Supporting Information

Dual Responsive Inverse Opal Films Based on a Crosslinked Liquid Crystal Polymer Containing Azobenzene

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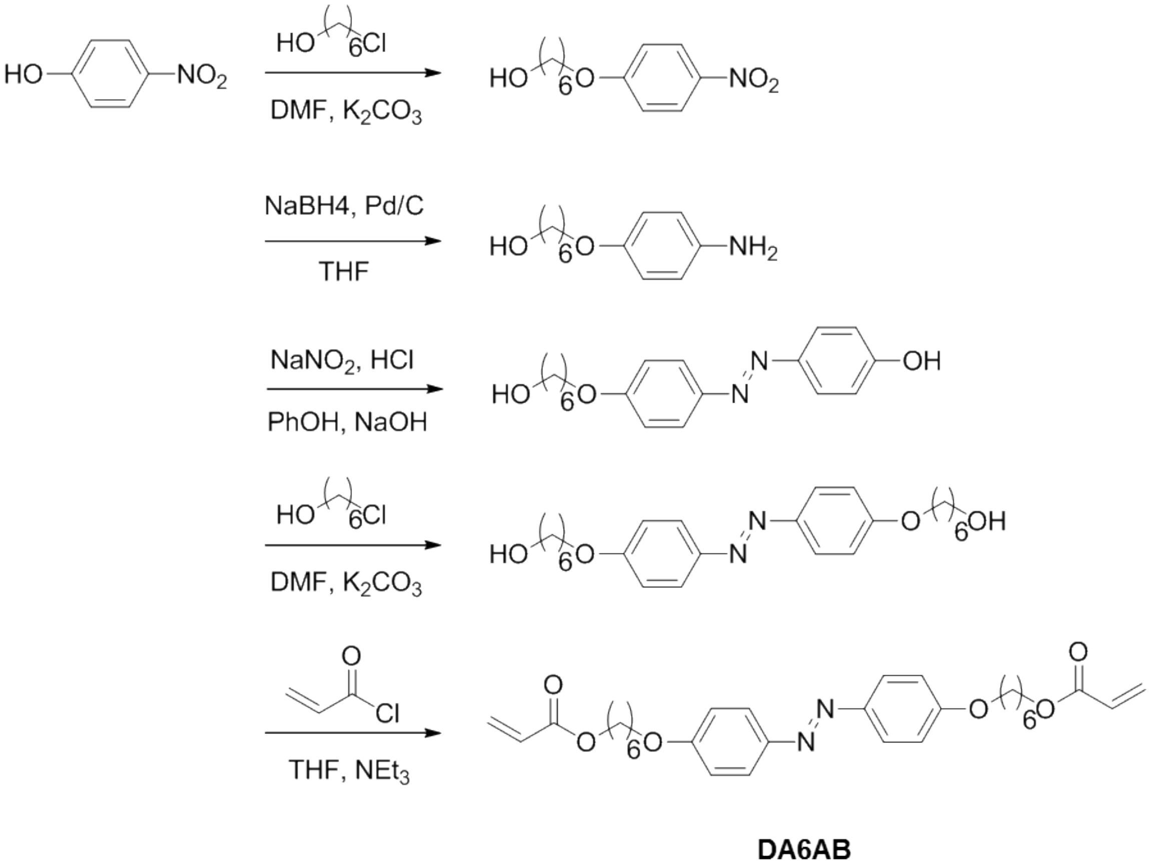
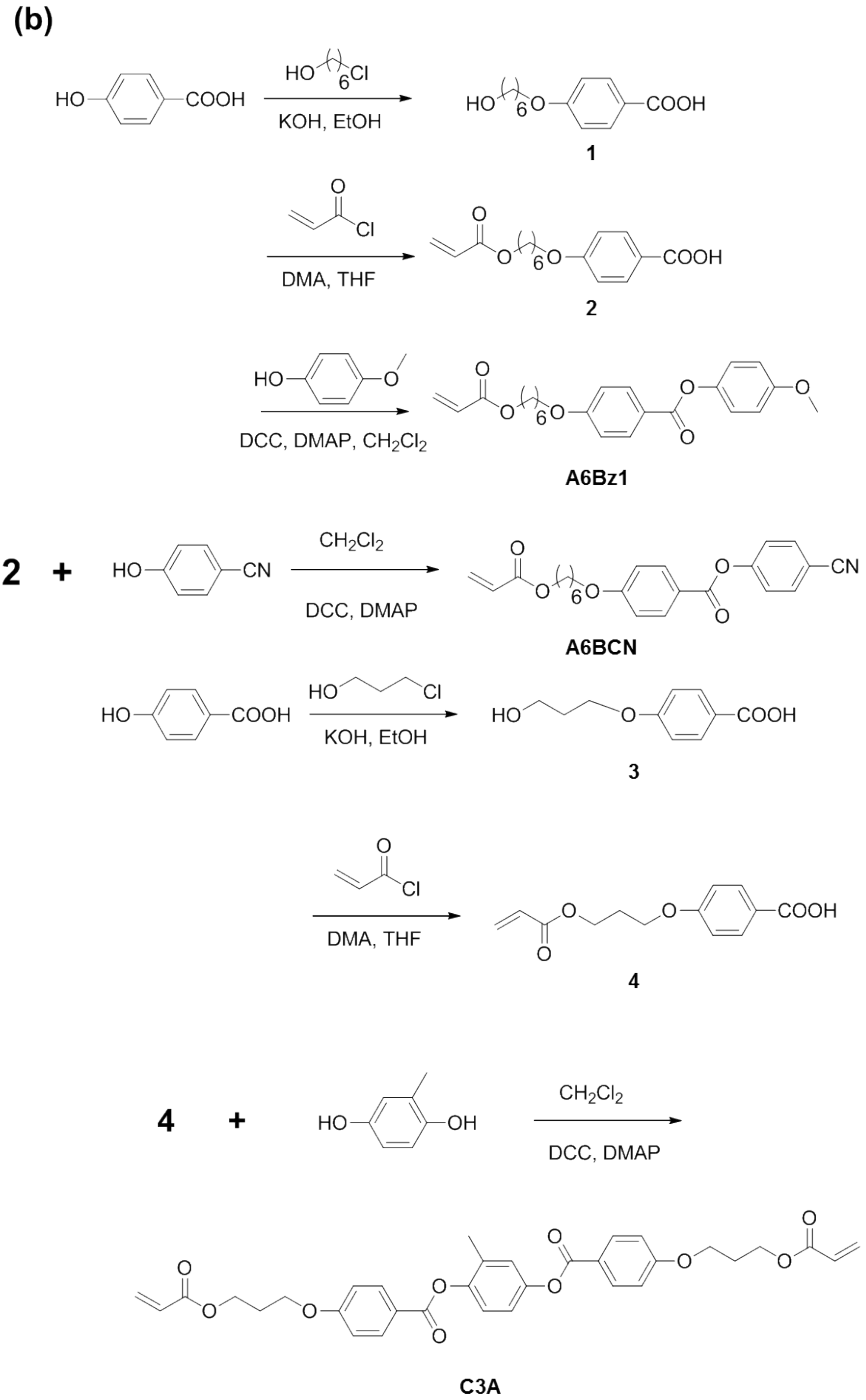
1. Synthesis

