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Chiral crystal-like droplets displaying unidirectional rotational sliding

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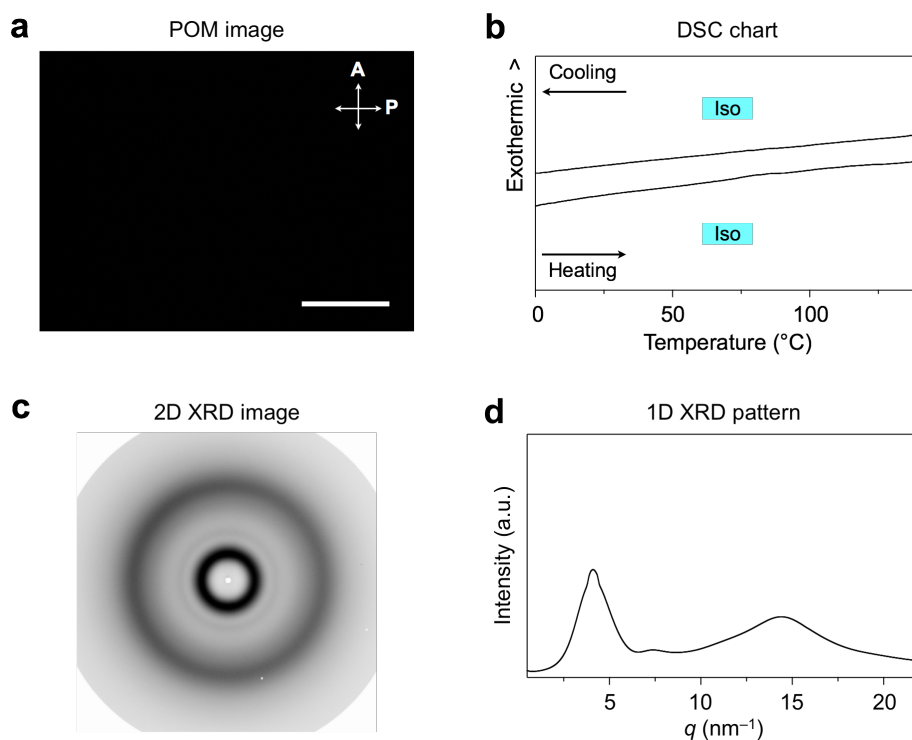
Supplementary Information

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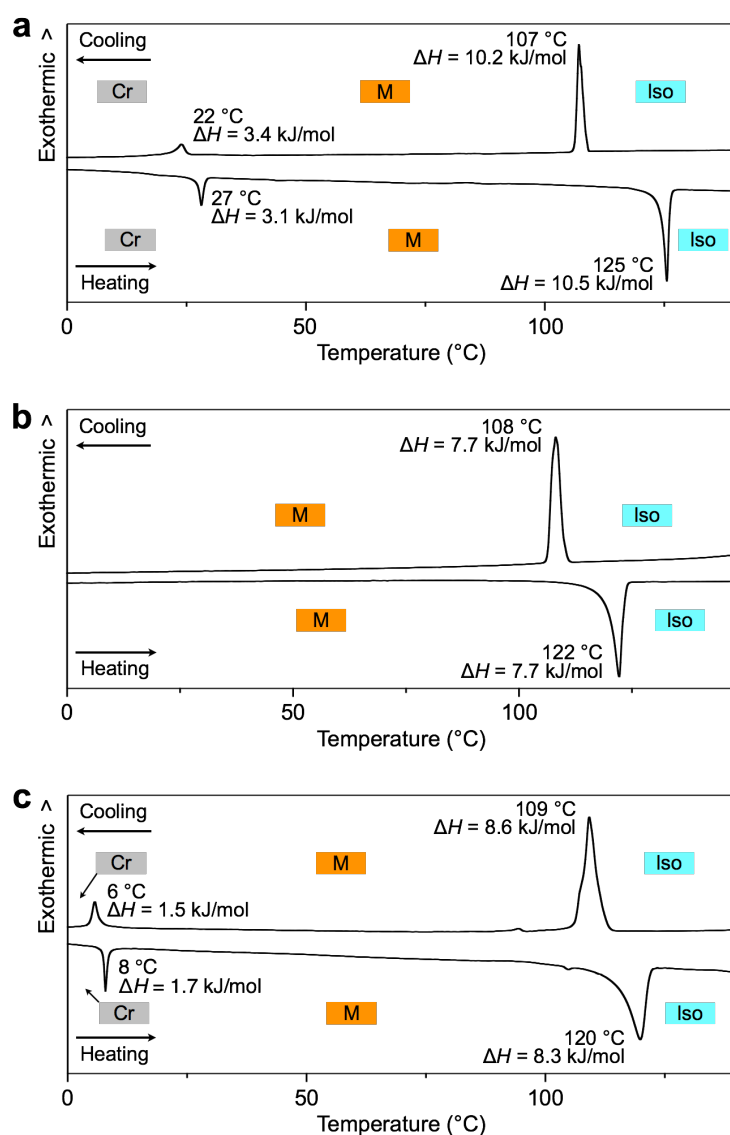
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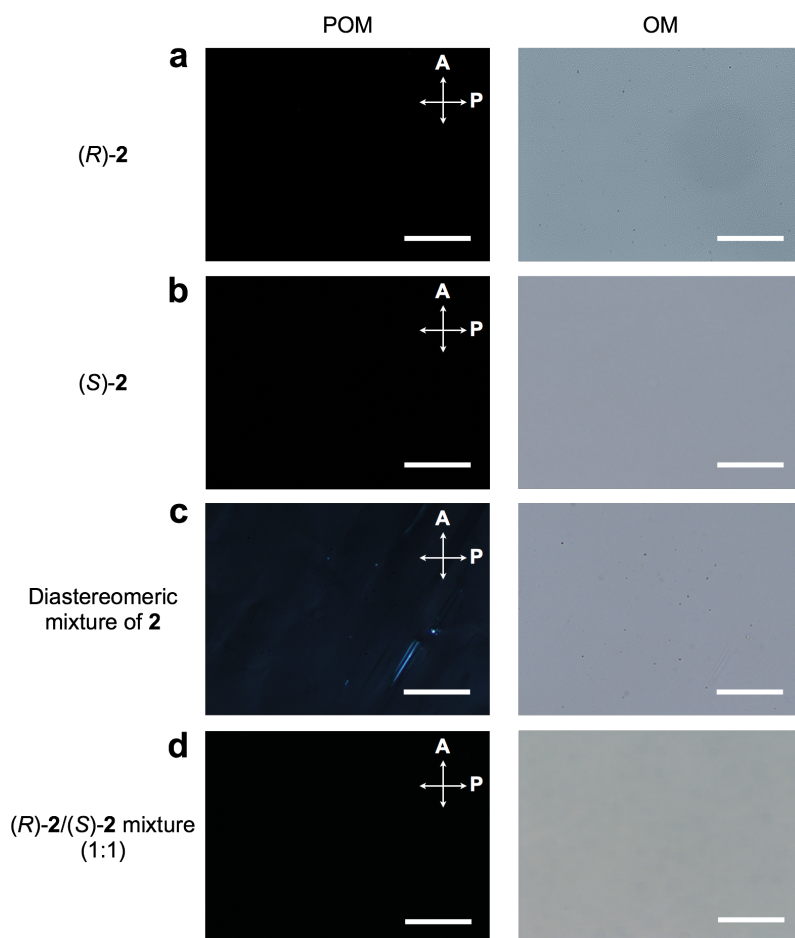
Supplementary Figures



