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Encrypted mirror prepared based on the linearization of circularly polarized light

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Experimental Section

Materials

4-(*trans*-4-Ethylcyclohexyl)benzoic acid, 4-(*trans*-4-*n*-propylcyclohexyl)benzoic acid, 4-(*trans*-4-*n*-butylcyclohexyl)benzoic acid, 4-(*trans*-4-*n*-pentylcyclohexyl)benzoic acid and *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC) were bought from Macklin Biochemical Technology Co., Ltd (Shanghai, China). (*S*)-(-)-1,1'-Bi-2-naphthol was bought from Lianyungang Chiral Chemical Co., Ltd (Lianyungang, China). 4-Dimethylaminopyridine (DMAP) and Irgacure 907 were bought from Aladdin Biochem. Techn. Co., Ltd (Shanghai, China). Dichloromethane, petroleum ether, ethyl acetate, trichloromethane ($CHCl_3$), *N*,*N*-Dimethylformamide, cyclohexanone and cyclopentanone were purchased from Chinasun Specialty Products Co., Ltd. (Baimao Branch). $CDCl_3$ and ethylene glycol monomethyl ether were obtained from Anhui Senrise Technologies Co., Ltd. LC242 was purchased from GL Biochem Ltd (Shanghai, China). *S*5011 and CA-Acrylate were given by Soochiral Sci. & Tec. Co., Ltd (Suzhou, China). The rubbing-oriented PET film was purchased from Nanya Plastics Co., Ltd (Taiwan, China). E7 was purchased from Yantai Xianhua Technology Group Co., Ltd. Wedge cells were bought from Guining Experimental Equipment Co., Ltd (KCRK07, Japan). Azo dye SD1 and rebound photopolymerizable OCA were given by Wuxi Wanli Adhesive Materials Co., Ltd (Wuxi, China). Tree-patterned photomask was fabricated by printing directly onto PET film using an HP LaserJet P1007 printer. The printer was purchased from Beijing Disby Technology Co., Ltd (Beijing, China). Mayer bars were purchased from Suzhou Research Materials Microtech Co., Ltd (Suzhou, China).

Characterizations

The FT-IR spectra were performed on a Nicolet 6700 spectrometer at 2.0 cm^{-1} resolution by averaging over 16 scans (Bruker, Germany). The ^1H NMR spectrum was taken on a Varian NMR (400 MHz) spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard at room temperature (Agilent, USA). Mass spectra (MS) were obtained using an UltrafleXtreme MALDI TOF/TOF spectroscope (Bruker, USA). Elemental analysis was measured on a Flashsmart instrument (Thermo Scientific, Germany). The MINHIO 4012–20 UV curing machine composed of a high-pressure Hg lamp (280-450 nm, 1.0 kW) and a conveyer belt is produced by MINHIO Intelligent Equipment Co., Ltd (Shenzhen, China). The light intensities of UVV (> 390 nm), UVA (320-390 nm), UVB (280-320 nm) and UVC (< 280 nm) are 75.4, 96.0, 87.2, and 0 mW cm^{-2}, respectively. FE-SEM and EDS images were obtained using a Hitachi Regulus 8230 operating (Ibaraki prefecture, Japan) at 5.0 kV and 15 kV, respectively. CD spectra were measured by using a JASCO 815 spectrometer (Tokyo, Japan). UV–*vis*–NIR spectra were measured by a UV–*vis*–NIR spectrophotometer (UV1900i, Shimadzu, Japan). Polarized optical microscopy (POM) images of the target compounds were taken using a Leica Microsystems CMS GmbH fitted with a Linkam LTS420 hot stage (Leica, Germany). The CLCN mirrors were prepared using the golden GD-320 laminator (Beijing Disby Technology Co., Ltd, China). The UV LED series equipment (UVSF81T, 400 mW cm^{-2}, output power) was produced by FUTANSI Electronic Technology Co., Ltd (Shanghai, China). And the 445-nm polarized laser equipment (FC445LD-2W-FC, 445 nm, 2000 mW, output power) produced by Kunshan Jiyang Optoelectronics Technology Co., Ltd (Jiangsu, China). The linear polarizer (12 cm × 12 cm) was purchased from Chuangcai Imaging Equipment Co., Ltd (Jiangsu, China). The circular polarizers (15 cm × 15 cm) were purchased from Nitto Denko Co., Ltd (Japan). The polarized UV–*vis* absorption spectra was measured by a polarizer accessory GTP10-A purchased from LBTEK Co., Ltd (Changsha, China).

