

Polymerization-induced diffusion driven the formation of cholesteric liquid crystal polymer network film with double helical pitches

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Table of Contents

Experimental Section

Scheme S1 Synthetic routes for C6C6 and CA-CF₃.

Table S1 Mass percentages of the compounds in the CLC mixtures.

Fig. S1 DSC curves of C6C6.

Fig. S2 POM images of C6C6 taken at (a) 98 and (b) 76 °C during the cooling process.

Fig. S3 SAXS pattern of C6C6 taken at 70.0 °C during the cooling process and the conformation of C6C6.

Fig. S4 UV-*vis* absorption spectra of C6C6 (7.5 x 10⁻⁵ M) in CHCl₃.

Fig. S5 UV-*vis* spectra of the CLC mixtures (a) without adding any photoinitiators (Sample 1), (b) without adding C6C6 (Sample 7) and the corresponding CLCN film and (c) with adding CA-iso-Acrylate (Sample 8) and the corresponding CLCN film.

Fig. S6 POM images of the CLCN films prepared using the CLC mixtures of (a) Sample 2 and (b) Sample 6 taken in reflection mode.

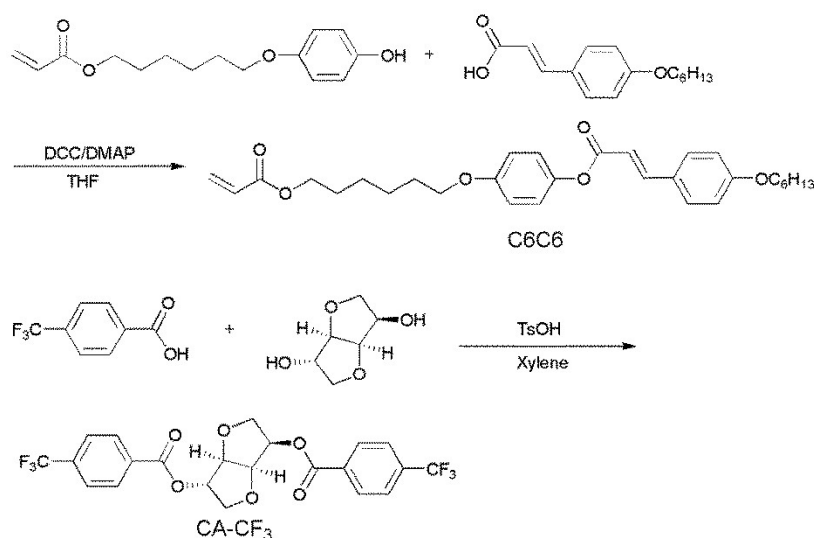
Fig. S7 UV-*vis* spectra of the CLCN films (a) with different thicknesses and (b) prepared at different temperatures using the CLC mixture of Sample 6.

Fig. S8 Curve of the viscosity of LC242/C6C6/CA-iso/369/907 (w/w/w/w/w, 82.8/10.0/3.8/1.8/1.6) mixture (Sample 6) at different temperatures.

Fig. S9 FT-IR spectra of the film taken during the preparation process.

Fig. S10 UV-*vis* spectra of the CLC mixture (Sample 9) and CLCN film.

Fig. S11 UV-*vis* spectra of (a) the screen-printed pattern before and after polymerization, and (b) the inject-printed pattern after polymerization.



Scheme S1 Synthetic routes for C6C6 and CA-CF₃.

Experimental Section

General information

4-(6-Acryloyloxyhex-1-yloxy)phenol, hexabromohexane and *trans-p*-hydroxycinnamic acid were bought from Shanghai Macklin Biochemical Co., Ltd. *N,N'*-Dicyclohexylcarbodiimide (DCC), cyclohexanone and 4-dimethylaminopyridine (DMAP) were bought from Shanghai Aladdin Biochem. Techn. Co., Ltd. 4-(Trifluoromethyl) benzoic acid, isosorbide and *p*-toluenesulfonic acid were bought from Shanghai Aladdin Biochemical Technology Co., Ltd. Methanol, acetone, ethyl acetate, DMAC, CDCl₃, xylene and tetrahydrofuran (THF) were obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. Cyclopentanone was bought from Chinasun Specialty Products Co., Ltd. LC242 was purchased from GL Biochem Ltd. CA-iso and CA-iso-Acrylate were given by Sochiral Sci. & Tec. Co., Ltd. Irgacure 369 was purchased from Shanghai 9 Ding Chemistry Co., Ltd. Irgacure 907 was purchased from Aladdin Chemical Co., Ltd (Shanghai, China). The rubbing-oriented and black PET films were purchased from Nanya plastics Co., Ltd. The screen with a serpentine pattern was bought from Shenzhen Deliou Technology development Co., Ltd.