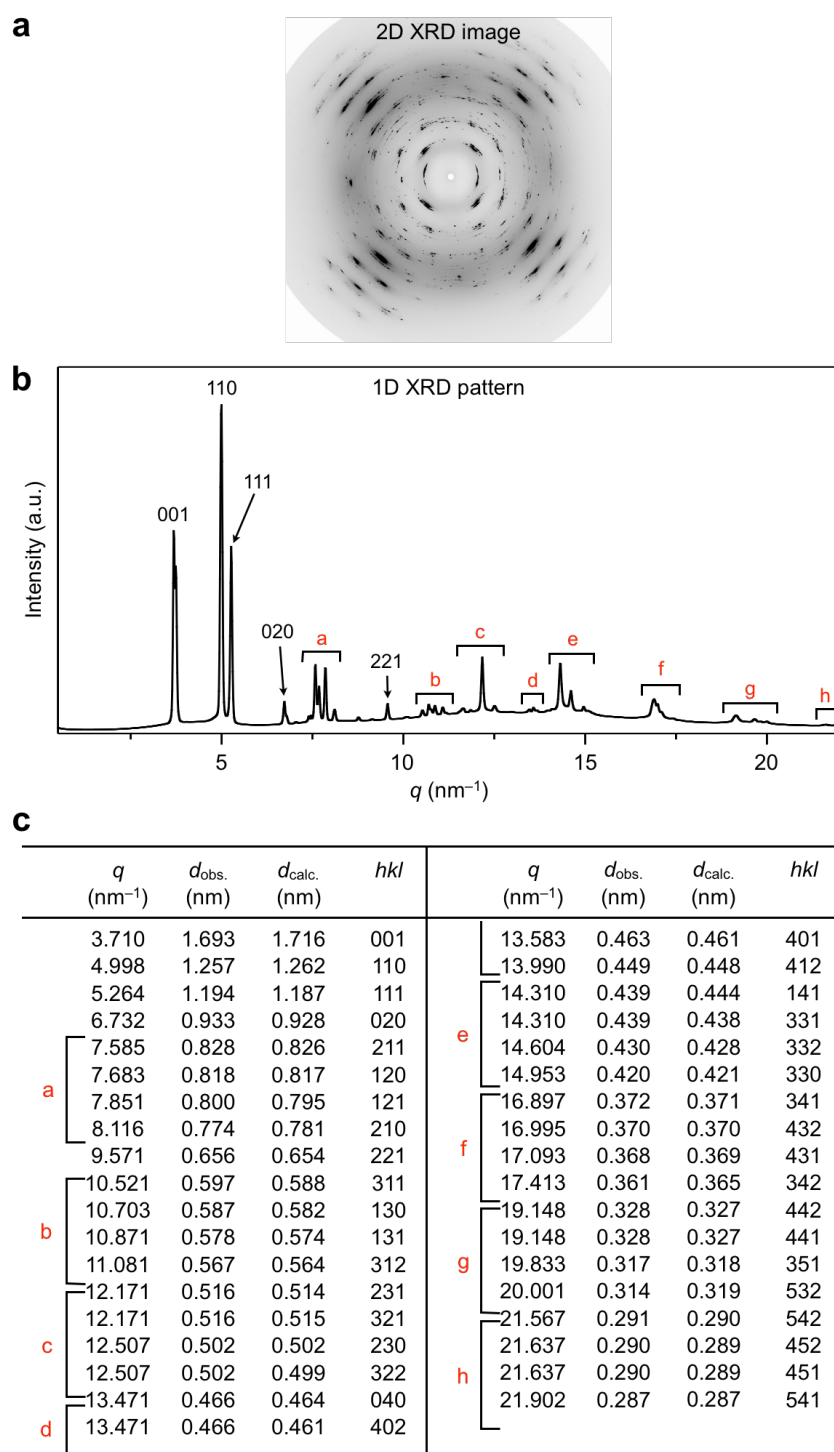
Supplementary Fig. 1 | Phase behaviour of (*R*)-3**.** **a**, Polarized optical micrograph (POM) of (*R*)-**3** at 30 °C; scale bar, 200 μm ; white arrows represent the transmission axes of the polarizer (P) and analyser (A). **b**, Differential scanning calorimetry (DSC) chart of (*R*)-**3**, measured at a scan rate of 10 °C/min (second heating/cooling cycle); Iso: isotropic liquid. **c**, Through-view two-dimensional (2D) X-ray diffraction (XRD) image of a bulk sample of (*R*)-**3** at 30 °C. **d**, One-dimensional (1D) XRD pattern obtained by converting the through-view 2D XRD image (**c**). The XRD profiles in (**c**) and (**d**) show a broad scattering feature, indicating that (*R*)-**3** is a liquid over a wide temperature range.