Synthesis of *S*-PCH2

A typical synthesis procedure was shown as follows. 4-(4-Ethylcyclohexyl)benzoic acid (4.3 g, 18.5 mmol), (*S*)-(-)-1,1'-Bi-2-naphthol (2.5 g, 8.7 mmol), DMAP (0.1 g, 0.9 mmol) and 100 mL of CH_2Cl_2 were added into a 250 mL round-bottomed flask. Then, EDC (4.4 g, 22.7 mmol) was added at 20 °C. The reaction mixture was stirred for 12 h under nitrogen. After the reaction, the solvent was removed by vacuum evaporation. The crude product was purified by a silica gel column using the petroleum ether/ethyl acetate ether (1:20) mixture as the eluent. White powder was obtained (yield: 5.4 g, 86.5%). $[\alpha]^{20}$ = +1.1° (c = 1.0, $CHCl_3$). FT-IR υ_{max}: 2916, 2850, 1733, 1608, 1508, 1261, 1178, 1068, 1016, 802, 744 and 700 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ = 0.89 (t, J = 7.3 Hz, 6H, $CH_2C\underline{H}_3$), 0.96–1.05 (m, 4H, $C\underline{H}_2CH_3$), 1.21–1.43 (m, 10H, aliphatic hydrogens), 1.78–1.88 (m, 8H, $ArCHC\underline{H}_2$), 2.43 (tt, J = 11.9, 3.2 Hz, 2H, $ArC\underline{H}CH_2$), 7.09 (d, J = 8.3 Hz, 4H, Ar$\underline{H}$), 7.29–7.37 (m, 4H, Ar$\underline{H}$), 7.44 (ddd, J = 8.1, 6.5, 1.5 Hz, 2H, Ar$\underline{H}$), 7.57 (dd, J = 17.3, 8.6 Hz, 6H, Ar$\underline{H}$), 7.90 (d, J = 8.2 Hz, 2H, Ar$\underline{H}$), 7.97 (d, J = 8.9 Hz, 2H, Ar$\underline{H}$) ppm. MS *m*/*z* (rel. int.): 737.214 ($[M+Na]^+$, 100). Elemental analysis: calculated (for $C_{50}H_{50}O_4$): C 84.00%, H 7.05%, found: C 84.11%, H 7.19%.

Synthesis of *S*-PCH3

Yield: 85.8%. $[\alpha]^{20}$ = +1.3° (c = 1.0, $CHCl_3$). FT-IR υ_{max}: 2918, 2849, 2362, 1733, 1608, 1259, 1210, 1178, 1068, 1014, 802, 744 and 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ = 0.89 (t, J = 7.2 Hz, 6H, $CH_2C\underline{H}_3$), 1.02 (td, J = 14.5, 13.6, 3.3 Hz, 4H, $C\underline{H}CH_2$), 1.16–1.22 (m, 4H, $C\underline{H}_2CH_3$), 1.28–1.43 (m, 10H, aliphatic hydrogens), 1.78–1.86 (m, 8H, ArCHC<u>H</u>$_2$), 2.42 (tt, *J* = 12.1, 3.3 Hz, 2H, ArC<u>H</u>CH$_2$), 7.09 (d, *J* = 8.4 Hz, 4H, Ar<u>H</u>) , 7.29–7.37 (m, 4H, Ar<u>H</u>), 7.44 (ddd, *J* = 8.1, 6.5, 1.5 Hz, 2H, Ar<u>H</u>), 7.57 (dd, *J* = 16.4, 8.6 Hz, 6H, Ar<u>H</u>), 7.90 (d, *J* = 8.2 Hz, 2H, Ar<u>H</u>), 7.97 (d, *J* = 8.9 Hz, 2H, Ar<u>H</u>) ppm. MS *m*/*z* (rel. int.): 766.421 ([M+Na]$^+$, 100). Elemental analysis: calculated (for $C_{52}H_{54}O_4$): C 84.06%, H 7.33%, found: C 83.99%, H 7.54%.