The FT-IR spectra were performed on a Nicolet 6700 spectrometer at 2.0 cm⁻¹ resolution by averaging over 16 scans. The ¹H NMR spectrum was taken on a Varian NMR (300 MHz) spectrometer in CDCl₃ using tetramethylsilane (TMS) as an internal

standard at room temperature. The ^{19}F NMR spectrum was taken on a BRUKER AVANCE NEO 400 MHz spectrometer in $\text{DMSO-}d_6$ using CFCl_3 as an internal standard at room temperature. The elemental analysis was measured on an EA-1106 instrument. The DSC measurement was conducted on a TA-Q200 under nitrogen at $10\text{ }^\circ\text{C min}^{-1}$. The POM images were taken using a CPV-900C polarization microscope fitted with a Linkam LTS420 hot stage. The transition temperatures reported in this paper were the peak values of the transition on DSC traces. The mass spectrum (MS) was measured with Ultraflex extreme MALDI TOF/TOF spectroscope. The FE-SEM images were obtained using a Hitachi S-4800 operating (Ibaraki prefecture, Japan) at 5.0 kV. UV-*vis* spectra were obtained with a UV-*vis* spectrophotometer (UV-1900i, Japan). The DRCD spectra were measured by using a JASCO 815 spectrometer (JASCO, Japan), and anhydrous barium sulfate was used as the blank. The UV LED series equipment (UVSF81T) produced by FUTANSI Electronic Technology Co., Ltd (Shanghai, China). The UV LED parallel light source is equipped with double aspherical quartz lenses to produce parallel light with a parallel half angle of less than 2° . The MINHIO 4012–20 UV curing machine composed of a high-pressure Hg lamp (280–450 nm, 1.0 kW) and a conveyer belt was produced by MINHIO Intelligent Equipment Co., Ltd (Shenzhen, China). The light intensities of UVV ($> 390\text{ nm}$), UVA (320–390 nm), UVB (280–320 nm) and UVC ($< 280\text{ nm}$) were measured to be 75.4, 96.0, 87.2, and 0 mW cm^{-2} , respectively. The distance between the lamp and the sample was about 3.6 cm. The irradiation time of the high-pressure Hg lamp was controlled by the speed of the conveyer belt. The A4UV printer was purchased from Shenzhen Songpu Industrial Group Co. Ltd.

Synthesis of 4-((6-(acryloyloxy)hexyl)oxy)phenyl (*E*)-3-(4-(hexyloxy)phenyl)acrylate (C6C6).

4-(6-Acryloyloxyhex-1-yloxy) phenol (5.0 g, 18.9 mmol), *trans*-3-(4-hexoxyphenyl) acrylic acid (5.2 g, 20.9 mmol) and 4-dimethylaminopyridine (0.2 g, 1.9 mmol) were dissolved in 100 mL of THF. Then, *N,N'*-dicyclohexylcarbodiimide (4.7 g, 22.7 mmol) was added into the solution portion by portion at $0\text{ }^\circ\text{C}$. Twenty four hours

later, THF was removed by rotary evaporation. The crude product was purified by recrystallization in a mixture of acetone and methanol (4.1 g, yield: 51.1%). FT-IR ν_{\max} : 2935, 2865, 1721, 1630, 1598, 1504, 1471, 1410, 1286, 1247, 1147, 1008 and 833 cm^{-1} . ^1H NMR (300 MHz, CDCl_3 , TMS): δ = 0.85 (d, J = 6.2 Hz, 3H, RCH_3), 1.26–1.29 (m, 4H, RCH_2), 1.33–1.49 (m, 6H, RCH_2), 1.57–1.80 (m, 6H, RCH_2), 3.88–3.92 (m, 4H, RCH_2O), 4.06–4.14 (m, 2H, RCH_2O), 5.73–5.76 (m, 1H, CH_2CH), 5.98–6.13 (m, 1H, CH_2CH), 6.28–6.48 (m, 2H, CHCH), 6.77–6.91 (m, 4H, CH_2CH), 6.98–7.02 (m, 2H, ArH), 7.42–7.52 (m, 2H, ArH), 7.73 (d, J = 15.9 Hz, 1H, ArH) ppm. MS m/z (rel. int.): 517.27 ($[\text{M}+\text{Na}]^+$, 100). Elemental analysis: calculated for $\text{C}_{30}\text{H}_{38}\text{O}_6$: C, 72.85%; H, 7.74%; found: C, 72.82%; H, 7.79%.

