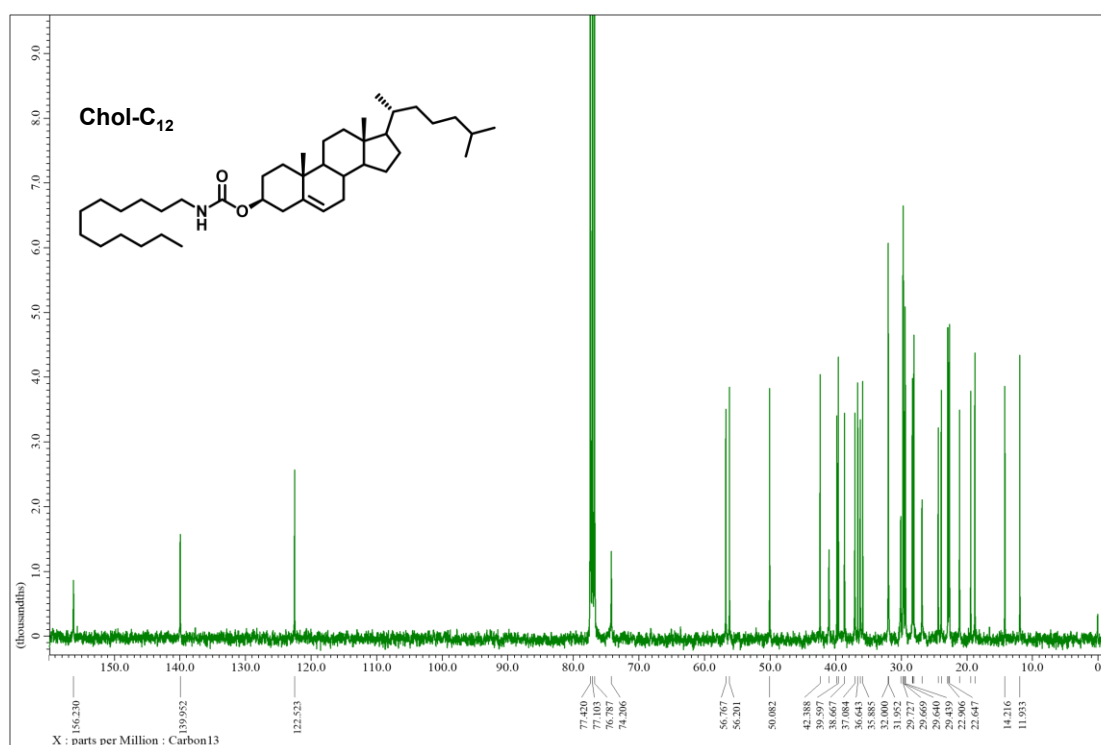
Supplementary Fig. 2.

¹³C NMR (100 MHz) spectrum of **Chol-C₆** in CDCl₃ at 298 K.



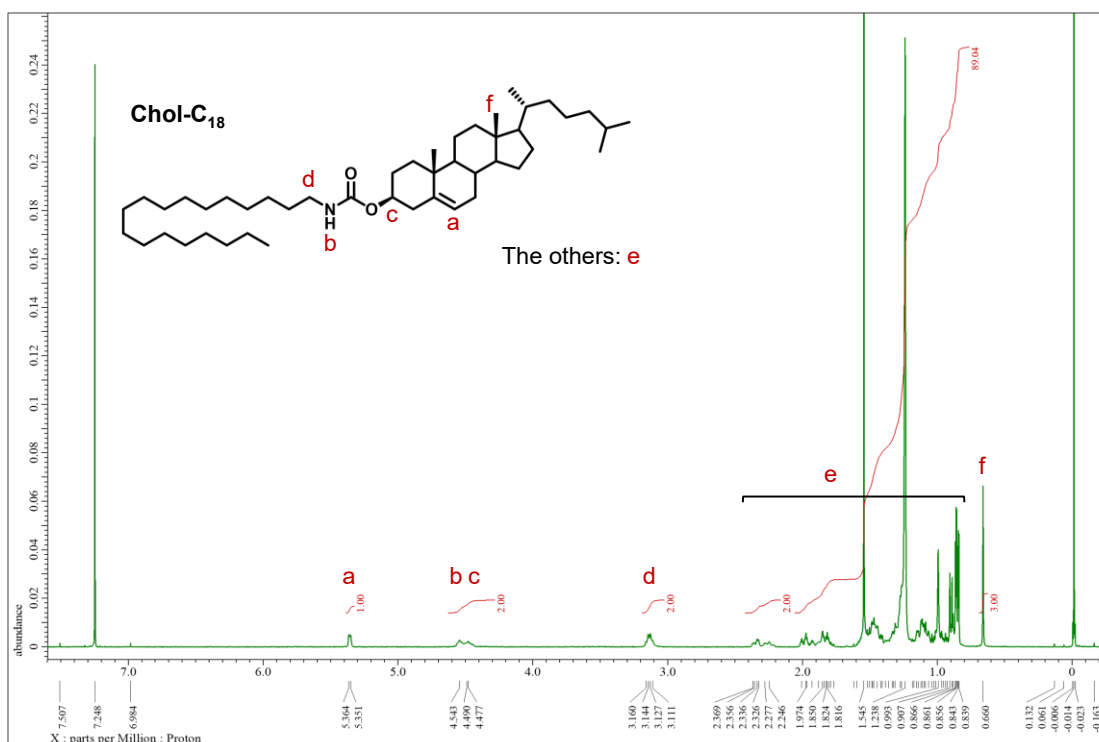
Supplementary Fig. 3.

¹H NMR (400 MHz) spectrum of **Chol-C₁₂** in CDCl₃ at 298 K.



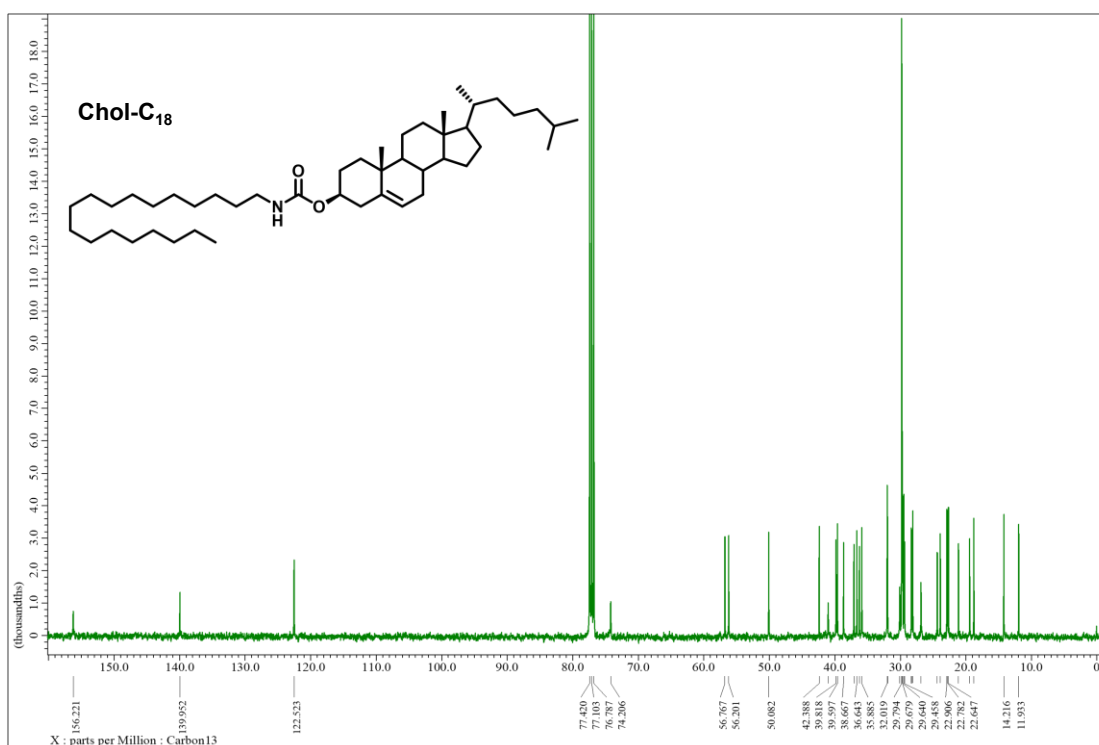
Supplementary Fig. 4.

¹³C NMR (100 MHz) spectrum of **Chol-C₁₂** in CDCl₃ at 298 K.



Supplementary Fig. 5.

¹H NMR (400 MHz) spectrum of **Chol-C₁₈** in CDCl₃ at 298 K .

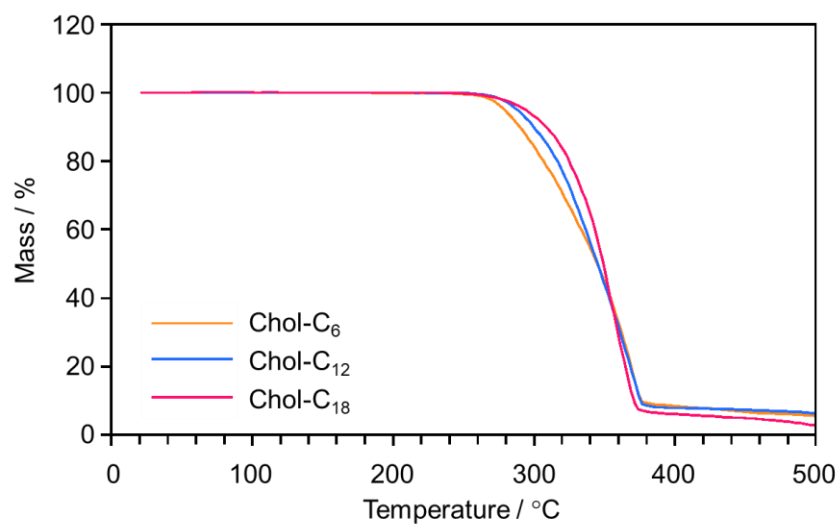


Supplementary Fig. 6.