Synthesis of *S*-PCH4

Yield: 84.1%. $[\alpha]^{20}$ = +1.0° (c = 1.0, $CHCl_3$). FT-IR υ_{max}: 2920, 2850, 1734, 1608, 1261, 1207, 1178, 1068, 1016, 804, 744 and 700 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ = 0.88–0.91 (m, 6H, CH$_2$C<u>H</u>$_3$), 0.98–1.06 (m, 4H, C<u>H</u>CH$_2$), 1.21–1.25 (m, 4H, C<u>H</u>$_2$CH$_3$), 1.26–1.43 (m, 14H, aliphatic hydrogens), 1.78–1.86 (m, 8H, ArCHC<u>H</u>$_2$) , 2.42 (tt, *J* = 12.2, 3.3 Hz, 2H, ArC<u>H</u>CH$_2$), 7.09 (d, *J* = 8.4 Hz, 4H, Ar<u>H</u>) , 7.29–7.37 (m, 4H, Ar<u>H</u>), 7.44 (ddd, *J* = 8.1, 6.4, 1.5 Hz, 2H, Ar<u>H</u>), 7.57 (dd, *J* = 16.5, 8.6 Hz, 6H, Ar<u>H</u>), 7.90 (d, *J* = 8.2 Hz, 2H, Ar<u>H</u>), 7.97 (d, *J* = 8.9 Hz, 2H, Ar<u>H</u>) ppm. MS m/z (rel. int.): 793.272 ([M+Na]$^+$, 100). Elemental analysis: calculated (for $C_{54}H_{58}O_4$): C 84.12%, H 7.58%, found: C 83.85%, H 7.75%.

Synthesis of *S*-PCH5

Yield: 83.3 %. $[\alpha]^{20}$ = +1.8° (c = 1.0, $CHCl_3$). FT-IR υ_{max}: 2920, 2846, 1734, 1608, 1259, 1209, 1178, 1067, 1015, 802, 744 and 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ = 0.89 (t, *J* = 7.0 Hz, 6H, CH$_2$C<u>H</u>$_3$), 1.02 (td, *J* = 11.8, 10.9, 3.1 Hz, 4H, C<u>H</u>CH$_2$), 1.20–1.39 (m, 22H, aliphatic hydrogens), 1.78–1.86 (m, 8H, ArCHC<u>H</u>$_2$), 2.42 (tt, *J* = 11.9, 3.2 Hz, 2H, ArC<u>H</u>CH$_2$), 7.09 (d, *J* = 8.3 Hz, 4H, Ar<u>H</u>), 7.30–7.37 (m, 4H, Ar<u>H</u>), 7.44 (ddd, *J* = 8.2, 6.5, 1.5 Hz, 2H , Ar<u>H</u>), 7.57 (dd, *J* = 16.6, 8.6 Hz, 6H, Ar<u>H</u>), 7.90 (d, *J* = 8.2 Hz, 2H, Ar<u>H</u>), 7.97 (d, *J* = 8.9 Hz, 2H, Ar<u>H</u>) ppm. MS *m*/*z* (rel. int.): 821.449 ([M+Na]$^+$, 100). Elemental analysis: calculated (for $C_{56}H_{62}O_4$): C 84.17%, H 7.82%, found: C 84.11%, H, 8.06%.

Synthesis of *S*-PCH5Br

Yield: 83.6%. $[\alpha]^{20}$ = −38.6° (c = 1.0, $CHCl_3$). FT-IR υ_{max}: 2920, 1735, 1610, 1261, 1211, 1176, 1068, 1014, 811, 763, 700 and 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ = 0.89 (t, *J* = 7.0 Hz, 6H, CH$_2$C<u>H</u>$_3$), 0.96–1.06 (m, 4H, C<u>H</u>CH$_2$), 1.20–1.41 (m, 22H, aliphatic hydrogens), 1.83 (t, *J* = 11.6 Hz, 8H, ArCHC<u>H</u>$_2$), 2.44 (ddd, *J* = 12.1, 9.2, 2.9 Hz, 2H, ArC<u>H</u>CH$_2$), 7.14 (dd, *J* = 15.3, 8.7 Hz, 6H, Ar<u>H</u>), 7.38 (dd, *J* = 9.0, 1.9 Hz, 2H, Ar<u>H</u>), 7.58 (dd, *J* = 26.5, 8.6 Hz, 6H, Ar<u>H</u>), 7.88 (d, *J* = 9.0 Hz, 2H, Ar<u>H</u>), 8.06 (d, *J* = 1.8 Hz, 2H, Ar<u>H</u>) ppm. MS *m*/*z* (rel. int.): 979.026 ([M+Na]$^+$, 100). Elemental analysis: calculated (for $C_{56}H_{60}Br_2O_4$): C 70.29%, H 6.32%, found: C 71.07%, H, 6.32%.