Synthesis of (3*R*,3*aS*,6*S*,6*aS*)-hexahydrofuro[3,2-*b*] furan-3,6-diyl bis(4-(trifluoromethyl)benzoate) (CA-CF₃).

4-(Trifluoromethyl) benzoic acid (19.0 g, 99.9 mmol), isosorbide (7.3 g, 49.9 mmol) and *p*-toluenesulfonic acid (5.0 g, 29.0 mmol) were dissolved in 300 mL of xylene. The mixture was heated to 175 °C under nitrogen and refluxed for 12 h. Then, the solvent was removed by spin evaporation. A white solid was obtained by column chromatography (15.0 g, yield: 61.2%). M.P.: 153.0 °C. $[\alpha]_{\text{D}}^{20}$ = +25.6° (c = 1.0, CHCl_3). FT-IR ν_{\max} : 2930, 1722, 1273, 1096, 1060, 1013, 857, 774 and 698 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 3.94–4.11 (m, 4H, RCH_2O), 4.61–4.64 (m, 1H, OCH), 5.02 (t, J = 5.2 Hz, 1H, OCH), 5.32–5.48 (m, 2H, OCH), 7.58–7.73 (m, 4H, ArH), 8.05–8.16 (m, 4H, ArH) ppm. MS m/z (rel. int.): 513.08 ($[\text{M}+\text{Na}]^+$, 100). ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$, CFCl_3): δ = -61.43 (s, CF_3). Elemental analysis: calculated for $\text{C}_{22}\text{H}_{16}\text{F}_6\text{O}_6$: C, 53.89%; H, 3.29%; found: C, 53.82%; H, 3.31%.

Preparation of the CLCN Films.

A typical preparation procedure was shown as follows. A mixture of LC242/C6C6/CA-iso/Irgacure 369/Irgacure 907 was prepared at the weight ratio of 82.8/10.0/3.8/1.8/1.6 (Sample 6), which was dissolved in a mixture of cyclohexanone/ethyl acetate (w/w, 4/1) to form a solution with 20 wt% of solid content. The solution was coated on the surface of a rubbing-oriented PET film using

a 40- μm Mayer bar. After the solvents were removed at 120 °C, polymerization was carried out under the irradiation of the high-pressure Hg lamp (1.0 kW) at 80 °C for 20 s. Then, a blue CLCN film was obtained. The other CLCN films were prepared by changing the concentration of CA-iso (Samples 1-5). For the CLCN film prepared without adding C6C6, the weight ratio of the LC242/CA-iso/Irgacure 369/Irgacure 907 mixture was 92.8/3.8/1.8/1.6 (Sample 7). For the CLCN film prepared using the reactive CA-iso-Acrylate as the chiral dopant, the weight ratio of the LC242/C6C6/CA-iso-Acrylate/Irgacure 369/Irgacure 907 mixture was 82.8/10.0/3.8/1.8/1.6 (Sample 8). The fluorinated CLCN film was prepared using the LC242/C6C6/CA-F/Irgacure 369/Irgacure 907 mixture at the weight ratio of 78.6/10.0/8.0/1.8/1.6 (Sample 9).

Preparation of the CLCN pattern through screen printing.

A LC242/C6C6/CA-iso/Irgacure 369/Irgacure 907 (w/w/w/w, 82.8/10.0/3.8/1.8/1.6) mixture was dissolved in a cyclohexanone/ethyl acetate (v/v, 4/1) mixture to form a transparent solution at a solid content of 50 wt%. Then, the solution was coated on the surface of the PET film through screen-printing. After removing the solvents at 80 °C for 5.0 min and photopolymerization as described above, the CLCN pattern was obtained.

Preparation of the CLCN pattern through inject printing.

