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Knotting a molecular strand can invert macroscopic effects of chirality

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Transferring structural information from the nanoscale to the macroscale is a promising strategy for developing adaptive and dynamic materials. Here we demonstrate that the knotting and unknotting of a molecular strand can be used to control, and even invert, the handedness of a helical organization within a liquid crystal. An oligodentate tris(2,6-pyridinedicarboxamide) strand with six point-chiral centres folds into an overhand knot of single handedness upon coordination to lanthanide ions, both in isotropic solutions and in liquid crystals. In achiral liquid crystals, dopant knotted and unknotted strands induce supramolecular helical organizations of opposite handedness, with dynamic switching achievable through in situ knotting and unknotting events. Tying the molecular knot transmits information regarding asymmetry across length scales, from Euclidean point chirality (constitutional chirality) via molecular entanglement (conformation) to liquid-crystal (centimetre-scale) chirality. The magnitude of the effect induced by the tying of the molecular knots is similar to that famously used to rotate a glass rod on the surface of a liquid crystal by synthetic molecular motors.

The tying of a knot can be considered a special kind of folding that causes entangled strand regions to become mechanically restricted in their positions with respect to others, unable to pass through the strand backbone. Knotted strands are found in some proteins¹ and DNA², and form spontaneously in any polymer of sufficient length and flexibility³. At the nanoscale, such chain entanglements have been found to influence the volume, stability and mechanical properties of individual molecules^{4–7}, but the consequences that molecular-level knotting can have for larger assemblies and at greater length scales have received less attention^{8–11}. The transmission of structural information from molecules to the macroscale generally requires hierarchical interactions, such as those present in supramolecular polymers^{12–14}, at interfaces¹⁵, in rigid three-dimensional frameworks^{16,17} or in liquid crystals^{18–22}. Chirality is often a key component of such information transfer^{23–25}. Recently, it was demonstrated that weak electric fields can induce micrometre-sized knotted defect lines in a chiral liquid crystal^{26–28}. Here we investigate effects induced by tying a nanometre-sized molecular strand into an overhand knot of single handedness in the anisotropic environment provided by a liquid crystal.

In recent years, a number of synthetic molecular knots have been prepared^{29–41}. One class of knot-forming molecules is based on a tris(2,6-pyridinedicarboxamide) motif, that is, three tridentate groups joined in a linear thread. Such strands can be folded into overhand-knotted conformations—that is, trefoil knots with open ends—through coordination to lanthanide(III) ions^{42–46}. Inserting a series of chiral centres into the strand causes only one handedness of the entanglement to form, as the steric limitations imposed by the substituents enforce a single helical orientation around the Ln(III) core⁴⁵. The coordination-induced knotting restricts the degrees of freedom of the strand and results in a substantial change in the chiral environments of the aromatic rings, as evidenced by circular dichroism (CD) spectroscopy⁴⁶.

We decided to investigate whether the changes in structural asymmetry resulting from tying such a knotted conformation can be expressed in soft matter and, if so, what and how large the effects of such a transformation can be. Liquid crystals are media in which chirality can be transmitted to larger length scales effectively because of their inherent anisotropy, their long-range order and their responsiveness to small changes in chemical composition. In nematic liquid crystals, individual molecules are oriented preferentially along a ‘director’ vector with their centres of mass randomly distributed⁴⁷. When a small amount of a chiral dopant is added, a chiral nematic (cholesteric) liquid crystal is formed, characterized by helical organization of the molecules on a length scale ranging from nanometres to centimetres. At low concentrations of dopant, small changes can lead to substantial differences in the helical pitch, p , according to equation (1):

$$\text{HTP} = (c \times p \times \text{e.e.})^{-1} \quad (1)$$

where HTP is the helical twisting power (positive value for right-handed chiral nematic phases; negative for left-handed chiral nematic phases), e.e. is enantiomeric excess and c is the concentration of chiral dopant.