¹³C NMR (100 MHz) spectrum of **Chol-C₁₈** in CDCl₃ at 298 K.

S3. Supplementary figures

S3a. Thermogravimetric analysis (TGA)

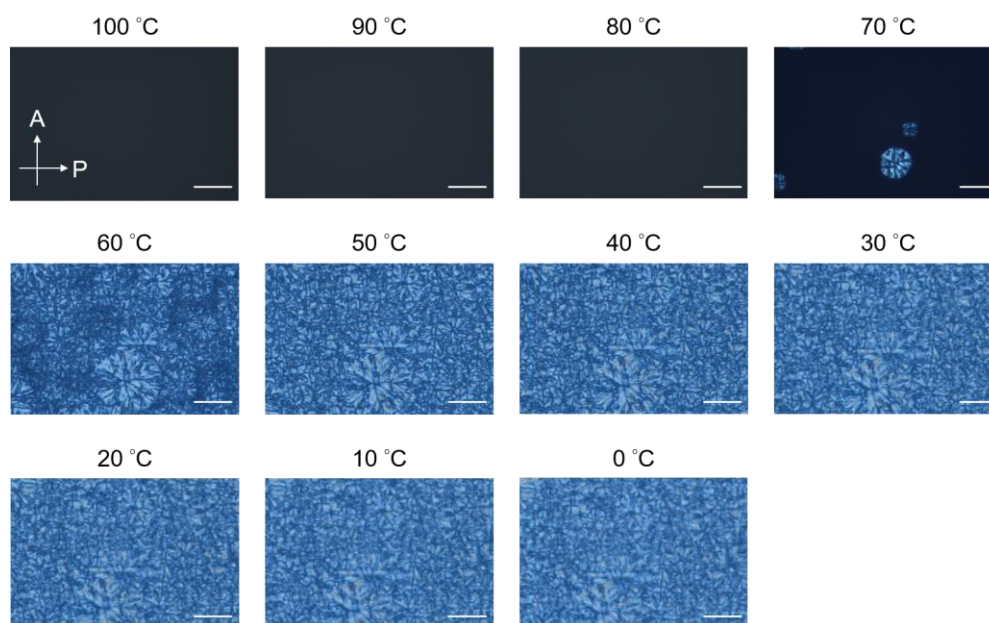


Supplementary Fig. 7.

TGA curves of **Chol-C₆**, **Chol-C₁₂**, and **Chol-C₁₈** from 25 to 500 °C obtained at a scan rate of 10 °C/min under a N₂ atmosphere.

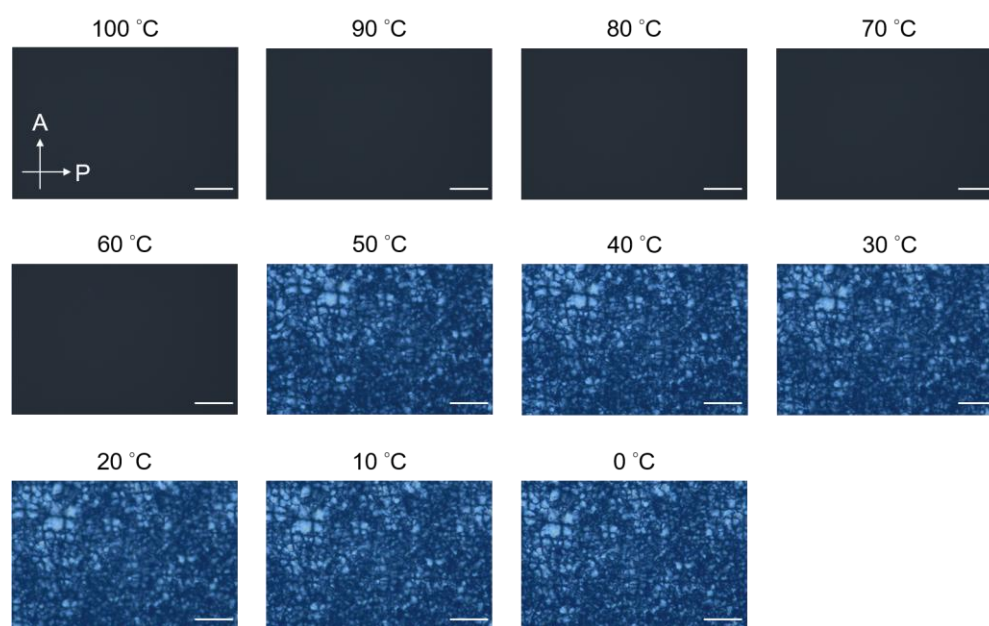
S3b. Characteristic texture observed via polarized optical microscopy (POM)

After melting, the samples were cooled from 100 °C to 0 °C at a cooling rate of 10 °C/min, and images were acquired at 10 °C intervals. In the isotropic molten state (100 °C), both **Chol-C₆** and **Chol-C₁₂** appeared a dark field of view under crossed Nicols. Upon cooling, characteristic textures emerged, indicating that **Chol-C₆** and **Chol-C₁₂** formed LC phases.



Supplementary Fig. 8.

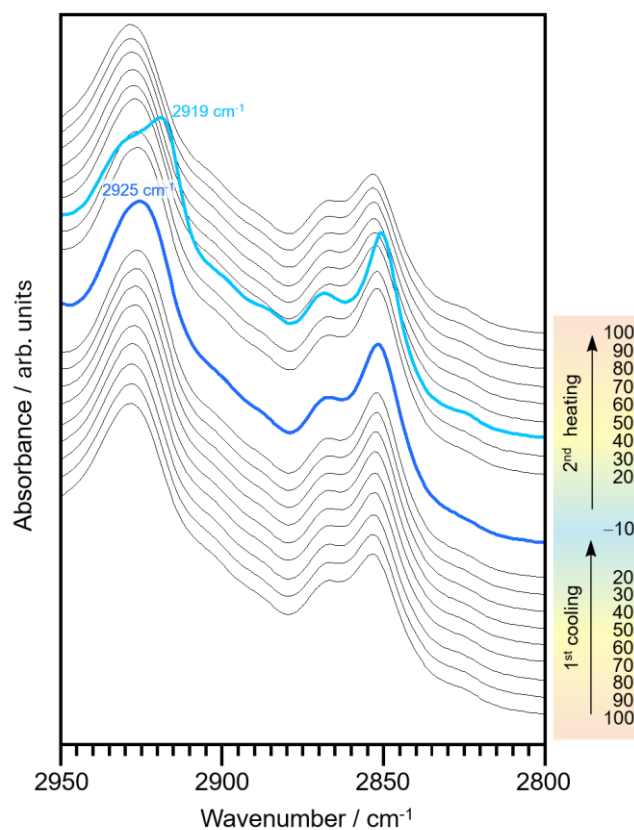
Polarized optical microscopy images of **Chol-C₆** from 100 °C to 0 °C at a cooling rate of 10 °C/min under a N₂ atmosphere: scale bar = 50 μm.



Supplementary Fig. 9.

Polarized optical microscopy images of **Chol-C₁₂** from 100 °C to 0 °C at a cooling rate of 10 °C/min under a N₂ atmosphere: scale bar = 50 μm.

S3c. Temperature-dependent FT-IR spectra of methylene stretching

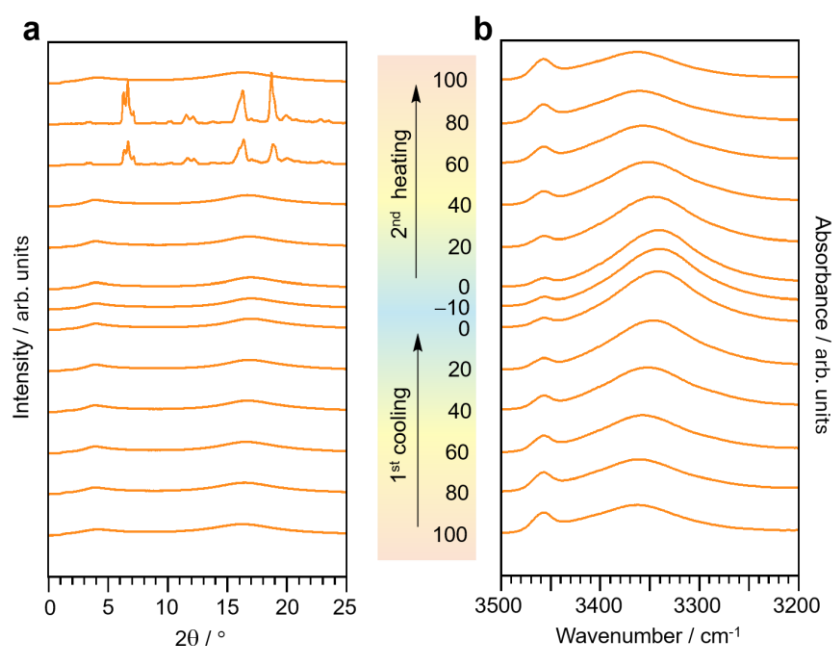


Supplementary Fig. 10.