Three inks were prepared at the LC242/C6C6/CA-iso/ Irgacure 369/ Irgacure 907 weight ratios of 82.8/10/3.8/1.8/1.6, 83.4/10/3.2/1.8/1.6 and 84.1/10/2.5/1.8/1.6, which were dissolved in a mixture of DMAc/cyclopentanone (v/v, 4/6) to form solutions with a solid content of 30 wt%. After the pattern shown in Fig. 7c was printed using the A4UV inject printer, the solvents were removed at 80 °C for 5.0 min. After photopolymerization as described above, the CLCN pattern was obtained.

Table S1 Mass percentages of the compounds in the CLC mixtures.

Sample No.	1	2	3	4	5	6	7	8	9
LC242 (wt%)	86.2	84.1	83.8	83.4	83.1	82.8	92.8	82.8	78.6
C6C6 (wt%)	10.0	10.0	10.0	10.0	10.0	10.0	0	10.0	10.0
CA-iso (wt%)	3.8	2.5	2.8	3.2	3.5	3.8	3.8	0	0
CA-iso-Acrylate (wt%)	0	0	0	0	0	0	0	3.8	0
369 (wt%)	0	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
907 (wt%)	0	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
CA-CF ₃ (wt%)	0	0	0	0	0	0	0	0	8.0

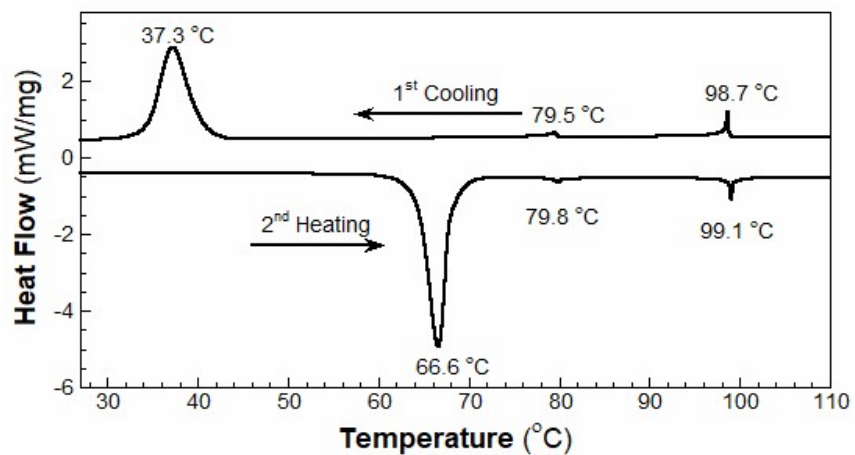


Fig. S1 DSC curves of C6C6.

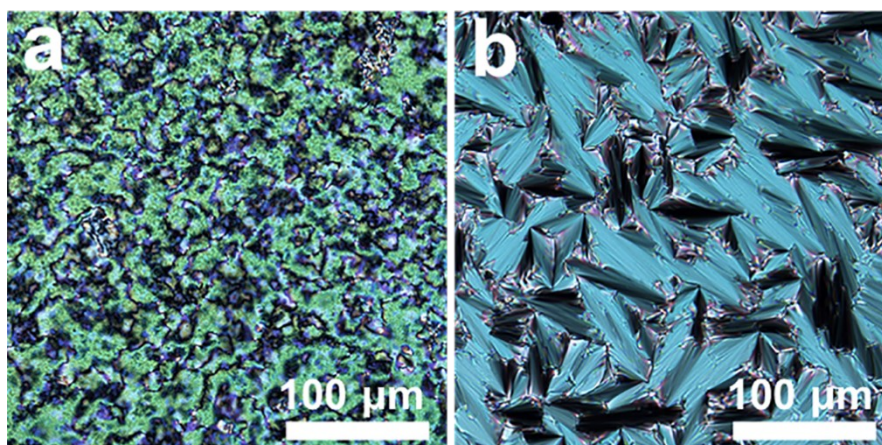


Fig. S2 POM images of C6C6 taken at (a) 98 and (b) 76 °C during the cooling process.