Inverting the handedness of chiral nematic liquid crystals by means of external stimuli has the potential to support information transmission in dynamic responsive systems^{25,48–50} as well as developments in the fields of optoelectronics, photonics and sensors^{51,52}. However, inverting the effective handedness of a molecular shape requires a large, and usually energetically demanding, structural change: to give a macroscopic analogy, a left hand cannot become right-handed through a trivial process such as threading a ring onto a finger; a much more drastic transformation of the collective structure of the palm and digits is necessary for them to preferentially fit into a right-handed glove. To date only a few chiral dopants have been shown to drive in situ inversion of liquid crystal pitch

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handedness^{18,25,50,51,53,54}, and they all use light and/or heat as the switching stimulus. Here we show that a metal-coordinated molecular overhand-knot dopant induces a twist in an otherwise achiral liquid crystal. We find that the changes in asymmetry of the strand caused by the metal-ion-induced knot tying produces large changes in helical twisting power, by modifying the pitch and switching the handedness of the liquid crystal (Fig. 1). This work demonstrates that folding a molecular strand into a well-defined entanglement whose asymmetry is well expressed to its immediate environment can be used to transmit chiral information across length scales.

Results and discussion

Effective chirality transmission from molecules to a liquid crystal requires effective intermolecular interactions between the achiral liquid crystal molecules and the chiral dopant. We tried to engineer such compatibility into our designs of dopant strands (1–3), including incorporating into two of them (2 and 3) structural features reminiscent of liquid-crystal-forming molecules. The three strands used (1–3) are shown in Fig. 2 (for their synthesis and characterization, see Supplementary Information Section 5.1). Solutions of each of 1–3 in MeCN were treated with one equivalent of Lu(OTf)₃ and stirred at 80 °C for 16 h, at which point the formation of the ligand-metal complexes (Λ -Lu1, Λ -Lu2 and Λ -Lu3) was confirmed by electrospray ionization mass spectrometry (ESI-MS) and ¹H nuclear magnetic resonance (NMR) spectroscopy. Complexes Λ -Lu1 and Λ -Lu2 were isolated in 62% and 51% yield, respectively, by trituration with CH₂Cl₂. By contrast, analysis of the product mixture from the reaction of 3, which bears the most rigid and sterically demanding end groups, with Lu(OTf)₃ indicated only partial formation of overhand knot Λ -Lu3. Accordingly, an additional step of size exclusion chromatography was required to purify Λ -Lu3, which was isolated in 16% overall yield.

The ¹H NMR and CD spectra of Λ -Lu1–3 (for example, Fig. 3) bear a close similarity to those of related lanthanide-coordinated trefoil knots whose structures have been confirmed by X-ray crystallography. Due to the conformational constraints induced by the entanglement, several NMR shifts characteristic of the

Fig. 1 | Doping nematic liquid crystals with molecular strands and knots.

Addition of a molecular strand featuring point-chiral centres as a dopant to an achiral liquid crystal results in a chiral nematic phase. Addition of the same strand in the form of an overhand knot coordinated to a metal ion leads to helix inversion and a pitch change in the liquid crystal.

overhand-knot structure are apparent for Λ -Lu1–3 (for example, the signals for the H₂ protons on both terminal coordinating motifs shift from 8.0 to 6.2 ppm due to π - π interactions with adjacent aromatic rings). The wrapping of the tris(2,6-pyridinedicarboxamide) motif

Fig. 2 | Entanglement of molecular strands into overhand knots. The knotting and unknotting of molecular strands 1–3 is brought about by complexation and removal, respectively, of lutetium(III) ions. Reagents and conditions (acetonitrile solution): (i) Lu(OTf)₃, MeCN, 80 °C (Λ -Lu1 62%, Λ -Lu2 51%, Λ -Lu3 16%). (ii) Me₄NF, MeCN, room temperature (quantitative). For the same transformations carried out in liquid crystal ZLI-1083, see Fig. 5. For synthetic procedures and characterization data, see Supplementary Information Section 5.1.

Fig. 3 | Solution-phase characterization of ligand strands and overhand knots. **a**, ^1H NMR spectrum (600 MHz, 298 K, CDCl_3) of strand **1**, highlighting the high degree of symmetry in the strand. **b**, ^1H NMR spectrum (600 MHz, 298 K, MeCN-d_3) of overhand knot $\Lambda\text{-Lu1}$. The reduction of symmetry, and corresponding increase in number of signals, in spectrum **b** compared to spectrum **a** indicates well-expressed diastereotopic proton environments in $\Lambda\text{-Lu1}$ due to the chiral knotted shape. Chemical shift differences between **a** and **b** of various protons, for example H_i , H_j and $\text{H}_{i'}$, are characteristic of the unfolded versus knotted environments of the two structures^{45,46}. **c**, CD spectra of overhand knots $\Lambda\text{-Lu1}$, $\Lambda\text{-Lu2}$ and $\Lambda\text{-Lu3}$ (MeCN , 0.1 mM). **d**, CD spectra of strands **1–3** (CH_2Cl_2 , 0.025 mM). The CD spectra in **c** and **d** show a difference in chiral expression in isotropic solution between the unconstrained molecular strands and the corresponding folded knotted conformations. $\Delta\epsilon$, molar circular dichroism; λ , wavelength.