Temperature-dependent FT-IR spectra of **Chol-C₁₂** in the range of 2950 to 2800 cm⁻¹ obtained during cooling from 100 to -10 °C, followed by reheating to 100 °C.

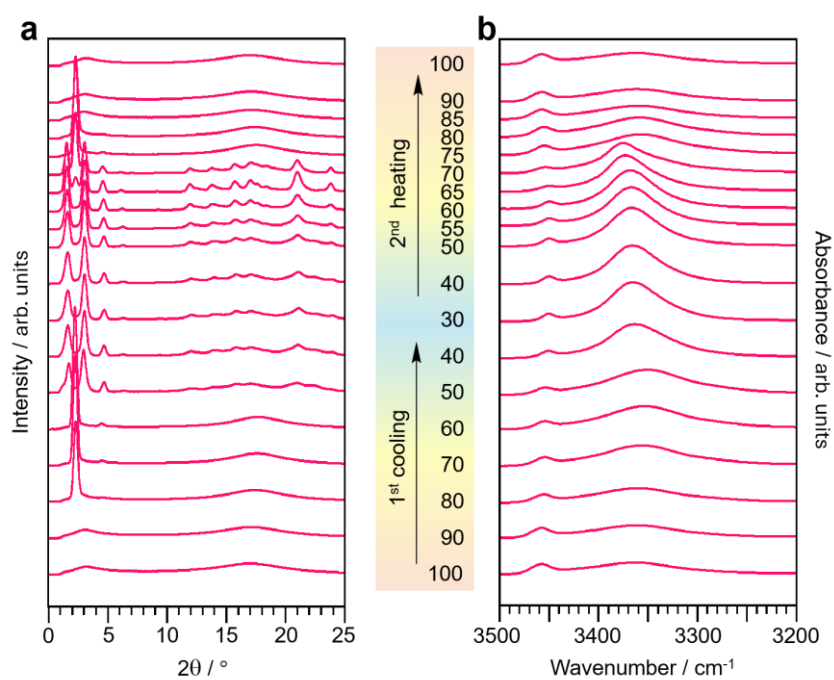
S3d. Temperature-dependent XRD profiles and FT-IR spectra

The phases transitions of **Chol-C₆**, **Chol-C₁₂**, and **Chol-C₁₈** were examined across temperatures. For XRD and FT-IR measurements, the samples were placed in capillaries or on a sapphire substrate, respectively, and subjected to controlled temperature variations. After reaching the thermal equilibrium at designated temperatures, measurements were conducted. As shown in **Supplementary Fig. 11**, **Chol-C₆** remained its nematic LC phase while cooling to $-10\text{ }^{\circ}\text{C}$. In contrast, as shown in **Supplementary Fig. 12**, **Chol-C₁₈** started forming lamellar crystalline structures when cooled to $50\text{ }^{\circ}\text{C}$. Correspondingly, a blue shift in the N–H stretching vibration was observed in the FT-IR spectra, consistent with the weakening of hydrogen bonding accompanying the enhanced packing of cholesteryl groups as is the case of **Chol-C₁₂**.



Supplementary Fig. 11.

a,b, Temperature-dependent XRD profiles (a) and FT-IR spectra (b) of **Chol-C₆** obtained during cooling from 100 to $-10\text{ }^{\circ}\text{C}$, followed by reheating to $100\text{ }^{\circ}\text{C}$.

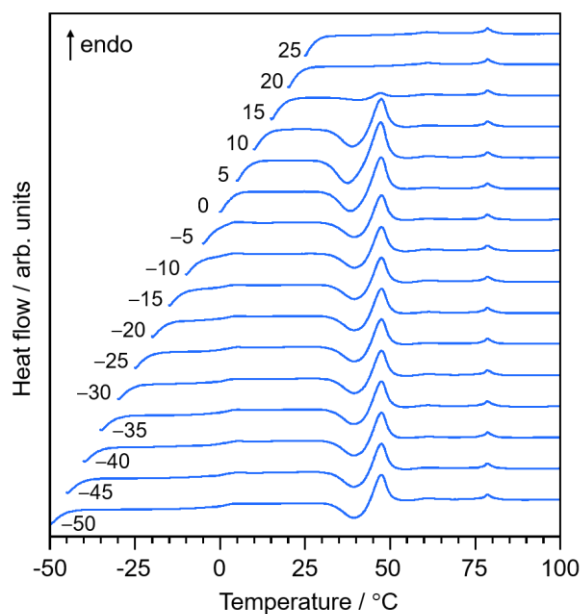


Supplementary Fig. 12.

a,b, Temperature-dependent XRD profiles (a) and FT-IR spectra (b) of **Chol-C18** obtained during cooling from 100 to 30 °C, followed by reheating to 100 °C.

S3e. Quenching temperature effect

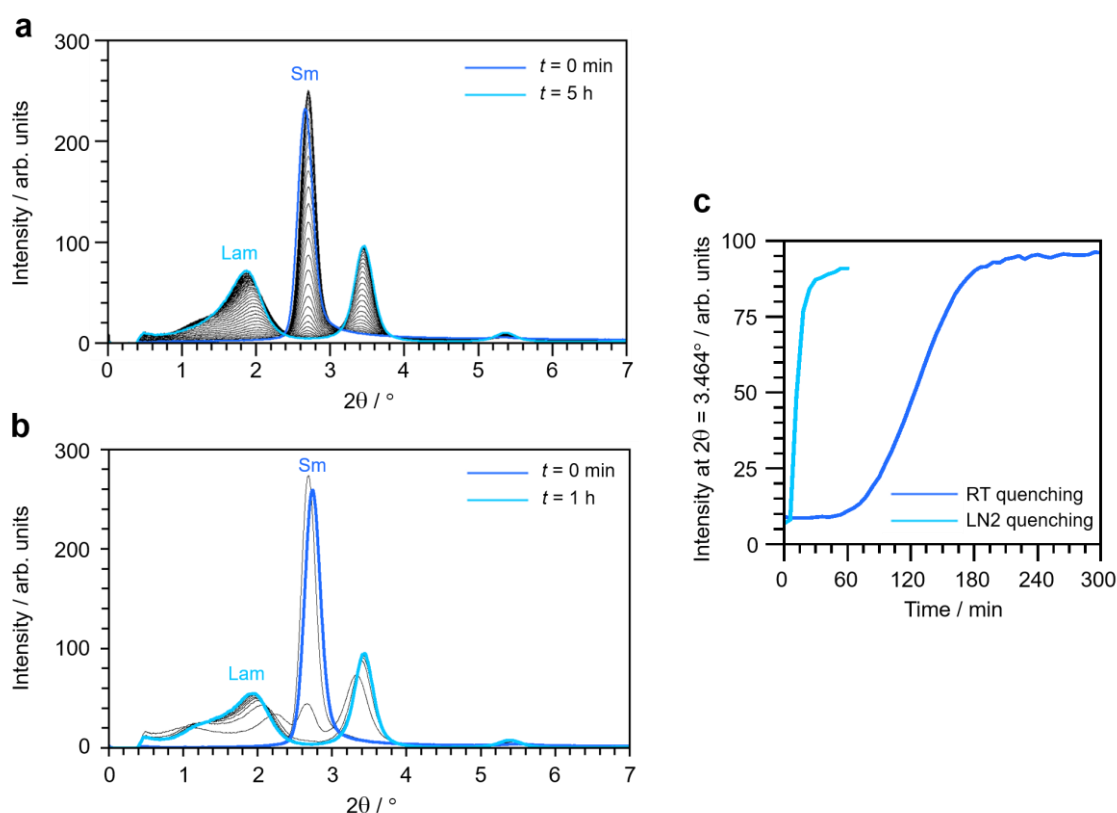
A **Chol-C₁₂** sample was first melted at 100 °C to eliminate thermal history if any. The sample was then quenched at a cooling rate of -50 °C/min to designated temperatures (-50 to 25 °C) and held for 5 min for reaching thermal equilibrium. The crystallization behaviour was monitored in the following heating trace.



Supplementary Fig. 13.

DSC curves of **Chol-C₁₂** from each quenched temperature to 100 °C at a scan rate of 10 °C/min under a N_2 atmosphere.

A **Chol-C₁₂** sample was first melted at 100 °C to eliminate thermal history if any. The sample plate was then subsequently quenched on an aluminium block cooled in a liquid-nitrogen bath or at room temperature prior to measurements.

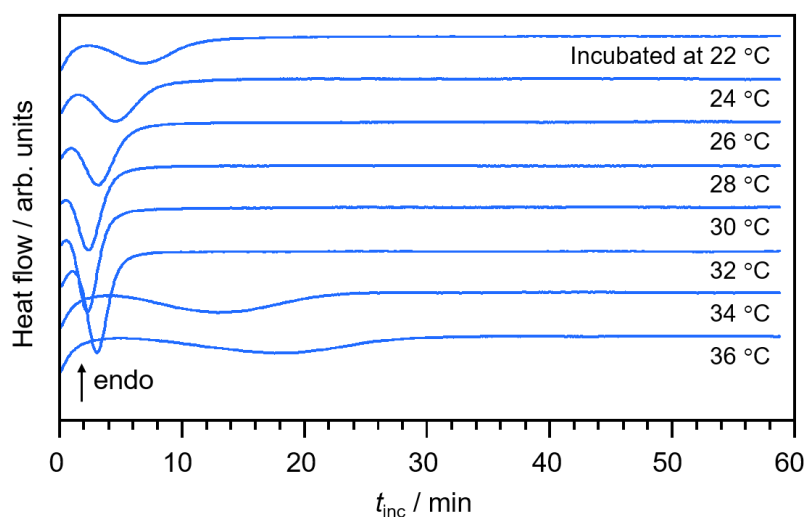


Supplementary Fig. 14.

a,b, Time-dependent XRD profiles of **Chol-C₁₂** recorded at 6-min intervals via shallow quenching (25 °C) from 0 min to 5 h (a) and deep quenching (−196 °C) from 0 min to 1 h (b). **c,** A change in the diffraction intensity at $2\theta = 3.464^\circ$ as a function of time.