Preparation of the CLCN films through the one-step approach

A typical preparation procedure is shown as follows. A CLC mixture was prepared at a LC242/*S*-PCH5/Irgacure 907 weight ratio shown in Table S1, which was dissolved in a mixture of cyclohexanone/cyclopentanone (v/v, 4/6) to form a solution with 30.0 wt % of solid content. The solution was coated on the surface of the rubbing-oriented PET film using a 60-μm Mayer bar. After the solvents were removed at 120 °C for 3.0 min, the CLC film was photopolymerized at 70 °C under the irradiation of the high-pressure Hg lamp (1.0 kW) for 5.0 s. Then, a CLCN film was obtained. The other CLCN films were prepared by changing the LC242/*S*-PCH5/Irgacure 907 weight ratio and the polymerization temperature.

Preparation of the CLCN films through the two-step approach

A typical preparation procedure is shown as follows. The LC242/*S*-PCH5/Irgacure 907 (w/w/w, 94.10/3.30/2.60) mixture or the CLC mixture shown in Table S2 was coated on the PET film surface as described above. Then, photopolymerization was carried out at 70 °C under the 365-nm LED lamp (120 mW cm^{-2}) irradiation for 1.0 s. After the film was annealed at 70 °C for 5.0 s to 12 min, photopolymerization was carried out under the high-pressure Hg lamp irradiation for 5.0 s. The other CLCN films with different thicknesses were prepared by changing the specification of the Mayer bar.

Preparation of the quadruple-layered CLCN mirror

OCA was first applied to the surface of the blue CLCN film. Subsequently, a green CLCN film was laminated face-to-face onto the blue film using a laminator. The OCA was then cured by exposure to the high-pressure Hg lamp at 25 °C for 15 s. Following this, the PET substrate of the green CLCN film was peeled off to obtain a double-layered CLCN film. A triple-layered film was fabricated by repeating this lamination process with the double-layered film and a red CLCN film. Finally, a quadruple-layered CLCN mirror was produced by similarly integrating the triple-layered film with a NIR reflecting CLCN film.

Preparation of the quarter-wave plate film with a tree pattern

SD1 was dissolved in a mixed solvent of ethylene glycol monomethyl ether and cyclohexanone (w/w, 1/1) at a concentration of 1.0 mg mL^{-1}. The solution was then coated onto a glass substrate using a Mayer bar with a 5.0-μm wet gap. After baking at 80 °C for 20 s, the SD1 layer was irradiated with 445-nm LPL (260 mW cm^{-2}, defined as polarization azimuth θ = 0°) for 20 s. Subsequently, a second irradiation was performed through a photomask using LPL with an orthogonal polarization direction (θ = 90°) for 40 s to create the patterned alignment. Separately, a NLC mixture was prepared by combining LC242 and the photoinitiator Irgacure 907 at a weight ratio of 97/3. This mixture was dissolved in a co-solvent of cyclohexanone and cyclopentanone (v/v, 4/6) to obtain a coating solution with a solid content of 10.0 wt%. The solution was coated onto the glass substrate using a 50-μm Mayer bar. The solvents were subsequently evaporated in an oven at 120 °C for approximately 50 s. Finally, the NLC film was photopolymerized at 70 °C under irradiation from a high-pressure Hg lamp for 5.0 s.