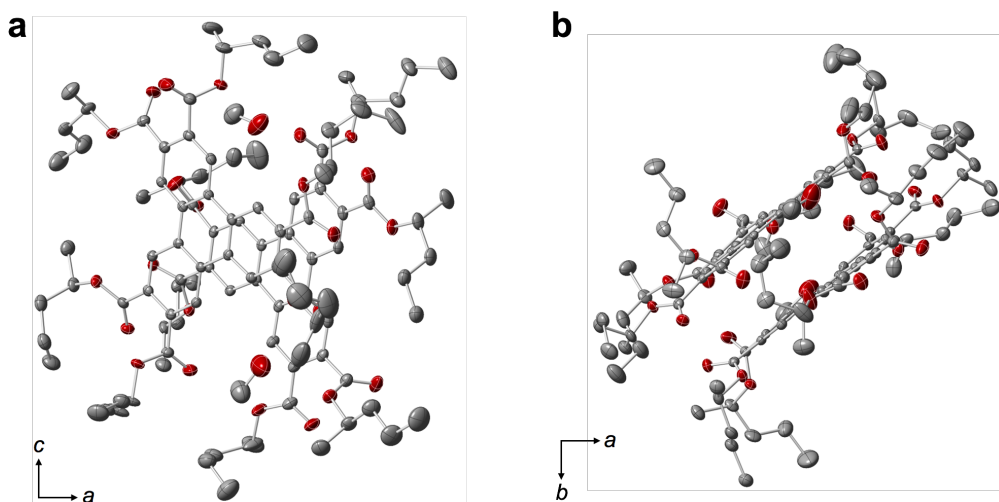
Supplementary Fig. 2 | DSC profiles. **a–c**, Enantiomerically pure **2** [(*R*)-**2**], **b**, a diastereomeric mixture of **2** and **c**, a 1:1 mixture of (*R*)-**2** and (*S*)-**2** measured at a scan rate of 10 °C/min (second heating/cooling cycle); Cr: crystal; M: mesophase (H^* phase); Iso: isotropic liquid.



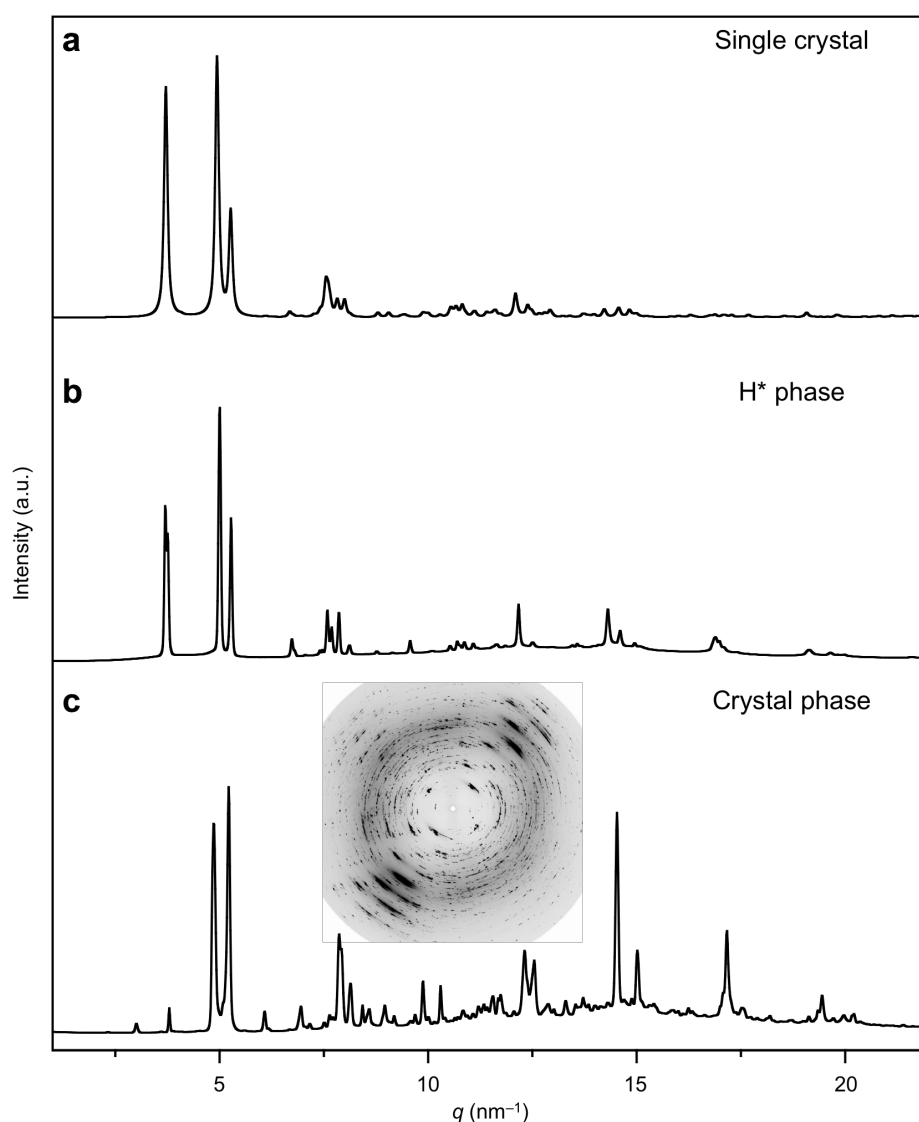
Supplementary Fig. 3 | POMs and optical micrographs (OMs). **a–d**, POMs (left) and OMs (right) of (*R*)-**2** (**a**), (*S*)-**2** (**b**), a diastereomeric mixture of **2** (**c**) and a 1:1 mixture of (*R*)-**2** and (*S*)-**2** (**d**). The samples were sandwiched between two glass substrates, heated once to their melting points and subsequently cooled to 30 °C; scale bars, 200 μm ; white arrows represent the transmission axes of the polarizer (P) and analyser (A). As described later in the main text, the mesophase of enantiomerically pure **2** was identified as H* phase with structural anisotropy, which would potentially display birefringence in POM. However, in the H* phase, the dimers of enantiomerically pure **2** are arranged in a herringbone-like manner to form a 2D sheet structure (Figs 1e and 2e). Due to multiple local orientations of the disc-shaped molecules in the 2D sheet, the optical anisotropy of the molecular assembly may become small, resulting in a nearly dark POM image.