S3f. Isothermal crystallization of Chol-C₁₂

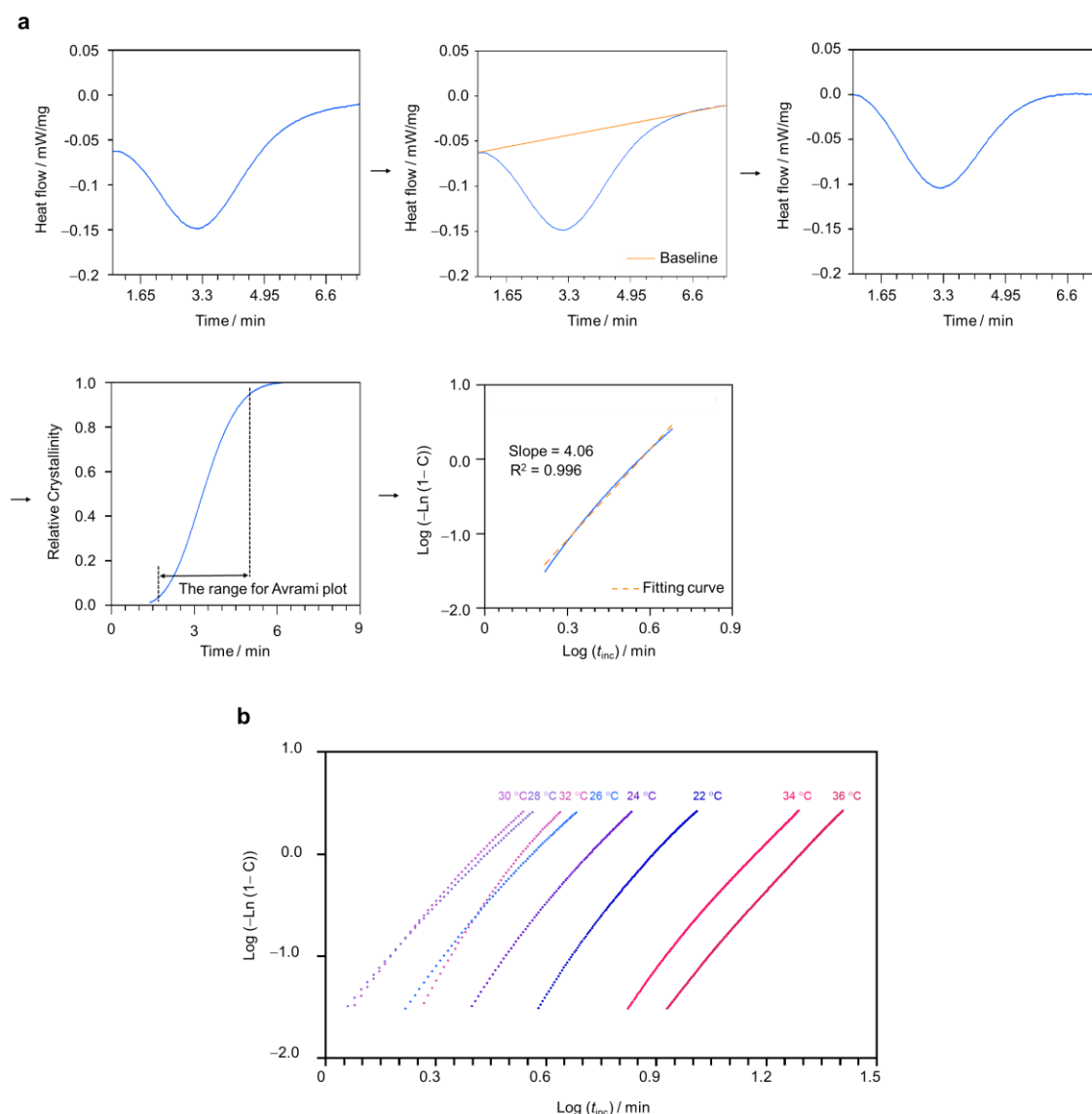
A Chol-C₁₂ sample was first melted at 100 °C to eliminate thermal history if any. It was then rapidly cooled to −50 °C at a rate of −50 °C/min and held for 10 min to reach thermal equilibration. Subsequently, the temperature was raised to the designated incubation temperatures (22 to 36 °C) at a heating rate of 50 °C/min, and the crystallization behaviour was monitored in the ensuing isothermal stage.



Supplementary Fig. 15.

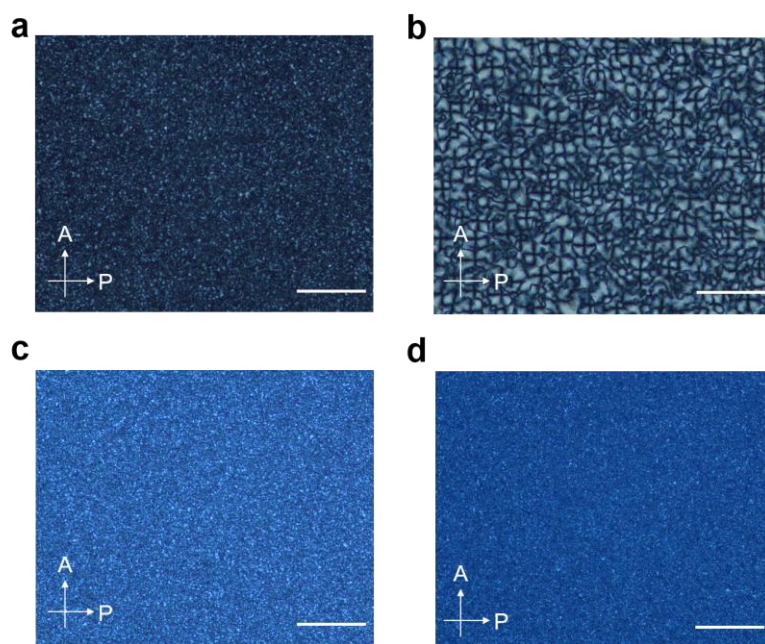
Isothermal DSC curves of Chol-C₁₂ obtained at various incubation temperatures ranging from 22 °C to 36 °C for 1 h.

The degree of relative crystallinity was evaluated from the integrated area of the exothermic peak obtained from isothermal DSC traces. To calculate the area of the crystallization peak, a linear baseline correction was applied across the crystallization peak to eliminate artifacts from the preceding heating process. The linear portion of the relative crystallinity-time curve was subsequently extracted to construct the Avrami plot (Supplementary Fig. 16a). A linear fit to the Avrami plot yielded an Avrami constant of approximately 4 (Supplementary Fig. 16b).^{S1}



Supplementary Fig. 16.

a, The method for the Avrami plot construction. The representative Avrami plot was derived from relative crystallinity-time data, using isothermal DSC measurements at 26 °C after baseline correction. **b**, Avrami plots of **Chol-C₁₂** derived from the data presented in Supplementary Fig. 15.

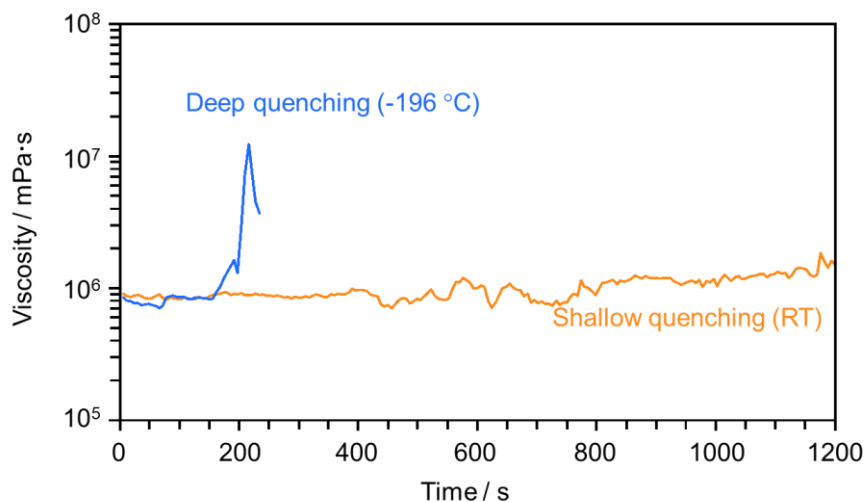


Supplementary Fig. 17.

a,b, Polarized optical microscopy images of **Chol-C₁₂** obtained via shallow quenching (25 °C) and subsequently aged for 0 min (a) and 1 day (b). Because of low nucleation density and sluggish crystallization kinetics, resulting in the formation of spherulites with visible sizes. **c,d,** Polarized optical microscopy images of **Chol-C₁₂** obtained via deep quenching (−196 °C) and subsequently aged for 0 min (c) and 1 day (d). Because of high nucleation density and rapid crystallization kinetics, significant changing is not observed under POM.: scale bar = 50 μm.