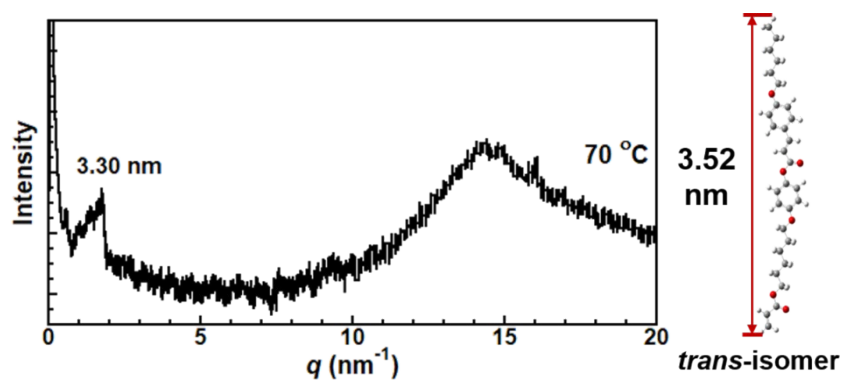


Fig. S3 SAXS pattern of C6C6 taken at 70.0 °C during the cooling process and the conformation of C6C6.^[S1]

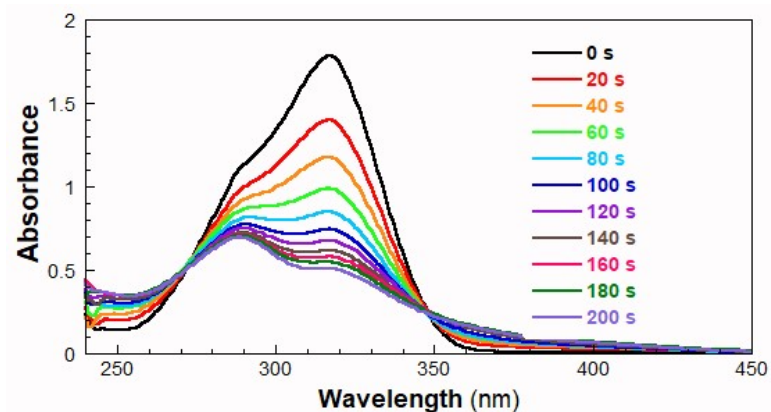


Fig. S4 UV-*vis* absorption spectra of C6C6 (7.5×10^{-5} M) in CHCl_3 .

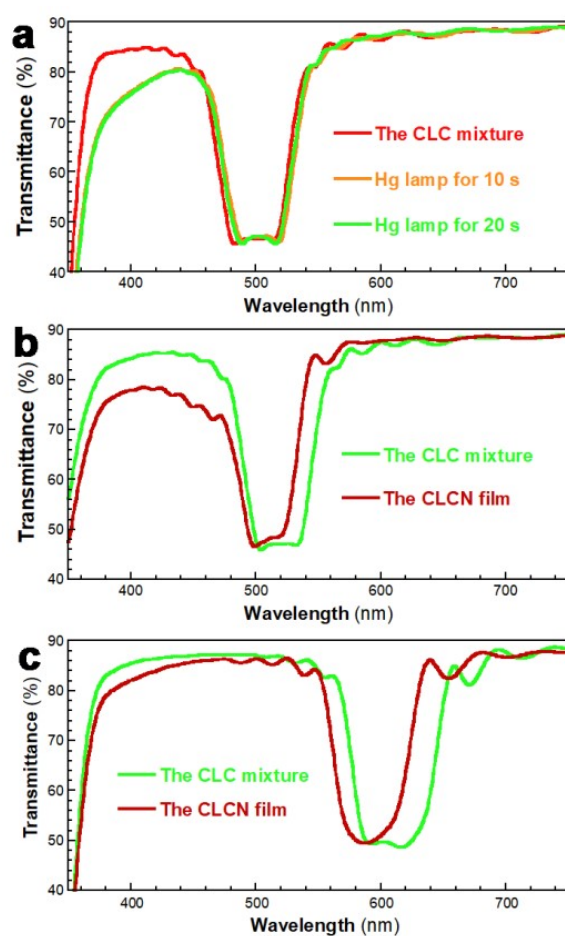


Fig. S5 UV-*vis* spectra of the CLC mixtures (a) without adding any photoinitiators (Sample 1), (b) without adding C6C6 (Sample 7) and the corresponding CLCN film and (c) with adding CA-iso-Acrylate (Sample 8) and the corresponding CLCN film.