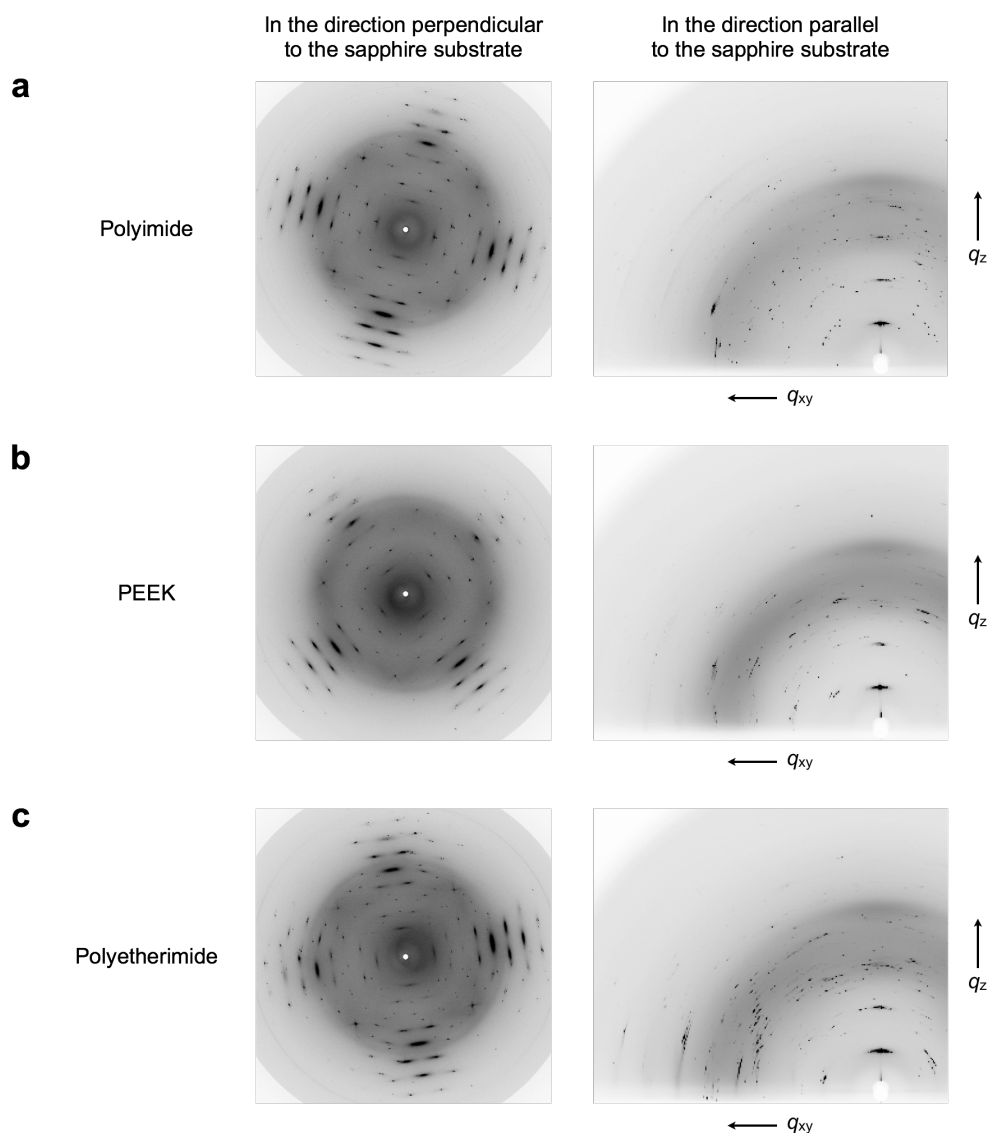
Supplementary Fig. 4 | XRD data of the mesophase (H^* phase) of (*S*)-2. **a**, Through-view 2D XRD image of a bulk sample of (*S*)-2 in a glass capillary (1.5 mm in diameter) at 105 °C upon cooling from its isotropic liquid phase; a.u., arbitrary units. **b,c**, 1D XRD pattern (**b**) obtained by converting the through-view 2D XRD image in **a** and its peak assignment (**c**); $P2_1$ monoclinic cell parameters of (*S*)-2 at 105 °C: $a = 1.861$ nm, $b = 1.855$ nm, $c = 1.856$ nm and $\beta = 112.39^\circ$.



Supplementary Fig. 5 | Crystal structure of (R) -2•MeOH (50% probability ellipsoids).
a,b, An asymmetric unit composed of a face-to-face dimer of (R) -2 and two molecules of MeOH, viewed along the directions of the b -axis (**a**) and the c -axis (**b**). For clarity, hydrogen atoms are not shown. Color code: carbon = gray, oxygen = red.

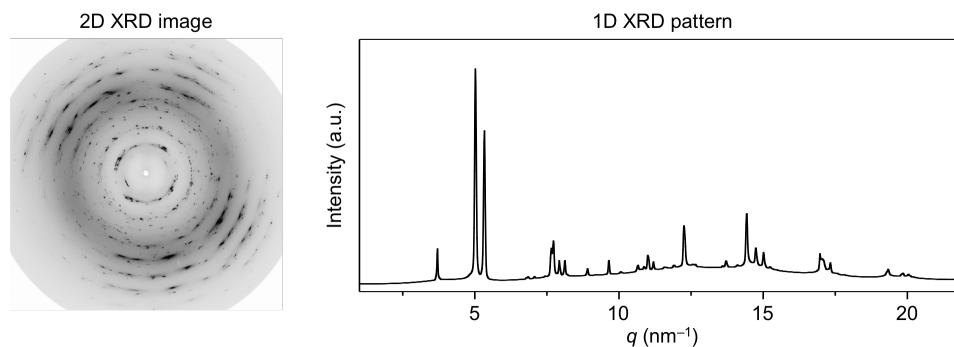


Supplementary Fig. 6 | 1D XRD patterns of enantiomerically pure 2. **a**, Calculated powder pattern using the crystallographic data for a (*R*)-**2**•MeOH single crystal. **b**, 1D XRD pattern of a bulk sample of (*S*)-**2** in a glass capillary (1.5 mm in diameter) at 105 °C. This profile is the same as that in Supplementary Fig. 4b and shown again for comparison. **c**, 1D XRD pattern of a bulk sample of (*S*)-**2** at 20 °C upon cooling from its isotropic liquid phase. This profile was obtained by converting a through-view 2D XRD image shown in the inset.

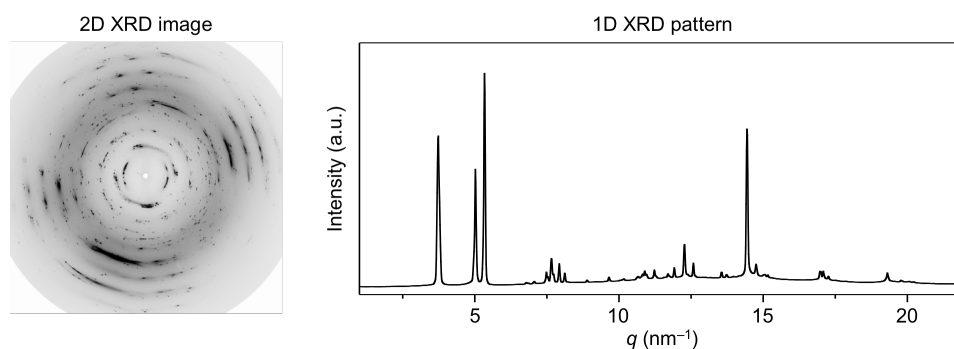


Supplementary Fig. 7 | XRD images of a droplet sample of (*R*)-2 in its H* phase (30 °C) on a polymer substrate. a–c, Through-view 2D XRD images obtained for a droplet sample on polyimide (**a**), polyetheretherketone (PEEK) (**b**) and polyetherimide (**c**) in the direction perpendicular (left) and parallel (right) to the substrate surfaces. The orientational behaviour of the molecular assembly is identical to those observed on inorganic substrates.