Preparation of the encrypted mirror with a tree pattern

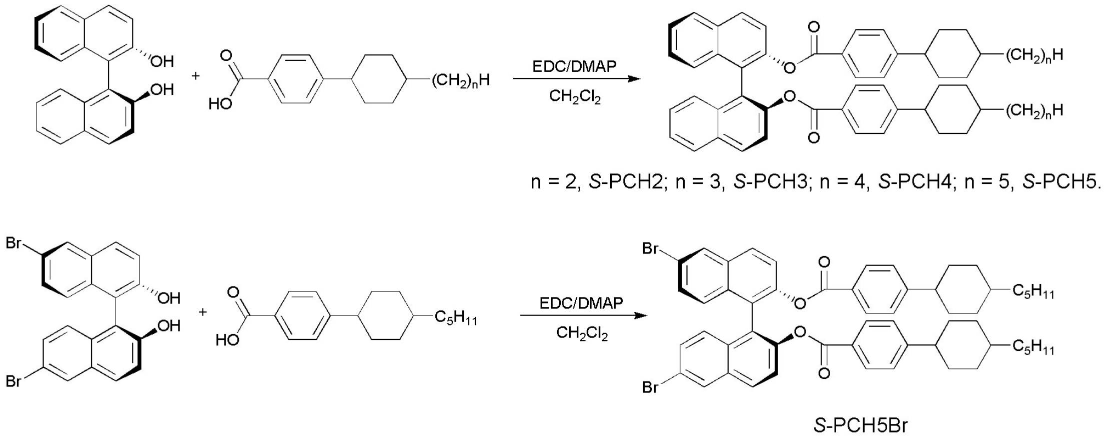
OCA was injected on the surface of the green CLCN film with a broad reflection band. Then, the quarter-waveplate film with a tree pattern was adhered to the green CLCN film face to face. OCA was cured under the irradiation of the high-pressure Hg lamp at 25 °C for 15 s. The green film with a tree pattern was obtained by peeling off the glass substrate of the quarter-wave plate film. Finally, the patterned mirror was prepared by stacking the blue and red CLCN films to this film as described above.

Table S1 Weight ratios of the compounds for the preparation of the CLCN films with single reflection band.

LC242	94.20	93.80	93.40	93.00	92.60	92.20
S-PCH5	3.20	3.60	4.00	4.40	4.80	5.20
Irgacure 907	2.60	2.60	2.60	2.60	2.60	2.60

Table S2 Weight ratios of the compounds for the preparation of the CLCN films with a broad reflection band.

CA-Acrylate/ *S*-PCH5	9/1 Blue	9/1 Green	9/1 Red	9/1 NIR	8/2	7/3
LC242	90.70	92.00	92.80	94.00	90.70	89.40
CA-Acrylate	6.03	4.86	4.14	3.60	5.36	5.60
S-PCH5	0.67	0.54	0.46	0.40	1.34	2.40
Irgacure 907	2.60	2.60	2.60	2.60	2.60	2.60



Scheme S1 Synthetic routes for the chiral dopants.

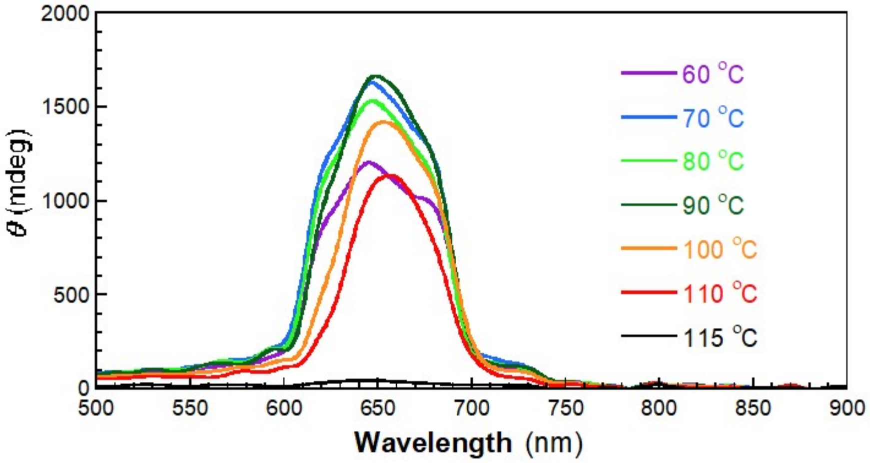


Fig. S1 CD spectra of the LC242/*S*5011/Irgacure 907 (w/w/w, 95.00/2.00/3.00) mixture taken at different temperatures.