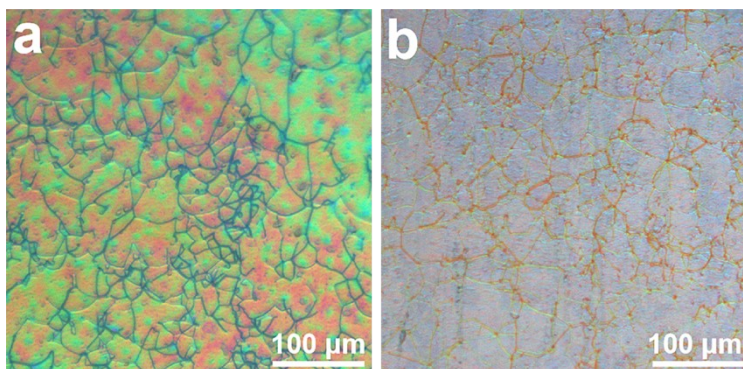


Fig. S6 POM images of the CLCN films prepared using the CLC mixtures of (a) Sample 2 and (b) Sample 6 taken in reflection mode.

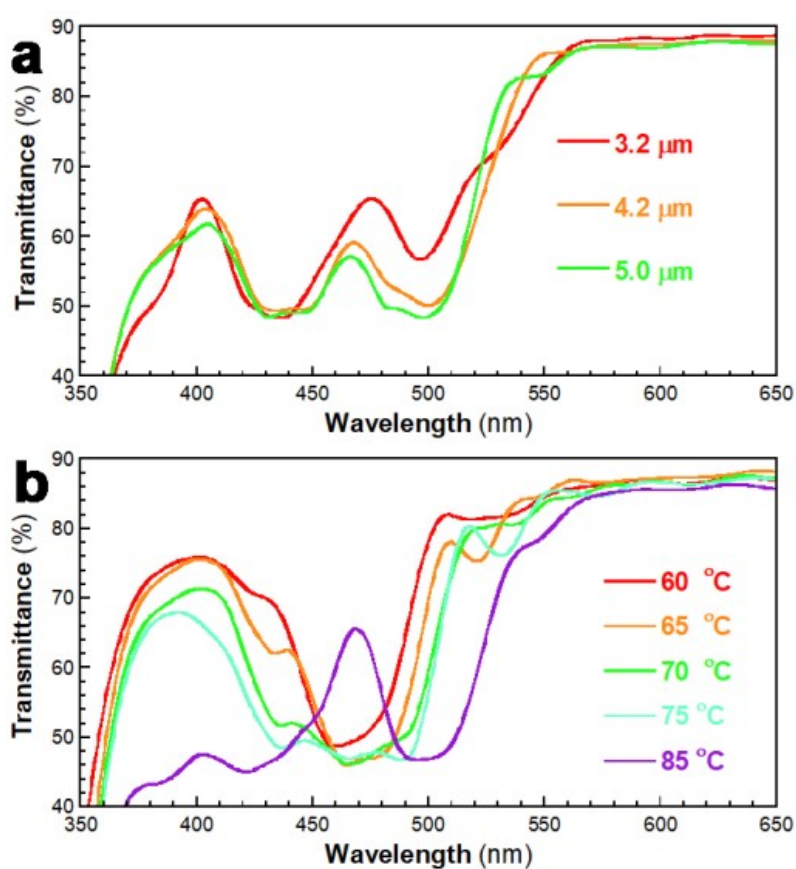


Fig. S7 UV-*vis* spectra of the CLCN films (a) with different thicknesses and (b) prepared at different temperatures using the CLC mixture of Sample 6.

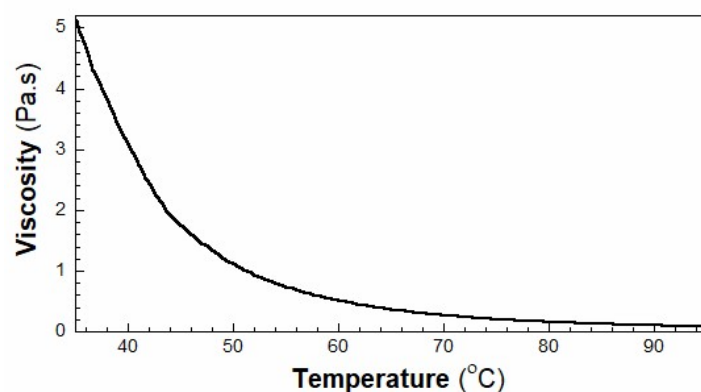


Fig. S8 Curve of the viscosity of LC242/C6C6/CA-iso/369/907 (w/w/w/w/w, 82.8/10.0/3.8/1.8/1.6) mixture (Sample 6) at different temperatures.