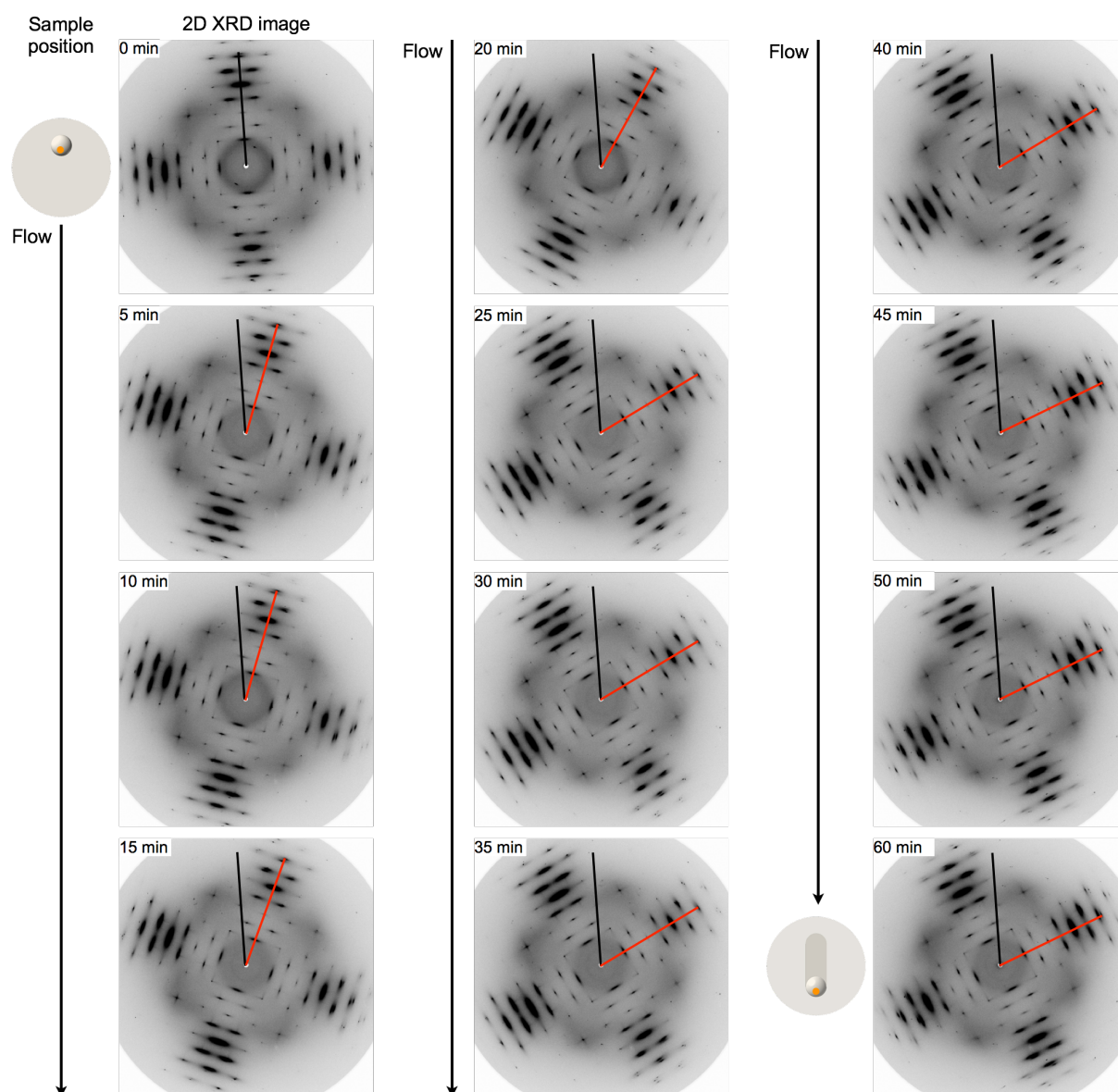
a Diastereomeric mixture of **2**



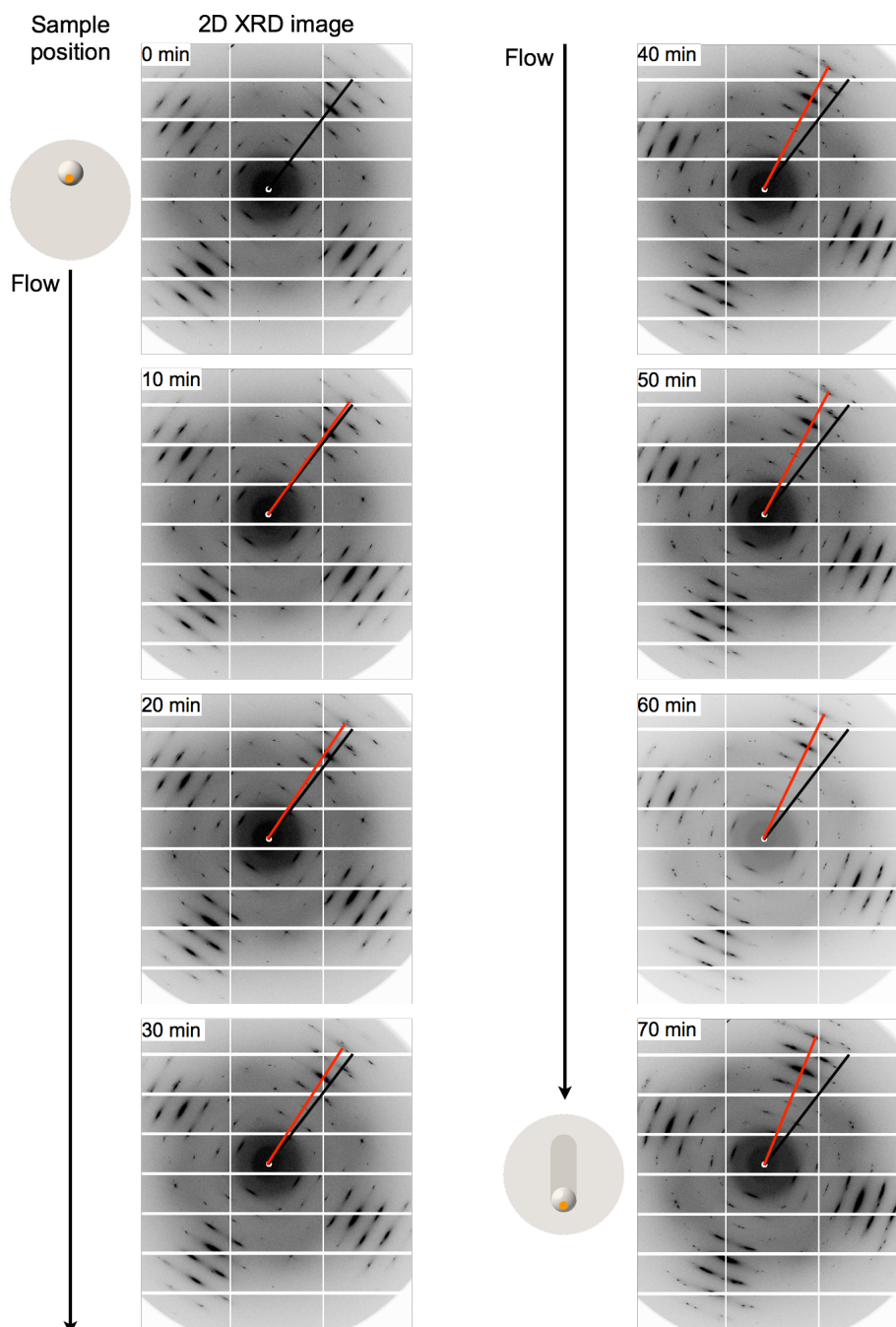
b (*R*)-**2**/*S*)-**2** mixture (1:1)