around the Lu(III) ion occurs stereoselectively, with an Λ -helical orientation when the strand has (*R*)-stereocentres. The CD spectra reflect the difference in the chiral environments experienced by the chromophores in the overhand knots (Fig. 3c) compared to the open ligand strands (Fig. 3d), with substantial shifts both in Cotton effects and the intensity of the exciton coupling maxima. The CD data show the large systemic change in chiral expression as a result of knotting the strands, and thus restricting their conformation to well-defined, helically chiral knotted shapes.

Ligand strands **1–3** and overhand knots $\Lambda\text{-Lu1–3}$ were each doped into (achiral) nematic liquid crystals (ZLI-1083 or 5CB; Extended Data Fig. 1). Upon doping, features typical of chiral nematic liquid crystals were observed by optical microscopy (Table 1 and Fig. 4). Wedge cells were used to measure the helical twisting powers of **1–3** in ZLI-1083 using the Grandjean–Cano method (Fig. 4 shows a typical micrograph of ZLI-1083 doped with 0.5 wt% of **3**)⁵⁵. The insufficient solubility of the metal-coordinated overhand knots in the liquid crystal meant that the same method could not

Table 1 | HTP values (in μm^{-1}) of molecular strands **1–3 (in mol%, that is the molar fraction $\times 100\%$) and of the corresponding overhand knots $\Lambda\text{-Lu1–3}$ (in mol%) in a nematic liquid crystal**

Strand	HTP ^a (mol%; μm^{-1})	Overhand knot	HTP ^b (mol%; μm^{-1})
1	−129.3	$\Lambda\text{-Lu1}$	+12.0
2	−141.9	$\Lambda\text{-Lu2}$	+27.6
3	−153.8	$\Lambda\text{-Lu3}$	+24.7

^aMeasured in wedge cells; 0.5 wt% solution of molecular strand in ZLI-1083. ^bMeasured in θ -cells; 0.1 wt% solution of molecular knot in ZLI-1083.

be used to determine the twisting power of the knots. We instead used an approach based on θ -cells (Fig. 5)⁵⁶. In θ -cells, the liquid crystal is confined between two glass substrates that are prepared differently, one promoting unidirectional alignment and the other

Fig. 4 | Polarized optical microscopy image of a strand-doped liquid crystal. Grandjean-Cano lines form when nematic (achiral) liquid crystal ZLI-1083 doped with 0.5 wt% of strand **3** is confined in a wedge cell. From the distance between the Grandjean-Cano lines, the HTP value of each strand can be calculated (Supplementary Information Section 4.3). Scale bar, 200 μm .

one promoting a circular alignment of the liquid crystal (Fig. 5b). Subject to such boundary conditions, the liquid crystal undergoes a twist deformation inhomogeneously in the plane of the layer, so that areas with left and right twists become distinguishable. Where areas of opposite twist meet, a disclination line appears in the plane of the layer. If an achiral substrate is introduced, the disclination line is parallel to the rubbing direction of the top substrate, but a chiral dopant can change the equilibrium configuration of the director field (Fig. 5c). The position of the disclination line, and specifically the magnitude and sign of the angle it makes with the rubbing direction, can be used to determine not only the handedness of the chiral nematic liquid crystal but also its pitch, up to the centimetre range.

The HTP values obtained for strands **1–3** and overhand knots **A–Lu1–3** in ZLI-1083 are shown in Table 1. Remarkably, inversion of the liquid crystal handedness occurs for each ligand strand and the corresponding overhand knot: the metal-free strands produce a left-handed liquid crystal organization while the overhand knots generate a right-handed liquid crystal organization. This effect is solely a result of conformational changes brought about by the knotting of the molecular strands; no additional chiral elements are used, with the role of the lutetium ions being only to direct the formation of the well-defined entanglement of single handedness. Understanding the role of molecular conformation in directing the handedness of cholesteric phases remains an unsolved problem in soft matter research⁵⁷. The profound effect (including the inversion of liquid crystal handedness) that the well-defined change of shape upon the knotting of strands **1–3** has, on both the local environment and the extended liquid crystal organization, may assist such understanding.