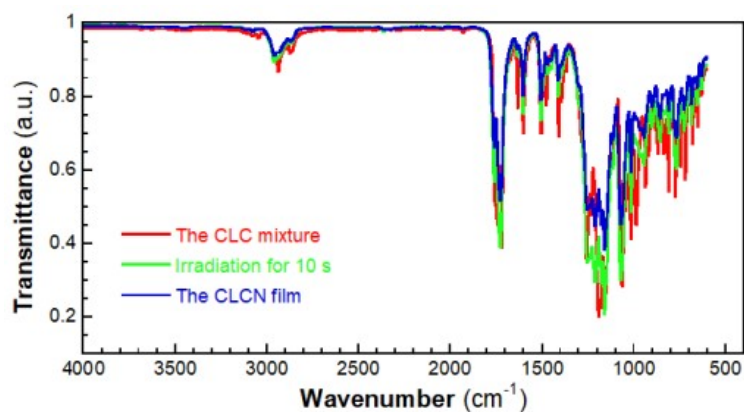


Fig. S9 FT-IR spectra of the film taken during the preparation process.

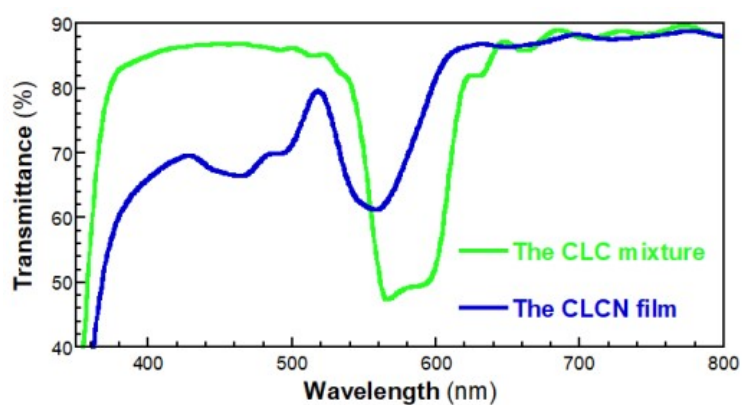


Fig. S10 UV-*vis* spectra of the CLC mixture (Sample 9) and CLCN film.

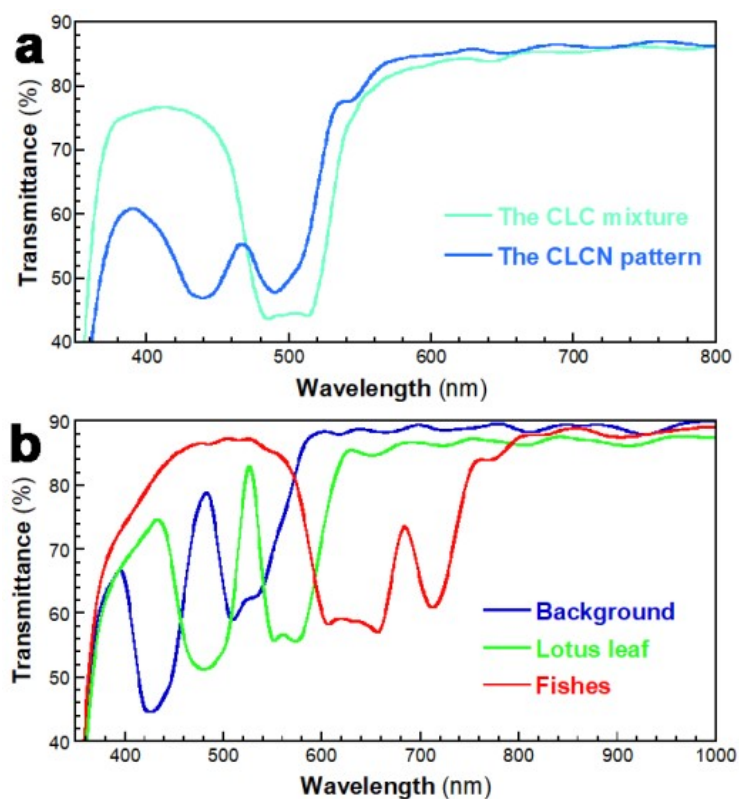


Fig. S11 UV-*vis* spectra of (a) the screen-printed pattern before and after polymerization, and (b) the inject-printed pattern after polymerization.

References

S1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. J. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, revision D.01 Gaussian, Inc.: Wallingford, CT, 2013.*