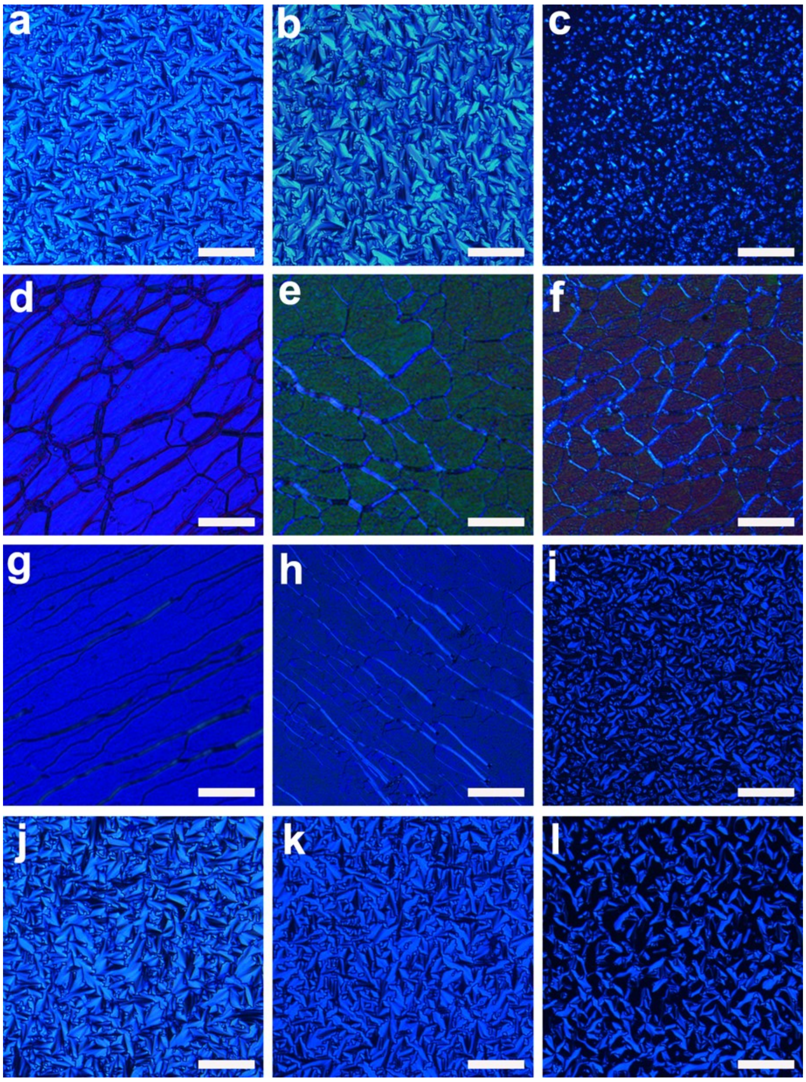


Fig. S2 POM images of the CLC mixtures prepared using *S*-PCH2 taken at (a) 60, (b) 80 and (c) 100 °C; *S*-PCH3 taken at (d) 70, (e) 90 and (f) 100 °C; *S*-PCH4 taken at (g) 70, (h) 90 and (i) 100 °C; *S*-PCH5 taken at (j) 70, (k) 80 and (l) 100 °C (scale bar, 50 μm).

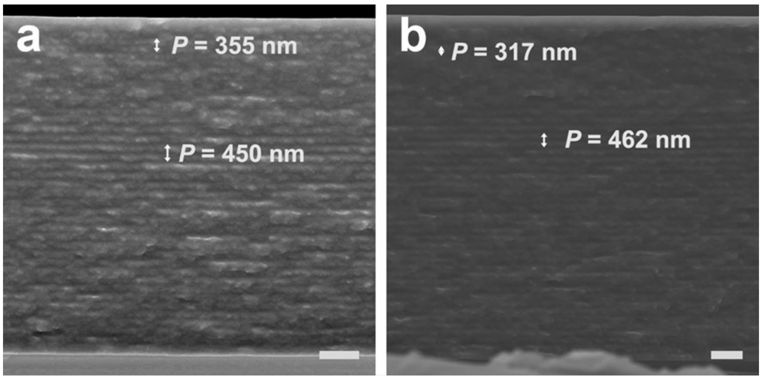


Fig. S3 Cross-sectional FE-SEM images of the CLCN films prepared with annealing time of (a) 1.0 min and (b) 12 min (scale bar, 1.0 μm).