The twisting powers of ligand strands **1–3** ($129.3\text{--}153.8\mu\text{m}^{-1}$) are large and similar in magnitude to those of overcrowded-alkene rotary motors, previously reported to have a helical twisting power of $144\mu\text{m}^{-1}$ in a nematic liquid crystal similar to that used in the present experiments¹⁸. The twisting powers of the overhand knots are an order of magnitude lower, but still substantial and clearly of the opposite sign. The presence of rigid phenyl ester groups in **2** and **3** positively affects the twisting powers compared to **1** for both the conformationally flexible strands and the entangled knots, indicating that the functionalization of molecular knots with liquid-crystal-like moieties is an effective means of designing chiral

dopants. However, there is little difference between either the values of the twisting powers of **2** and **3** or for the corresponding overhand knots. The similarity between twisting powers shows that, while the presence of groups promoting liquid crystallinity in the strands increases solubility by interaction with the surrounding liquid crystal molecules, this does not, in itself, necessarily lead to larger values of twisting power. In another nematic liquid crystal, 5CB, the twisting power values follow the same trends as for ZLI-1083 (Extended Data Fig. 1). The lower HTP values for the unknotted strands in 5CB may result from changes in conformation at different polarities, a feature apparent from CD titrations (Extended Data Fig. 1 and Supplementary Figs. 25–27) of (apolar) cyclohexane into solutions of the unknotted/knotted strands in (more polar) dichloromethane. The HTP values scale linearly with dopant concentration (Supplementary Fig. 9), indicating that the strand and knots are homogeneously dispersed within the liquid crystal with little or no aggregation.

The differences in sign and magnitude of twisting power between the open strands and the overhand knots indicate that the reason for the helix inversion is the handedness of the knotted entanglement produced by the coordination-driven folding. The twisting power values for a single 2,6-dicarboxamide unit and its lanthanide complex featuring three ligand molecules are consistent with this (Supplementary Table 1 and Supplementary Figs. 4–6), with pitch inversion of liquid crystal handedness a result of the arrangement of the three molecules around the metal-ion core (stereoisomerism analogous to that of three identical bidentate ligands in octahedral metal complexes).

The change of pitch and helix inversion of the liquid crystal could be achieved by in situ knotting of **1–3** in ZLI-1083 (Fig. 5a). The addition of $\text{Lu}(\text{OTf})_3$, followed by warming to disperse the metal ions, led to the inversion of the liquid crystal helix from left-handed to right-handed (Fig. 5d,e and Table 2). It was possible to determine the extent of knotting in the liquid crystal sample because helical twisting is an additive property at low concentrations, and the resulting helical twisting power is equal to the fraction-weighted sum of the twisting powers of all the species present. The helical pitch values measured suggest that 95–99% of strands **1–3** in ZLI-1083 are in the knotted state after treatment with $\text{Lu}(\text{OTf})_3$ (Table 2). It may be that this high knotting efficiency is a consequence of the liquid crystal environment aiding folding by restricting the conformations accessible to the strand outside of the knotting pathway. Other phenomena attributed to crowding effects in liquid crystals include rate and stereochemical enhancement in chemical reactions⁵⁸ and the synthesis of helical polymers⁵⁹.

The lanthanide ions could be removed from the overhand knots formed in situ by adding tetramethylammonium fluoride (Me_4NF) or potassium fluoride (KF) at 60°C . Removal of the lanthanide ions resulted in complete and spontaneous unknotting, with the liquid crystal helix consequently returning to its original pitch length and handedness (Fig. 5f and Supplementary Fig. 8). The helical pitch measurements before knotting, after knotting and after unknotting

Table 2 | Helical pitch values and knotting/unknotting yields for in situ knotting/unknotting of molecular stands **1–3 in a liquid crystal**

	Helical pitch ^a (μm); yield in parentheses		
	1	2	3
Initial (strand)	−57.3	−57.6	−57.0
After knotting	+952.4 (99%)	+652.2 (95%)	+779.3 (95%)
After unknotting	−60.4 (95%)	−103.2 (62%)	−106.3 (59%)

^a0.1 wt% solution in liquid crystal (ZLI-1083).