The synthesis of monomers A6Bz1, A6BCN and crosslinkers DA6AB, C3A is outlined in Scheme S1. The compounds were prepared using a procedure similar to the literature. [1, 2]

(a)





Scheme S1 (a) Synthetic route for azobenzene-containing crosslinker DA6AB. (b) Synthetic route for non-azobenzene monomers A6Bz1, A6BCN and crosslinker C3A.

^{1}H NMR spectra of the monomers and crosslinkers were recorded in CDCl$_3$ with a spectrometer. Chemical shifts of ^{1}H signals were quoted to internal standard CDCl$_3$ (δ=7.24).

A6Bz1: ^{1}H-NMR (CDCl$_3$): δ 1.4-1.8 (m, 8H), 3.8 (s, 3H), 3.6 (t, 2H), 4.0 (t, 2H), 5.8 (dd, 1H), 6.1 (m, 1H), 6.4 (m, 1H), 6.9-8.1 (m, 8H)

A6BCN: ^{1}H-NMR (CDCl$_3$): δ 1.4-1.8 (m, 8H), 4.0 (t, 2H), 4.1 (t, 2H), 5.8 (dd, 1H), 6.1 (m, 1H), 6.4 (m, 1H), 6.9-8.1 (m, 8H)

DA6AB: ^{1}H-NMR (CDCl$_3$): δ 1.4-1.9 (m, 16H), 3.9-4.1 (t, 8H), 5.8 (dd, 2H), 6.1 (dd, 2H), 6.4 (dd, 2H), 6.9 (m, 4H), 7.8 (m, 4H)

C3A: ^{1}H-NMR (CDCl$_3$): δ 1.5 (m, 4H), 2.2 (s, 3H), 4.1-4.4 (t, 8H), 5.8 (dd, 2H), 6.1 (m, 2H), 6.4 (m, 2H), 6.9 (m, 4H), 7.0-8.1 (m, 7H)

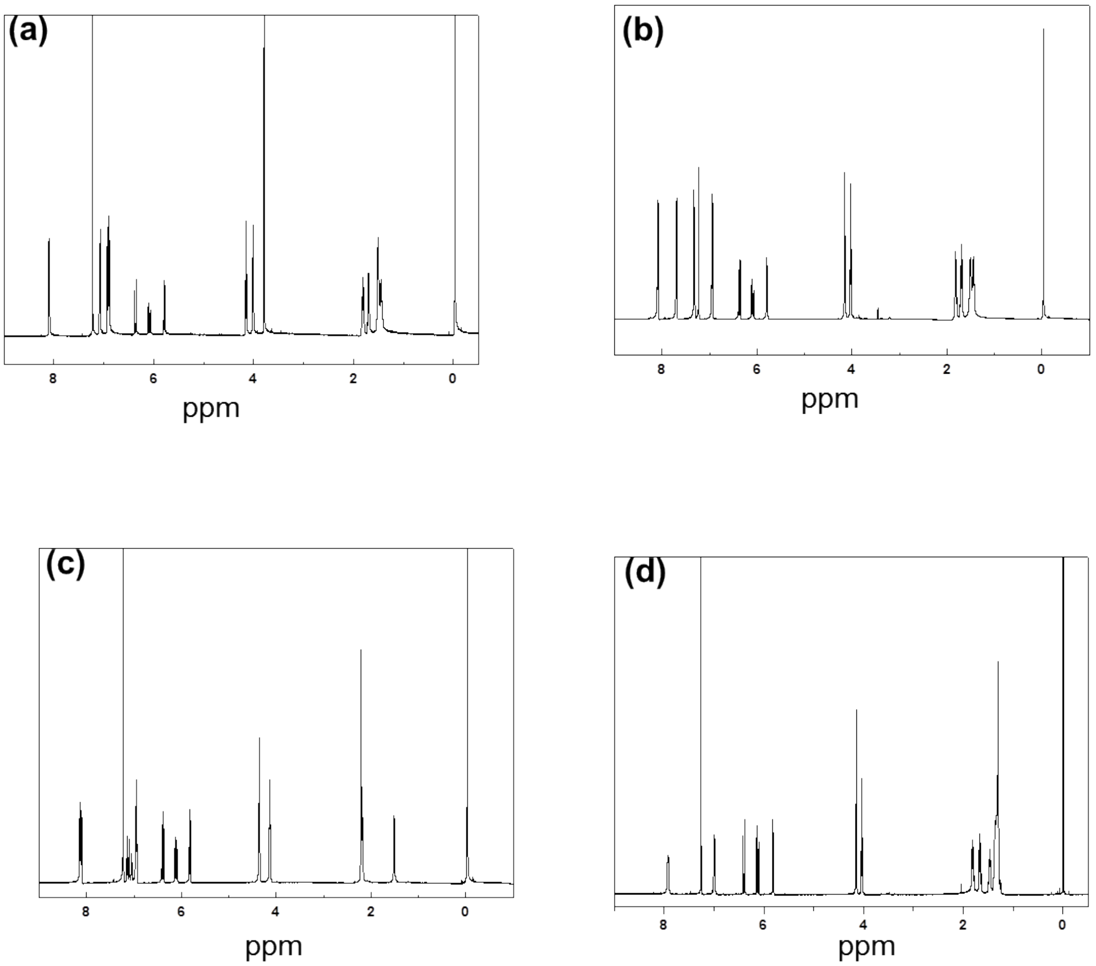


Fig. S1 ^{1}H NMR of the monomers (a) A6Bz1, (b) A6BCN and the crosslinkers (c) C3A, (d) DA6AB.