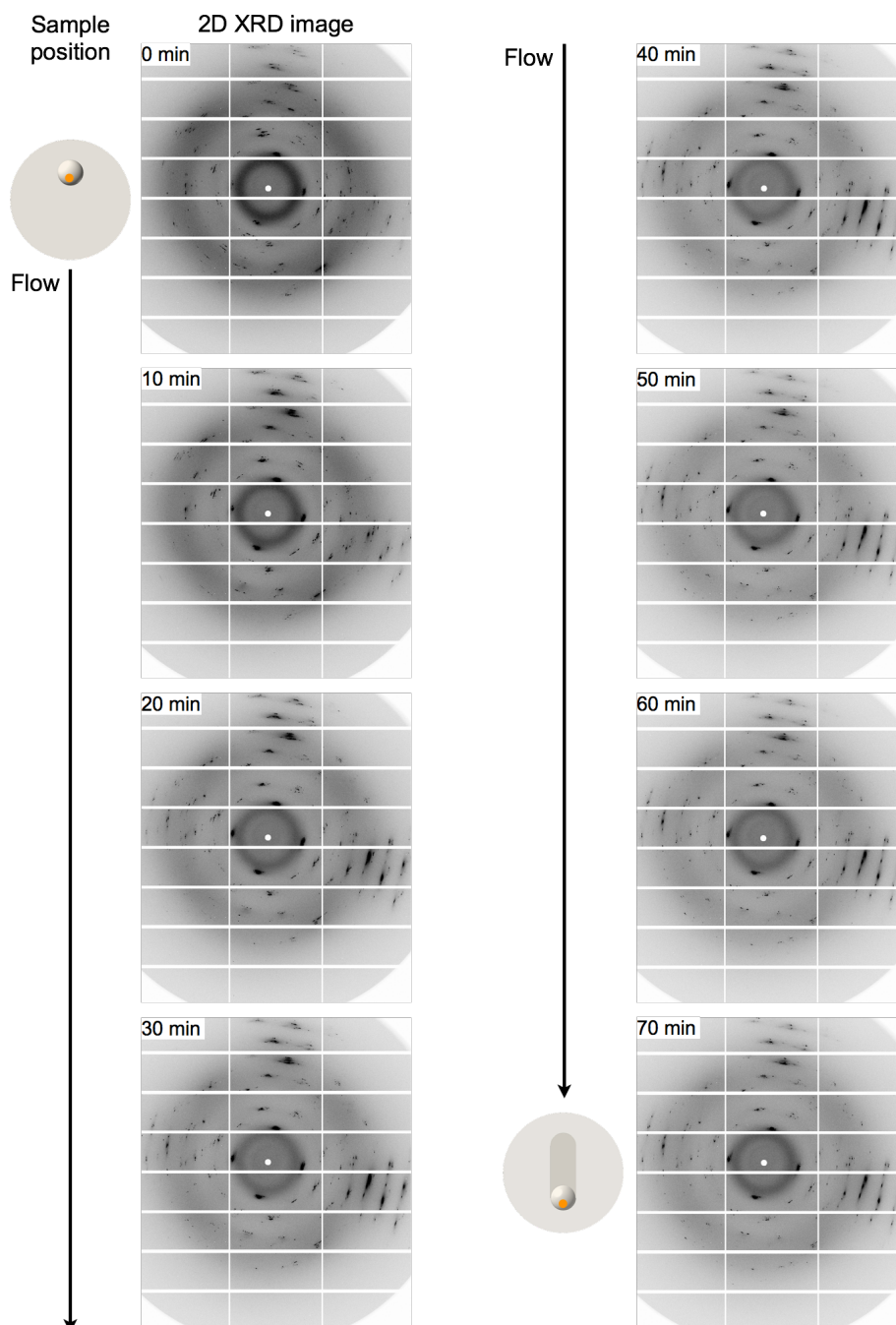
Supplementary Fig. 8 | Through-view 2D XRD images (left) and 1D XRD patterns (right) of the mesophase of a diastereomeric mixture of **2 and a 1:1 mixture of (*R*)-**2** and (*S*)-**2**.** **a,b**, Bulk samples of a diastereomeric mixture of **2** (**a**) and a 1:1 mixture of (*R*)-**2** and (*S*)-**2** (**b**) in a glass capillary (1.5 mm in diameter) at 105 °C upon cooling from their isotropic liquid phases; a.u., arbitrary units. The 1D XRD patterns were obtained by converting the corresponding through-view 2D XRD images.