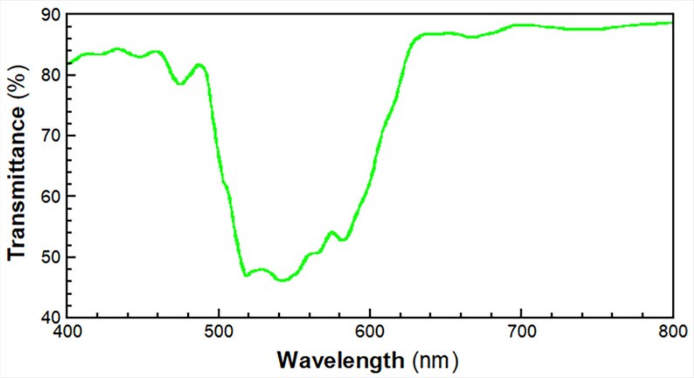


Fig. S4 UV–*vis* spectrum of the CLCN film prepared using LC242/CA-Acrylate/*S*-PCH5Br/Irgacure 907 (w/w/w/w, 92.00/4.86/0.54/2.60) mixture.

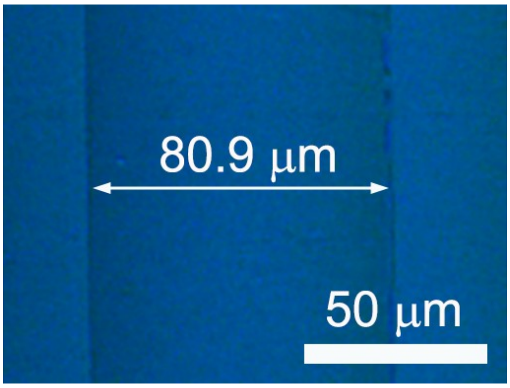


Fig. S5 POM image of the *S*-PCH5Br/E7 mixture (0.5 wt%) in a wedge cell taken at 26.5 °C.

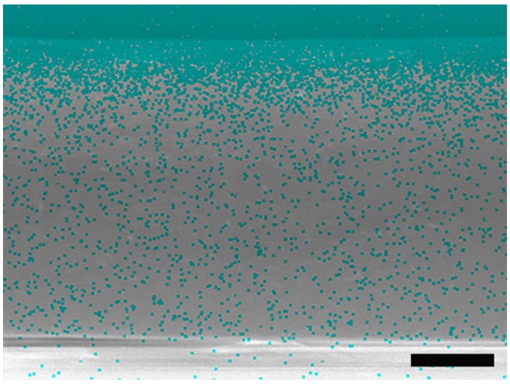


Fig. S6 EDS image of the CLCN film prepared using LC242/CA-Acrylate/*S*-PCH5Br/Irgacure 907 (w/w/w, 92.00/4.86/0.54/2.60) mixture (scale bar, 2.0 μm).