S3g. Viscosity of Chol-C₁₂

To measure the viscosity of the undercooled LC **Chol-C₁₂**, a **Chol-C₁₂** sample was first melted at 100 °C on a disposable dish and then subjected to either deep quenching (−196 °C) or shallow quenching (25 °C). A shear deformation at a rate of 30 s^{−1} was subsequently applied to the undercooled LC **Chol-C₁₂** at 25 °C. As shown in **Supplementary Fig. 18**, the viscosity of deeply quenched **Chol-C₁₂** increased from 10⁶ mPa·s to 10⁷ mPa·s after about 200 s due to cold crystallization. In contrast, the viscosity of the shallowly quenched sample remained nearly constant throughout the experimental period, reflecting a much sluggish crystallization kinetics.

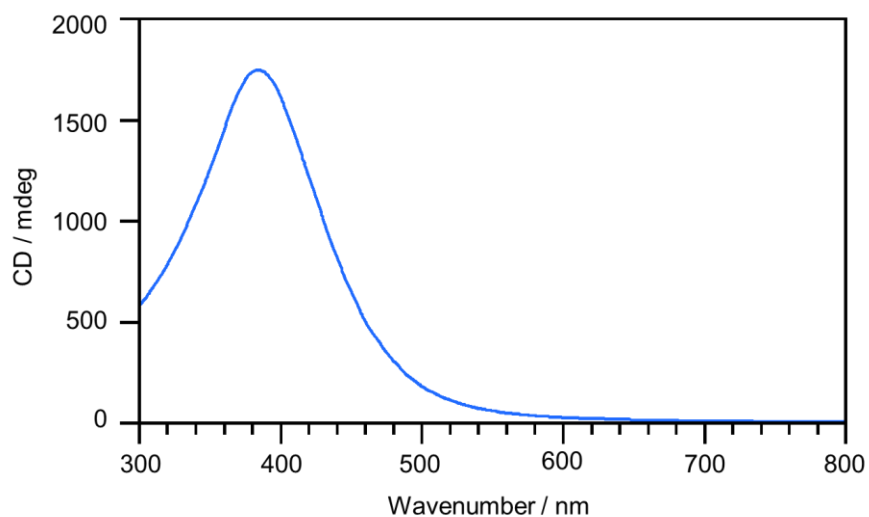


Supplementary Fig. 18.

Viscosity of **Chol-C₁₂** under deep quenching (−196 °C, blue line) and shallow quenching (25 °C, orange line) conditions.

S3h. Selective reflection by the chiral smectic phase of Chol-C₁₂

A Chol-C₁₂ sample was sandwiched between two calcium fluoride (CaF₂) windows and melted at 100 °C to eliminate previous thermal history if any. CD spectra were recorded after shallow quenching (25 °C).

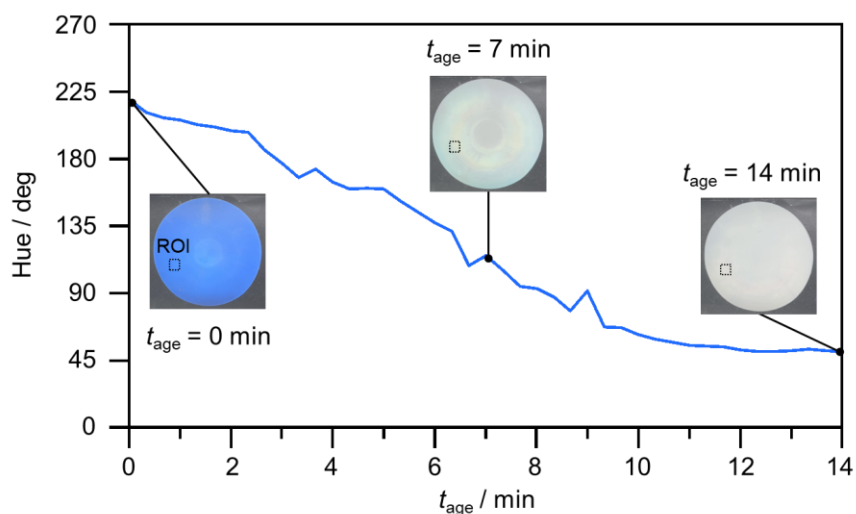


Supplementary Fig. 19.

CD spectra of Chol-C₁₂ recorded after shallow quenching (25 °C).

S3i. Temporal variation in hue degree of pressed Chol-C₁₂ (sheet-0)

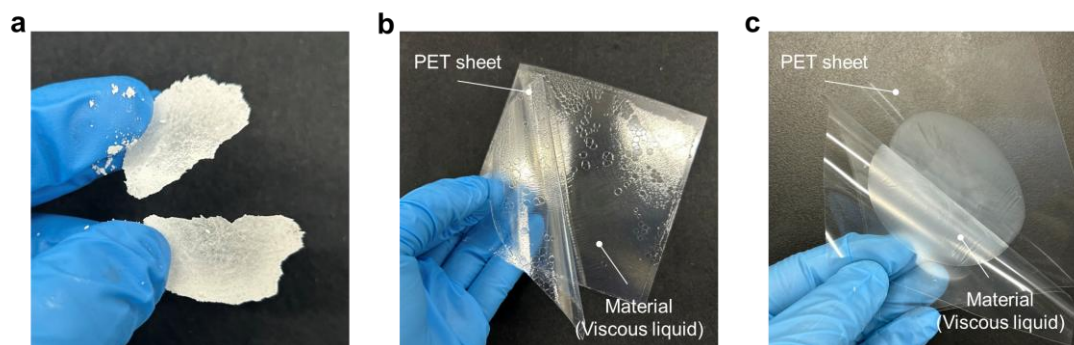
The colour information in the real-time video was quantified using the hue parameter. The video of pressed **Chol-C₁₂** (identified as sample **sheet-0** in the following paragraph of the main text) was sampled every 20 s, and the region of interest (ROI) from each extracted frame was converted from RGB (red, green, and blue) to the mean hue value in ImageJ (Fiji). These values were then rescaled to 360° scale (0° – 360°) from the 8-bit scale (0 – 255).



Supplementary Fig. 20.

Temporal variation in hue degree over a period of 14 min, indicating the disappearance of the selective reflection of chiral smectic LC phase upon cold crystallization.

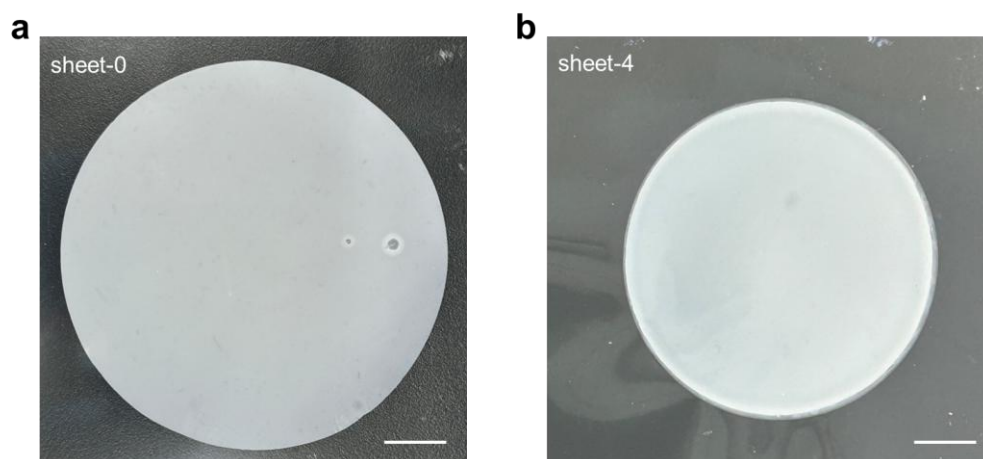
S3j. Comparison with another cholesteryl compound



Supplementary Fig. 21.

a-c, Cholesterol (a), cholesteryl oleyl carbonate (b), and a simple mixture of cholesterol and cholesteryl oleyl carbonate (1/1 in mol%) (c) were prepared under the same conditions as **sheet-0**. None of these materials were able to form a free-standing sheet.