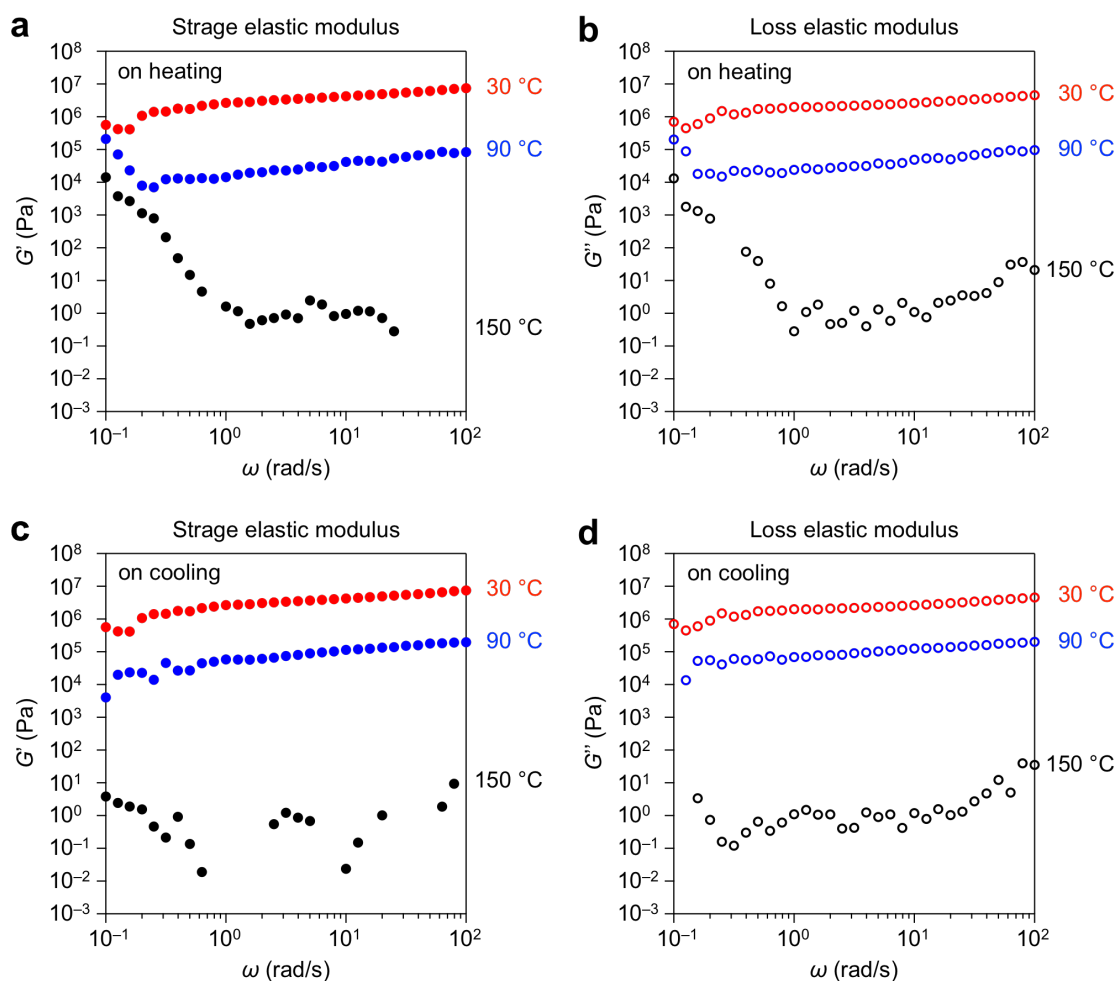
Supplementary Fig. 9 | Full data set of in situ through-view 2D XRD images of a droplet of (*R*)-2 sliding under the force of gravity. The droplet slid for 60 min at 105 °C (see also Fig. 3). An R-Axis IV++ (Rigaku) imaging-plate area detector was used for the measurement. The black (initial position) and red lines are a marker for showing the unidirectional rotating behaviour. Since the size of a droplet decreases upon sliding, the force of gravity received by the sliding droplet decreases, and eventually, when it cannot overcome the physical adsorption force between the material and substrate surface, the macroscopic sliding of the droplet stops.



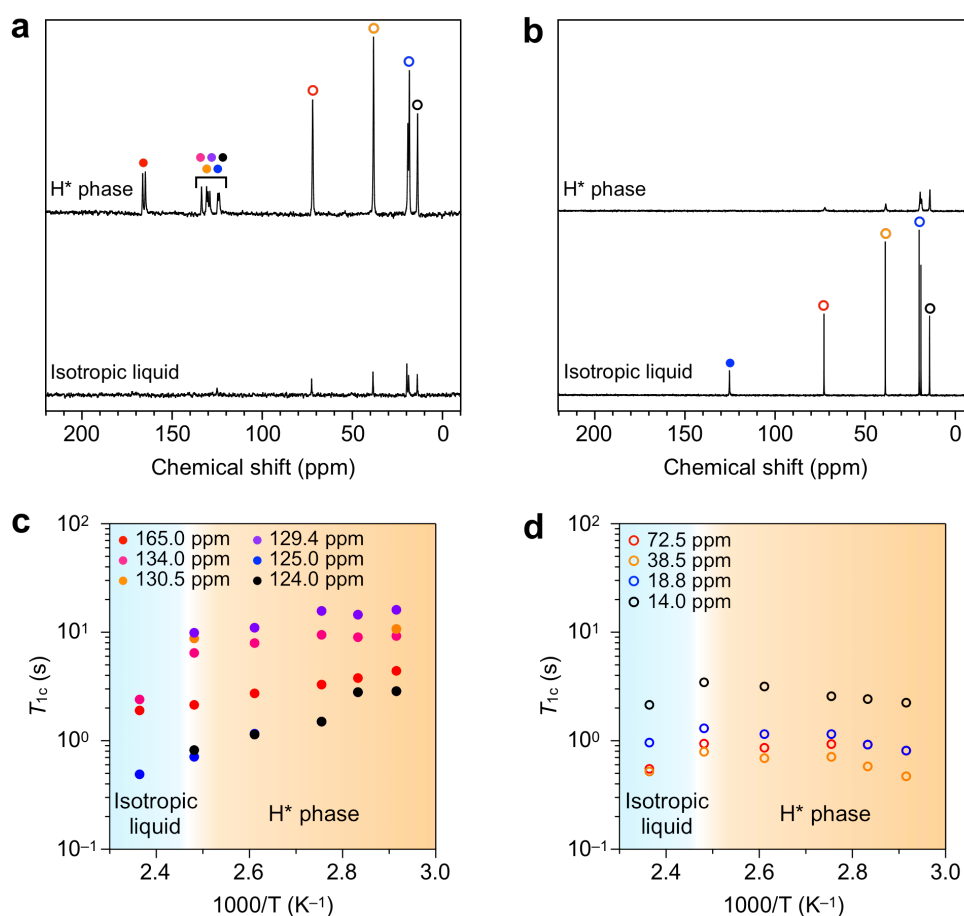
Supplementary Fig. 10 | In situ through-view 2D XRD images of a droplet of (S)-2 sliding under the force of gravity. The droplet slid for 70 min at 105 °C. A Pilatus3X 2M (Dectris) detector was used for the measurement. The black (initial position) and red lines are a marker for showing the unidirectional rotating behaviour. Since the size of a droplet decreases upon sliding, the force of gravity received by the sliding droplet decreases, and eventually, when it cannot overcome the physical adsorption force between the material and substrate surface, the macroscopic sliding of the droplet stops.