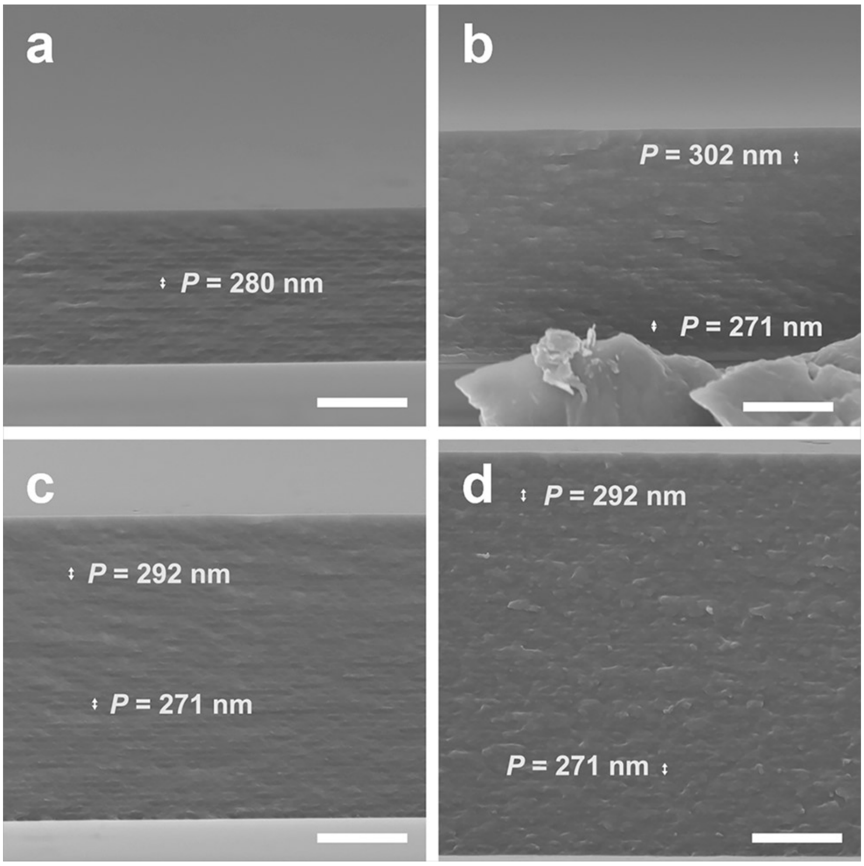


Fig. S7 Cross-sectional FE-SEM images of the CLCN films with the thickness of (a) 3.3, (b) 5.3, (c) 6.5 and (d) 7.9 μm (scale bar, 2.0 μm).

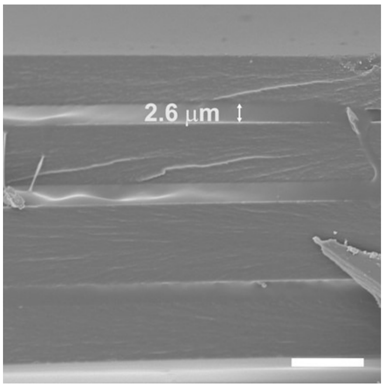


Fig. S8 Cross-sectional FE-SEM image of the CLCN mirror (scale bar, 10 μm).

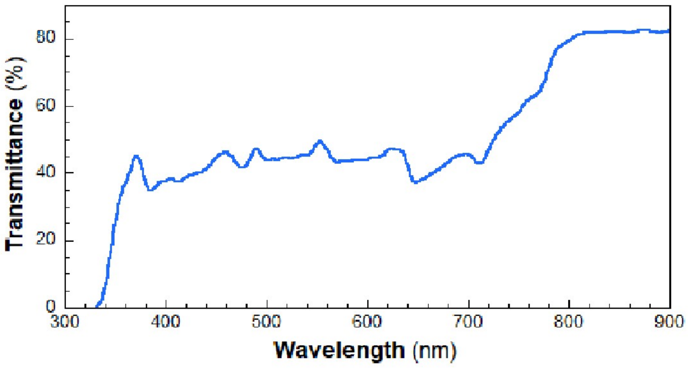


Fig. S9 UV–*vis* spectrum of the quadruple-layered CLCN film taken at the incident ray of 60° angle.

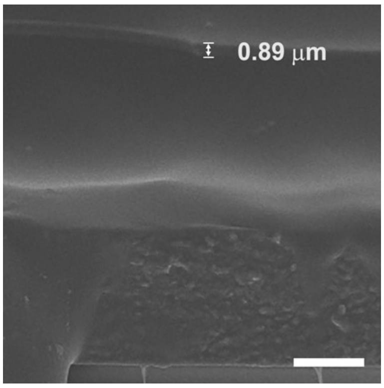


Fig. S10 Cross-sectional FE-SEM image of NLCN/OCA/CLCN film (scale bar, 5.0 μm).

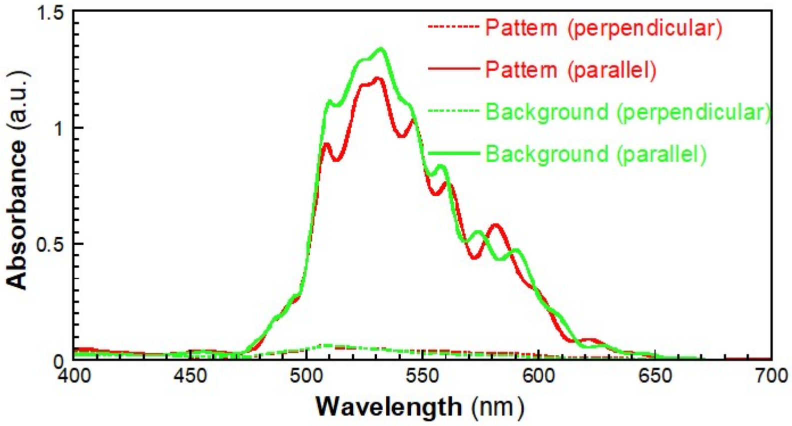


Fig. S11 UV–*vis* spectra of the patterned NLCN/OCA/CLCN film under LPL.