S3k. Appearance of sheet-0 and sheet-4

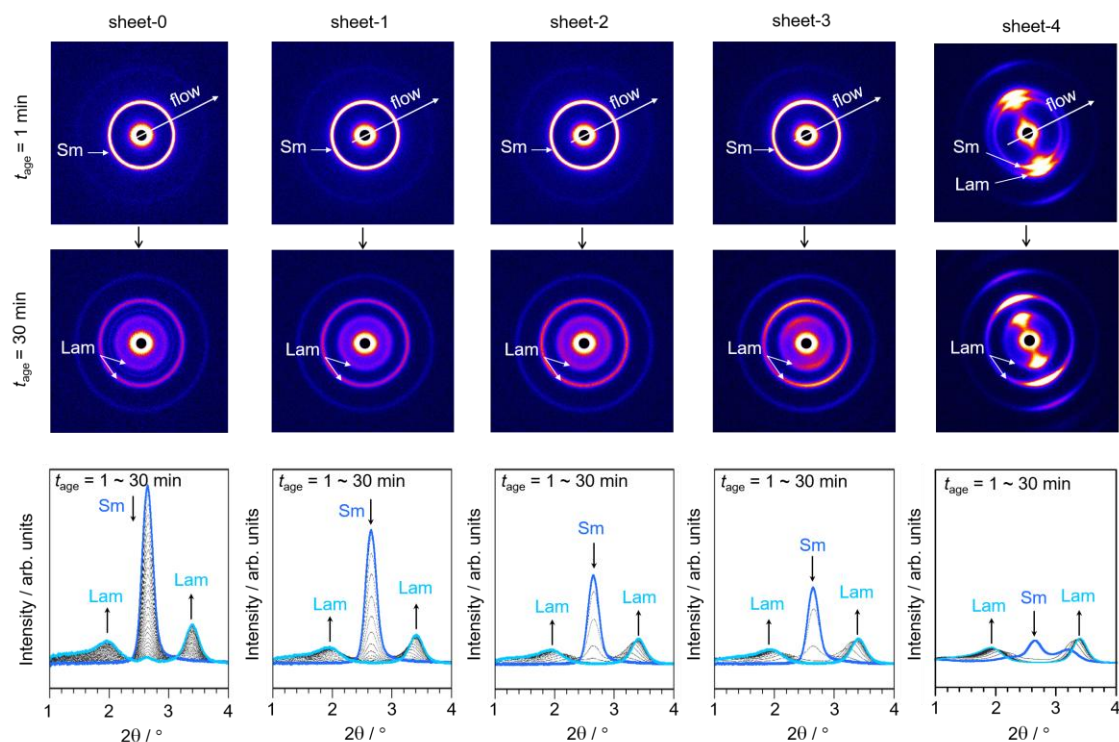


Supplementary Fig. 22.

a,b, The appearance of **sheet-0** (a) and **sheet-4** (b): scale bar = 2 cm.

S3I. Molecular alignment with different t_{inc}

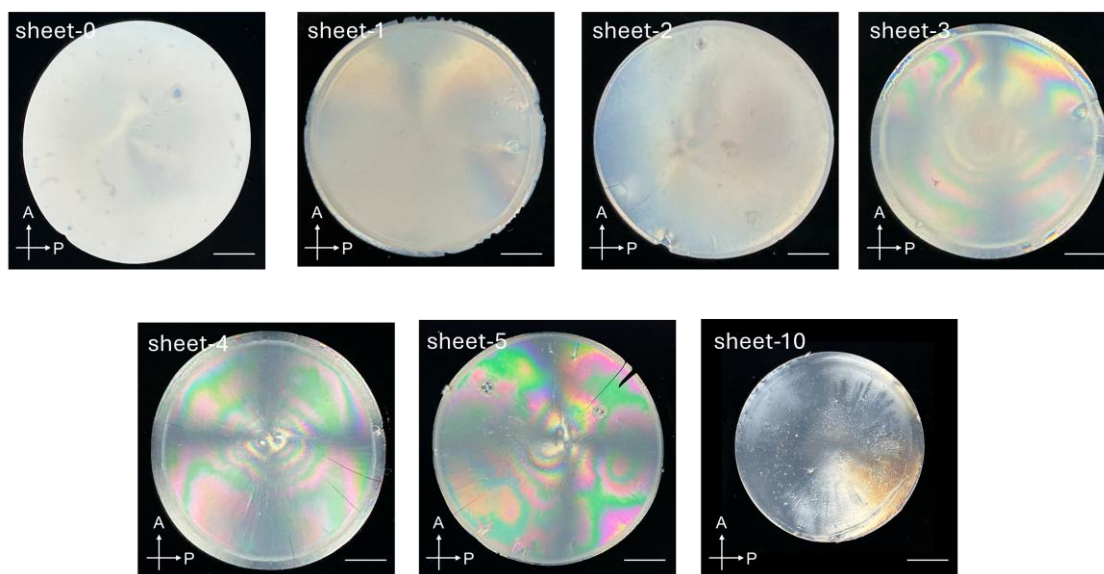
In this measurement, four PET films were used (two small pieces and two larger pieces). The metastable LC **Chol-C₁₂** sample was sandwiched between the two small pieces, then further laminated between two larger pieces. The stacked assembly was pressed at room temperature for 10 s. After compression, the two small pieces were peeled off and mounted directly onto a sample holder, followed by measurements performed at room temperature.



Supplementary Fig. 23.

2D-XRD images and time-dependent 1D-XRD spectra of **sheet- t_{inc}** ($t_{\text{inc}} = 0, 1, 2, 3$, and 4) obtained immediately after pressing ($t_{\text{age}} = 1 \text{ min}$) and after subsequent aging ($t_{\text{age}} = 30 \text{ min}$), upon exposure to an X-ray irradiation perpendicular to the sheets.

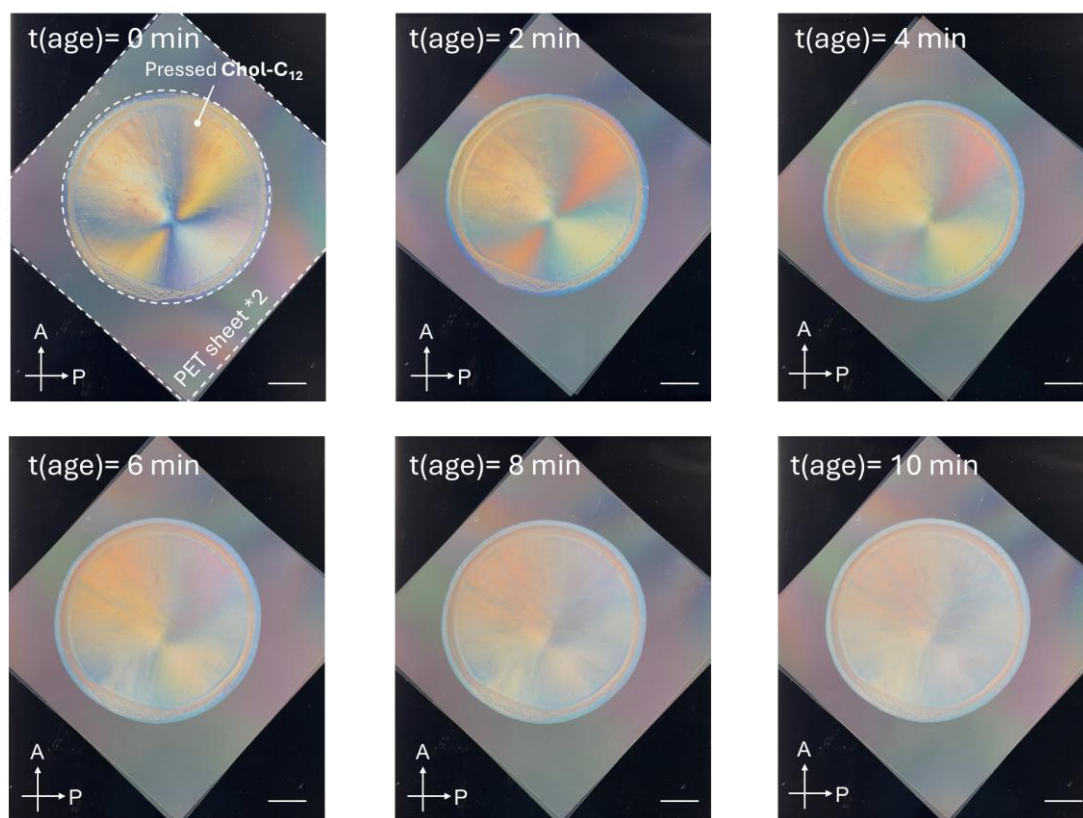
S3m. Polarized photographs of the obtained sheets with different t_{inc}



Supplementary Fig. 24.

Appearances of the obtained **sheet- t_{inc}** ($t_{inc} = 0, 1, 2, 3, 4, 5$, and 10) under crossed Nicols. Maltese cross patterns are absent in **sheet-0 to sheet-2** but faintly visible in **sheet-3**. **sheets-4 and sheet-5** exhibit distinct Maltese crosses, indicating macroscopic radial alignment of lamellae. In **sheet-10**, the pattern is no longer observed, which might be attributed to its higher crystallinity and resultant poor processability: scale bar = 2 cm.

S3n. Relaxation of molecular alignment via shallow quenching



Supplementary Fig. 25.

Time-dependent appearances of a **Chol-C₁₂** sheet prepared by compression after shallow quenching (25 °C) for $t_{\text{inc}} = 1 \text{ h}$. Observations were recorded from $t_{\text{age}} = 0 \text{ min}$ to 10 min. Due to the predominant LC phase of **Chol-C₁₂**, the sheet could not be detached from the PET sheets. The failure to preserve the induced orientation after compression demonstrated the alignment relaxation before the immobilization due to the sluggish crystallization: scale bar = 2 cm.