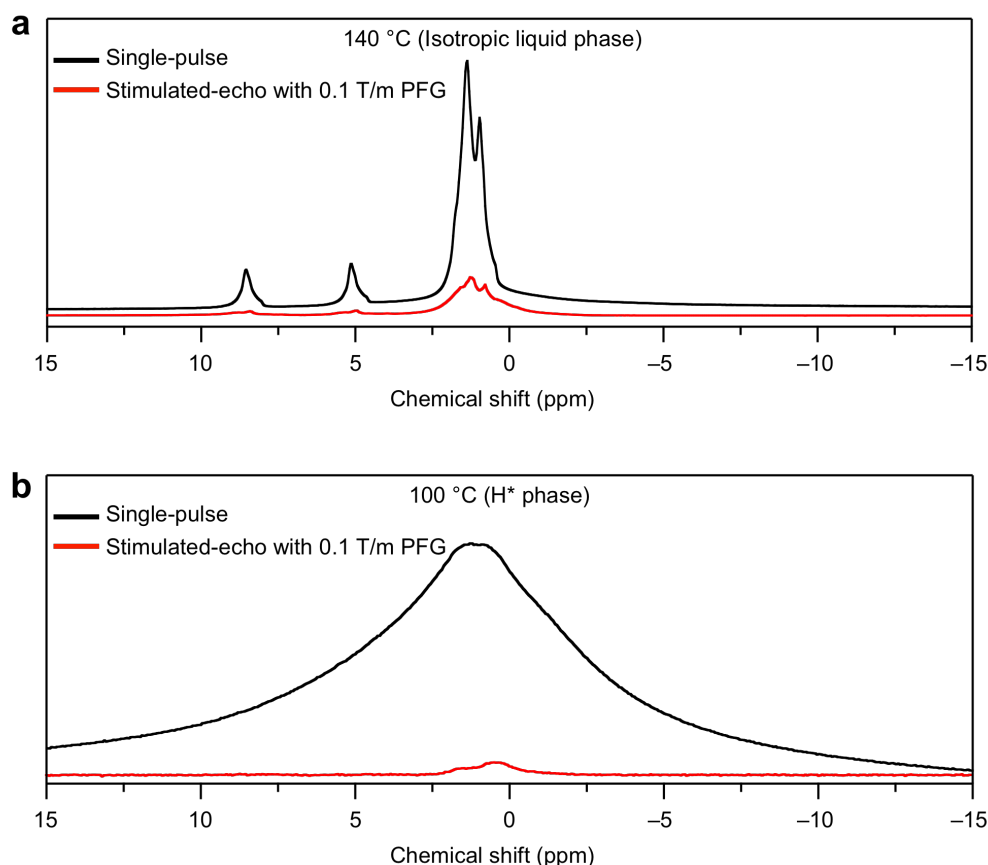
Supplementary Fig. 11 | In situ through-view 2D XRD images of a droplet of an equimolar mixture of (*R*)-2 and (*S*)-2 sliding under the force of gravity. The droplet slid for 70 min at 105 °C. A Pilatus3X 2M (Dectris) detector was used for the measurement. Since the size of a droplet decreases upon sliding, the force of gravity received by the sliding droplet decreases, and eventually, when it cannot overcome the physical adsorption force between the material and substrate surface, the macroscopic sliding of the droplet stops.



Supplementary Fig. 12 | Rheological properties of (R)-2. **a–d**, Angular frequency dependence of the storage elastic modulus (G') (**a,c**) and the loss elastic modulus (G'') (**b,d**) of (R)-2 observed under an applied strain (γ) of 0.1 at 30 °C (red), 90 °C (blue) and 150 °C (black) in a second heating (**a,b**) and cooling (**c,d**) cycle.



Supplementary Fig. 13 | Solid-state ^{13}C cross-polarization with magic-angle spinning (CP/MAS) and refocused insensitive nuclei enhanced by polarization transfer (RINEPT) spectral profiles. **a,b**, CP/MAS (**a**) and RINEPT (**b**) spectra of (*R*)-**2** in the H* phase (top) and the isotropic liquid phase (bottom), where the former technique can effectively detect immobile or ordered carbon atoms, while the latter technique allows the detection of very mobile carbon atoms¹. **c,d**, Plots of ^{13}C spin-lattice relaxation time (T_{1c}) versus $1000/T$ K⁻¹ for (**c**) the carbonyl (165.0 ppm) and aromatic carbons and (**d**) the aliphatic carbons of (*R*)-**2**. The ^{13}C spin-lattice relaxation measurements in the range of the temperatures of H*-phase provided an insight into the mobility of the segments of (*R*)-**2**. As the temperature was increased, the T_{1c} values of the aliphatic carbons increased. According to the Bloembergen-Pound-Purcell (BPP) theory², this tendency indicates that the alkyl side chains of (*R*)-**2** behave like a liquid. On the other hand, the T_{1c} values of the carbonyl and aromatic carbons decreased with increasing temperature, and thus, the triphenylene core behaves like a solid.



Supplementary Fig. 14 | Pulsed-field-gradient spin-echo (PGSE) NMR measurements of (S)-2. **a,b**, Single-pulse (black) and stimulated-echo with pulsed-field gradient (PFG) of 0.1 T/m (red) ^1H NMR spectra of (S)-2 at **(a)** 140 °C and **(b)** 100 °C upon cooling (cooling rate: 1 °C/min). Compound (S)-2 in the isotropic liquid phase (at 140 °C) displayed four peaks in a single-pulse ^1H NMR spectrum. Using a ^1H PGSE method under conditions in which diffusion time (Δ), PFG pulse length (δ) and PFG strength were 100 ms, 1 ms and 0.1–5.0 tesla/m, respectively, the self-diffusion coefficient (D) of (S)-2 in the isotropic liquid phase (T_2 : ca. 10 ms) was determined to be $6.4 \times 10^{-12} \text{ m}^2/\text{s}$. Upon cooling from the isotropic liquid phase to the H* phase (100 °C), a single-pulse ^1H spectrum significantly broadened due to ^1H - ^1H dipolar interaction, indicating that (S)-2 in the H* phase undergoes extremely fast decaying transverse magnetization ($T_2 < 1 \text{ ms}$).

Supplementary References

1. Morris, G. A., Freeman, R. Enhancement of nuclear magnetic resonance signals by polarization transfer. *J. Am. Chem. Soc.* **101**, 760–762 (1979).
2. Bloembergen, N., Purcell, E., Pound, R. Relaxation effects in nuclear magnetic resonance absorption. *Phys. Rev.* **73**, 679–712 (1948).