Fig. 5 | The in situ tying and untying of a molecular overhand knot dopant reversibly inverts the handedness of a chiral nematic liquid crystal.

a, Representation of the knotting and unknotting process. Reagents and conditions: (i) $\text{Lu}(\text{OTf})_3$, ZLI-1083, 80 °C. (ii) Me_4NF , ZLI-1083, 60 °C. **b**, Schematic representation of the θ -cell set-up. **c**, Origin of disclination lines upon introduction of chiral liquid crystals in θ -cells. Dashed lines correspond to rubbing direction. **d–f**, Polarized optical images of θ -cells filled with ZLI-1083 doped with 0.1 wt% of **2**: initial state (**d**; left-handed (LH) helix); after knotting (**e**; right-handed (RH) helix); and subsequent unknotting (**f**; back to left-handed helix). The absolute value of the angle ($\delta_{+/-}$) between the defect line and the rubbing direction (dashed line) is determined by the pitch of the chiral nematic liquid crystal. The sign of this angle is defined by the handedness of the liquid crystal: clockwise rotation corresponds to a right-handed helix; counterclockwise rotation to a left-handed helix. Thickness of θ -cell, 10 μm (**d,f**) and 50 μm (**e**). Scale bars, 200 μm .

(Table 2) indicate that unknotting (demetallation followed by unfolding) of Λ -**Lu1** with Me_4NF occurs with ~95% efficiency within the liquid crystal. The unknotting yields of Λ -**Lu2** and Λ -**Lu3** are more modest (62 and 59%, respectively), likely a result of partial naphthol ester hydrolysis under the switching conditions (Supplementary Scheme 10). The knotting–unknotting cycle with strand **1** could be repeated once more before the accumulation of waste products inhibited further switching.

To demonstrate that it is the entanglement of the strand to form the overhand knot that leads to switching, a macrocyclic (0_1 -unknot⁸) analogue of **1** (which cannot fold into a knot) was doped into ZLI-1083 and the resulting chiral nematic liquid crystal subjected to the same cycles of $\text{Lu}(\text{III})$ addition and removal as those shown in Fig. 5 (Extended Data Fig. 2 and Supplementary Information Section 5.5). No inversion of liquid crystal handedness occurred under these conditions.

Conclusions

The physical importance of knotting is increasingly becoming apparent across a range of disparate fields^{1–8,11,26–28}. Our findings demonstrate that tying or untying an overhand knot in a molecular strand (nanometre scale) can produce a large and measurable effect (helix inversion and pitch change) on a length scale six to seven orders of magnitude larger than the knotting event itself. When knotted, it is the handedness of the entanglement, rather than that of the individual chiral centres of the strand, that encodes for the handedness of the liquid crystal structure. Macroscopic structural helix

inversions brought about by molecular-level events (gene regulation or mutation) also occur in biology⁶⁰, although the mechanisms for the information transfer across multiple length scales remain unclear. The knotting of **1** in a liquid crystal is an artificial system in which a conformational transformation at the molecular scale induces helix inversion at the macroscopic level.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41557-020-0517-1>.

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Methods

Representative method for solution-phase tying of an overhand knot. To a vigorously stirred solution of **1** (34 mg, 0.0178 mmol) in MeCN (18 ml) was added lutetium triflate (11 mg, 0.028 mmol). The reaction was stirred for 16 h at 80 °C. The mixture was allowed to cool to room temperature, filtered and concentrated. The solid was repeatedly triturated with dichloromethane to give **Λ -Lu1** (28 mg, 62%) as an off-white powder.

General liquid crystal preparation. Low-molar-mass liquid crystals ZLI-1083 and 5CB (Merck) were used as host nematic matrices (Extended Data Fig. 1). ZLI-1083 and 5CB are liquid crystalline at room temperature with isotropization temperatures 51 °C and 35.5 °C, respectively. The molecular strands and knots were dissolved in the liquid crystal in either dichloromethane or acetonitrile, respectively. The solvent was slowly evaporated and the residue dried under vacuum at 50 °C for several hours.

HTP and handedness measurements. HTPs of enantiopure molecular strands were determined by the Cano method⁵⁵ using liquid crystal mixtures containing 0.5 wt% dopant. The handedness of the helix formed by the chiral nematic liquid crystal was determined using a rotatable analyser as reported previously⁶¹. Optical imaging and measurements were performed using a polarized optical microscope BX51 (Olympus) and Cell software (Olympus). The handedness and HTP values of the molecular knots (0.1 wt%) in liquid crystals were determined using so-called θ -cells⁶². For an in-depth description of these methods, see Section 4.3 of the Supplementary Information.