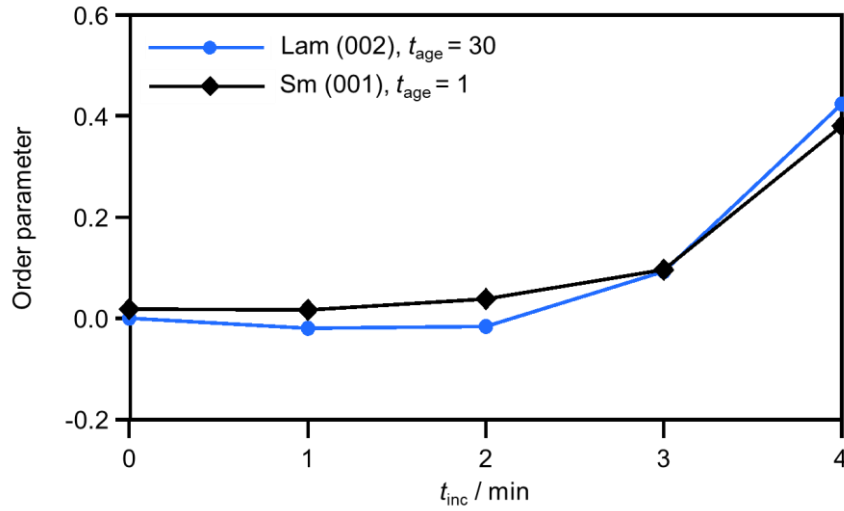
S3o. Order parameter (S) for various sheets (sheet-0 to sheet-4)

To characterize the degree of molecular alignment, the order parameter (S) was determined from the azimuthal (δ) - intensity (I) distributions which are extracted from the corresponding XRD patterns. Specifically, the (001) reflection was utilized for the smectic LC, as the (002) reflection was for the lamellae. The order parameter is given by^{S2}:

$$S = \frac{3\langle \cos^2 \delta \rangle - 1}{2}$$

,where

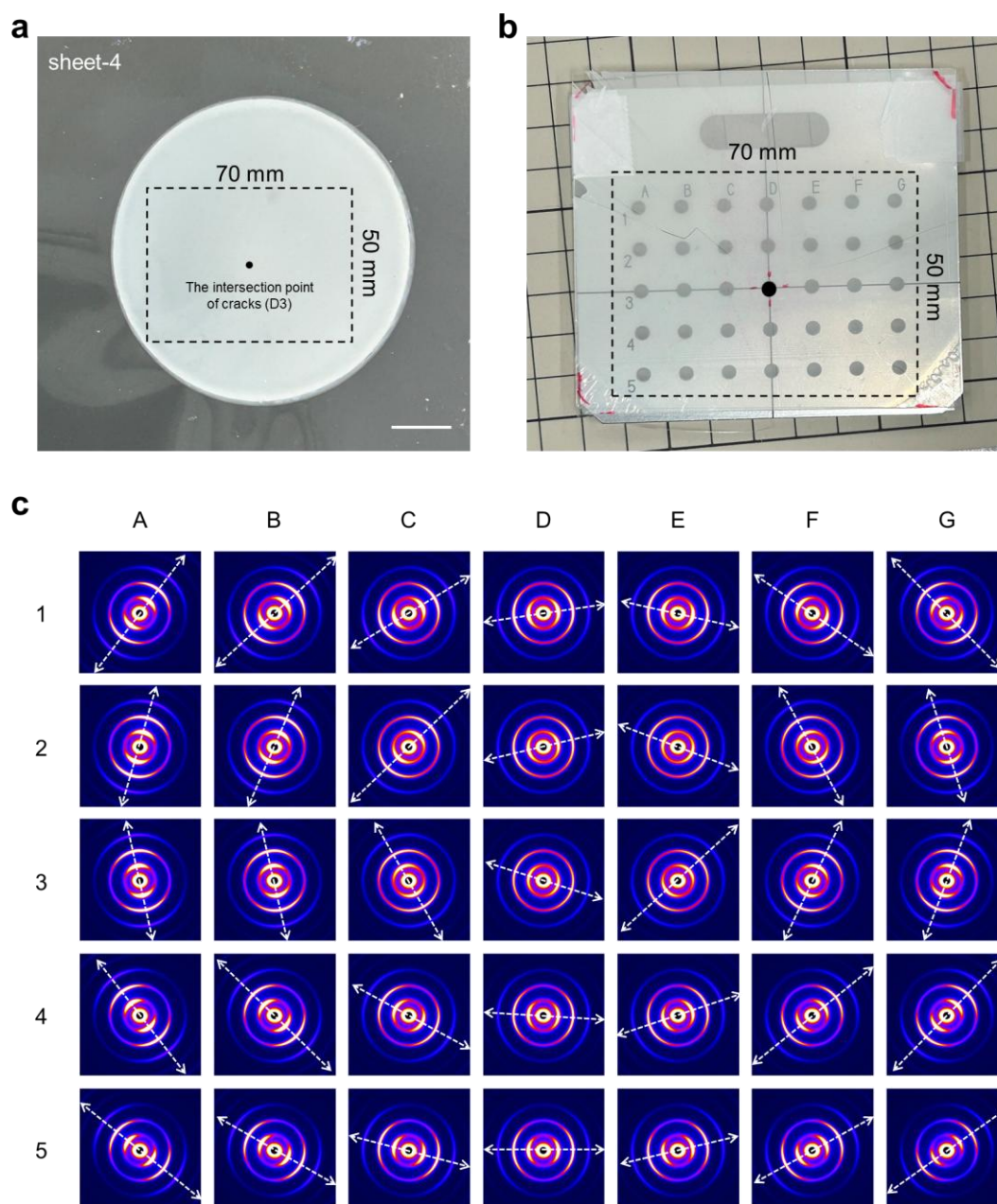
$$\langle \cos^2 \delta \rangle = \frac{\int_0^{\frac{\pi}{2}} I \cos^2 \delta \sin \delta d\delta}{\int_0^{\frac{\pi}{2}} I \sin \delta d\delta}$$



Supplementary Fig. 26.

Order parameter (S) of Lam (002) at tage = 30 min and Sm (001) at tage = 1 min for **sheet- t_{inc}** ($t_{\text{inc}} = 0, 1, 2, 3, 4$).

S3p. Macroscopic view of the molecular alignment in sheet-4

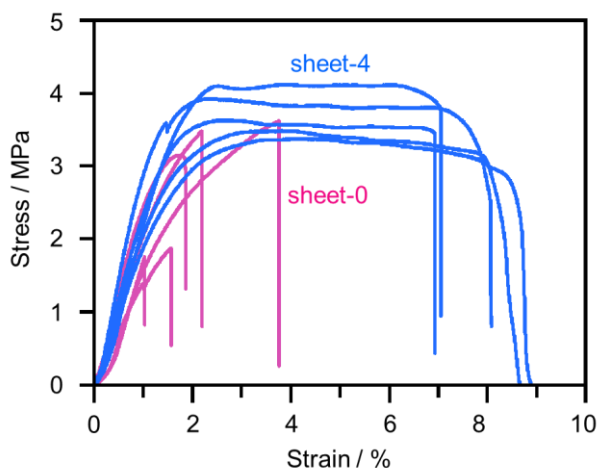


Supplementary Fig. 27.

a,b, After aligning the intersection point of cracks in **sheet-4** with the D3 position of the XRD sample stage: scale bar = 2 cm (a), a **sheet-4** was measured by 2D-XRD mapping measurement at 35 positions (7×5 grid) (b). As shown in **c**, the lamellar structures exhibit an orientation along the tangential direction (white double-headed arrow), indicating that the molecular alignment follows the flow direction.

S3q. Tensile testing results of sheet-0 and sheet-4

To minimize the influence of radial molecular orientation in wider samples, the **sheets** were cut into narrow strips (W 2 mm $\times$ L 24 mm) along the radial direction. For all tensile tests, each sample was then mounted onto a rectangular paper frame (W 10 mm $\times$ L 24 mm) featuring a central window (W 6 mm $\times$ L 10 mm). The top and bottom ends of the sample (7 mm) were attached to the frame using adhesive tape or glue. After mounting the samples onto the jigs, both sides of the paper frame were cut prior to the measurement to ensure that the load was applied uniaxially to the samples only.

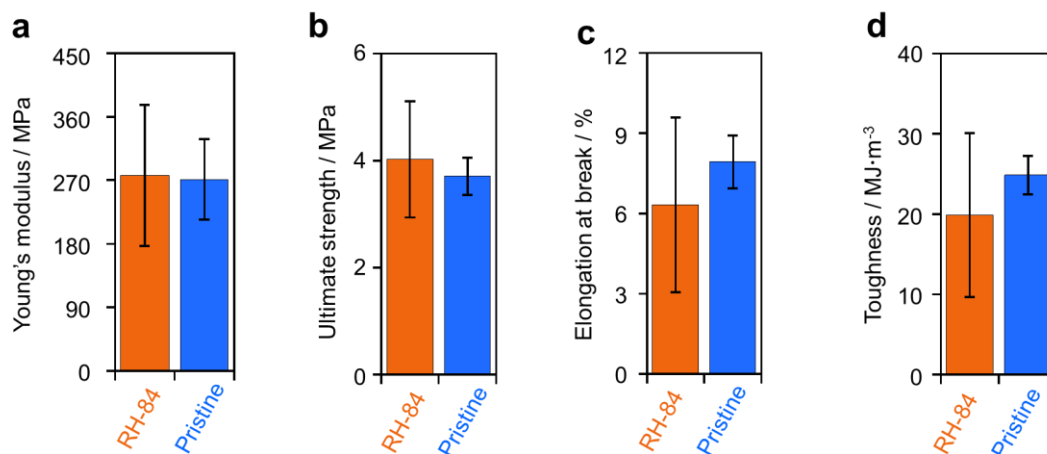


Supplementary Fig. 28.

Tensile stress–strain curves of **sheet-0** and **sheet-4** (strain rate = 0.1 min⁻¹, n = 5).

S3r. Tensile testing results after environmental moisture exposure

To generate a high-humidity environment,^{S2} the prepared **sheet-4**, a hygrometer, and a container of saturated brine were placed inside a transparent acrylic chamber. A brief vacuum (~30 s) was applied until the saturated brine began to boil, after which the vacuum was stopped applying. The humidity subsequently increased and stabilized at approximately 84% relative humidity (RH-84). **Sheet-4** was conditioned in this high-humidity environment for 24 h prior to tensile testing.

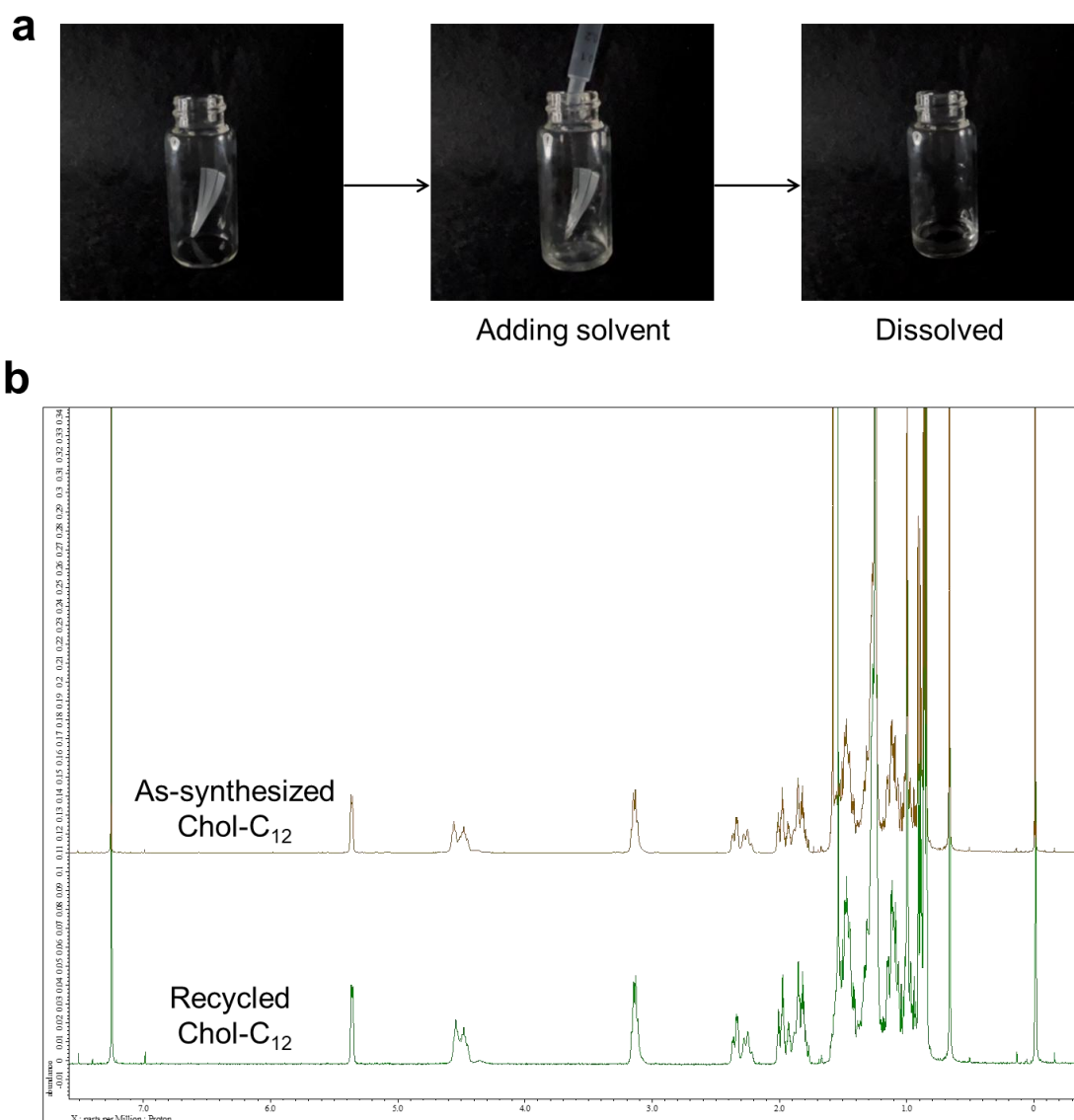


Supplementary Fig. 29.

a-d, Young's modulus (a), ultimate strength (b), elongation at break (c), and toughness of **sheet-4** (RH-84 and pristine) (d). The error bars represent 95% confidence intervals. (strain rate = 0.1 min⁻¹, n = 5). These results show that the mechanical properties of **Chol-C₁₂** exhibit only minimal changes under environmental humidity, demonstrating its durability against moisture exposure.

S3s. Recyclability of Chol-C₁₂

A part of **sheet-4** was placed in a sample vial, dissolved in 1 mL of CDCl₃, and analyzed by ¹H NMR spectral measurement (400 MHz).

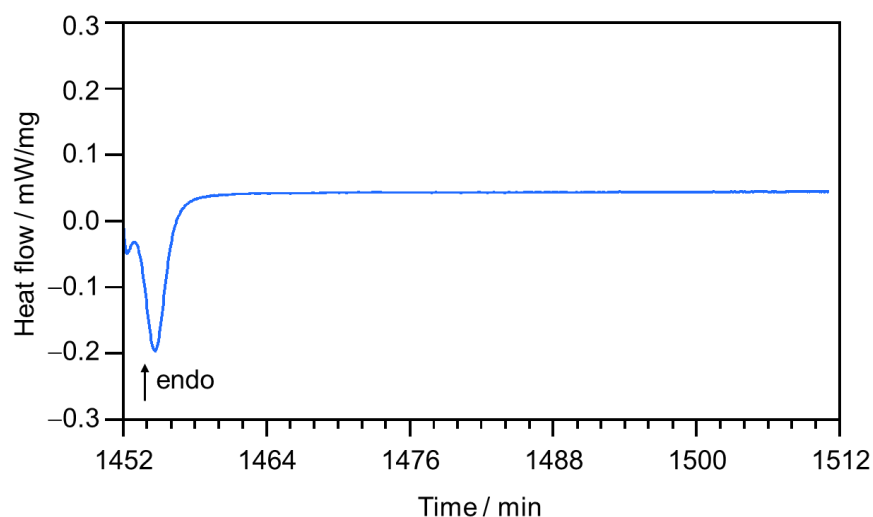


Supplementary Fig. 30.

a, The process of recycling **sheet-4**. **b**, ¹H NMR spectra (400 MHz) of a recycled Chol-C₁₂ from a processed **sheet-4** (green line) and as-synthesized Chol-C₁₂ (brown line) in CDCl₃ at 298 K.

S3t. Hibernation of metastable LC Chol-C₁₂

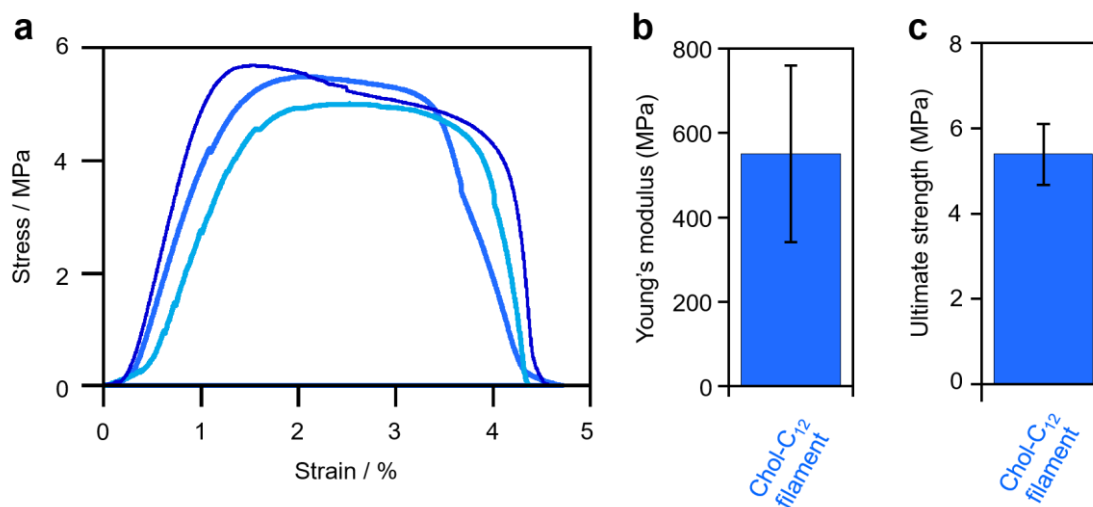
A **Chol-C₁₂** sample was first heated to 100 °C above its melting point to eliminate thermal history if any (5 min). It was then rapidly quenched to −50 °C at 50 °C/min (3 min) to kinetically arrest the material in a LC glassy state, and the temperature was maintained for 1 day (1440 min). Upon subsequent heating to 30 °C at 50 °C/min (1.6 min), isothermal crystallization occurred, indicating that **Chol-C₁₂** remains vitrified and unable to undergo crystallization when held below its glass-transition temperature.



Supplementary Fig. 31.

Isothermal DSC curve of the **Chol-C₁₂** sample incubated at 30 °C for 1 h after being previously frozen at −50 °C for 1 day (1440 min).

S3u. Tensile testing results of Chol-C₁₂ filaments



Supplementary Fig. 32.

a, Tensile stress–strain curves of **Chol-C₁₂** filaments (Ø1 mm × 24 mm) (strain rate = 0.1 min⁻¹, n = 3). **b,c**, Summary of the Young's modulus (**b**) and ultimate strength (**c**). The error bars represent 95% confidence intervals.

S4. Reference

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