Fabrication of θ -cells. Glass slides (Thermo Fischer Scientific) were cut into 10 × 10 mm squares. The glass squares were immersed in ethanol and sonicated for 30 min at room temperature. The slides were air dried and spin coated with a Sunever 150 alignment layer polyimide (Nissan Chemical Industries) using a Laurell WS-650 spin coater. The slides were heated on a hot plate at 180 °C for 1 h. Two kinds of aligning substrates were prepared: unidirectional planar alignment was applied by unidirectional rubbing of the slide with a velvet cloth, and circular planar alignment was achieved by rubbing of the rotating substrate. The thickness of the cells was defined by Teflon spacers of 10 μ m or 50 μ m in thickness that were placed on both edges of the slides. The cells were then assembled with NOA68 UV-curable glue. The chiral nematic liquid crystal was subsequently introduced into the cell by capillary forces at room temperature.

Knotting and unknotting experiments in liquid crystals. Knotting was performed in a liquid crystal (ZLI-1083) containing 0.1 wt% of a molecular strand by adding an excess of solid lutetium triflate. The mixture was stirred at 80 °C for 24 h, followed by cooling to room temperature and centrifugation in order to remove solid residue. The resulting material was introduced into the θ -cell (50 μ m) and the HTP value measured (Supplementary Fig. 7). In order to study the unknotting process, a liquid crystal (ZLI-1083) containing 0.1 wt% of a molecular

knot was mixed with an excess of tetramethylammonium fluoride (TMAF) and stirred at 60 °C for 24 h. The reaction mixture was cooled to room temperature and centrifuged to remove any solid residue. The resulting chiral nematic liquid crystal was introduced into the θ -cell (10 μ m) and the HTP value measured (Supplementary Fig. 8).

Data availability

The data that support the findings of this study are available within the paper and its Supplementary Information, or are available from the Mendeley data repository (<https://bit.ly/3e5chOf>) under <https://doi.org/10.17632/dw93cmxxs4.2>.

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Author contributions

F.S. and L.P. planned and carried out the synthetic work. F.L. and A.R. designed and performed the liquid crystal experiments. D.A.L. and N.K. directed the research. All authors contributed to the analysis of the results and the writing of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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Extended Data Fig. 1 | Effect of strand and knot doping in different liquid crystalline hosts. a, Molecular structures of ZLI-1083 and 5CB which form liquid crystalline phases. **b**, Table summarizing HTP values for strand **1–3** and knots Λ -Lu1– Λ -Lu3 in ZLI-1083 and 5CB. **c**, Polarized optical micrograph images (Grandjean-Cano lines and θ -cell measurements) highlighting the chiral helical organization induced by strands **1–3** and corresponding knots in different liquid crystalline hosts. The dashed line shows the rubbing direction of the top substrate. The red arrow shows the rotation of disclination line. Scale bars corresponds to 200 μm . **d**, CD spectra on ligands **1** (**d**) and **2** (**e**) in different solvent mixtures (0.025 mM, 298 K), highlighting how the chiral expressions change with decreasing polarity. Normalized for absorbance.

Extended Data Fig. 2 | Probing the effect of the knotted conformation with macrocyclic strands. **a**, Treatment of macrocycle **5** with $\text{Lu}(\text{OTf})_3$ does not produce a trefoil knot due to topological restrictions, nor does this operation invert macroscopic chirality in liquid crystals. Conditions: $\text{Lu}(\text{OTf})_3$, MeCN, 80 °C, 24 h. **b**, CD spectra of the mixture obtained upon complexation of **5** with $\text{Lu}(\text{OTf})_3$ (purple trace, MeCN, 298 K) overlaid with reference knot spectrum belonging to $\Lambda\text{-Lu1}$ (green trace, MeCN, 298 K). Normalized for absorbance. **c, d**, Polarized optical image of θ -cell filled with ZLI-1083 nematic host doped with 0.1 wt% of **5** after complexation with $\text{Lu}(\text{OTf})_3$ (**c**) and after decomplexation with tetramethylammonium fluoride (**d**). Notice that handedness of the chiral nematic liquid crystal is not modified. Thickness of the θ -cell is 50 μm . Scale bars correspond to 200 μm .