2. Characterization of monomers, crosslinkers, polymerizable mixture and CLCP inverse opal film

The thermodynamic properties of monomers, crosslinkers, polymerizable mixture and CLCP invese opal film were determined by a differential scanning calorimeter (DSC, TA Q2000) at a scanning rate of 3 ºC min^{-1} for the monomers, crosslinkers, mixture and 10 ºC min^{-1} for the CLCP inverse opal film. At least three scans were performed for each sample to check the reproducibility. Liquid crystal (LC) behavior and phase transition behavior were examined with a polarizing optical microscope (Leica DM4000M) equipped with a hot-stage (Linkam, T95-PE and LNP95). The results are shown in Table S1, Fig. S2 and Fig. S3.

Table S1 Phase transition temperatures of monomer, crosslinker and mixture.

	Phase transition T / ºC									
Name	Heating					Cooling				
A6Bz1		K	59	I		I	49	N	34	K
A6BCN		K	77	I			I	62	K	
C3A	K	75	N	129	I	I	129	N	73	K
DA6AB		K	75	I		I	81	N	74	K
Mixture	K	41	N	54	I	I	53	N	8	K

K, Crystal; N, nematic; I, isotropic

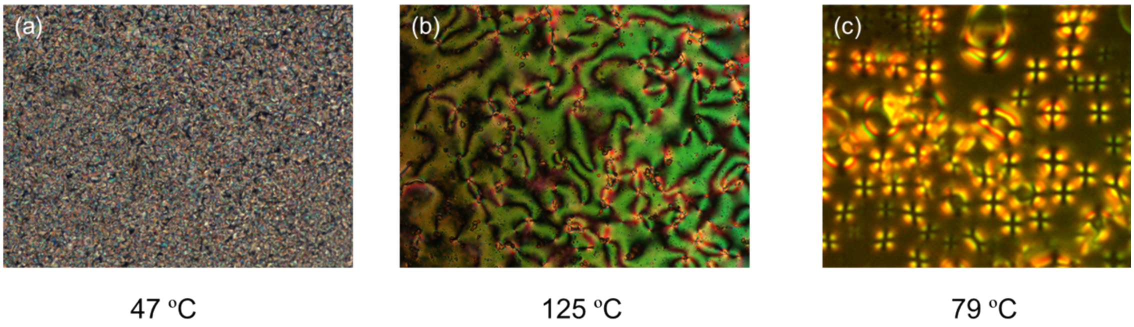


Fig. S2 POM images of the monomer (a) A6Bz1 and the crosslinkers (b) C3A, (c) DA6AB on the cooling process.

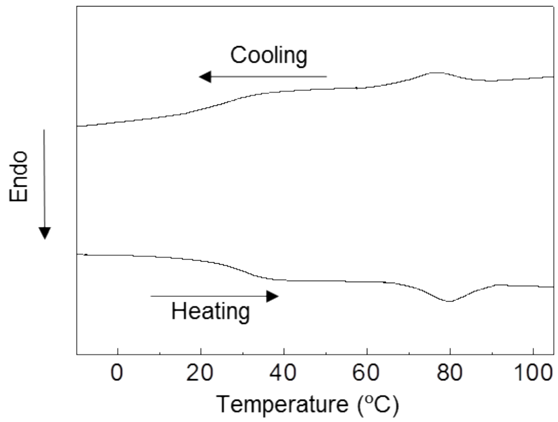


Fig. S3 DSC thermograms of the CLCP film on the third heating and cooling at a rate of 10 ºC min^{-1}.

3. The dynamic of the reflection peak

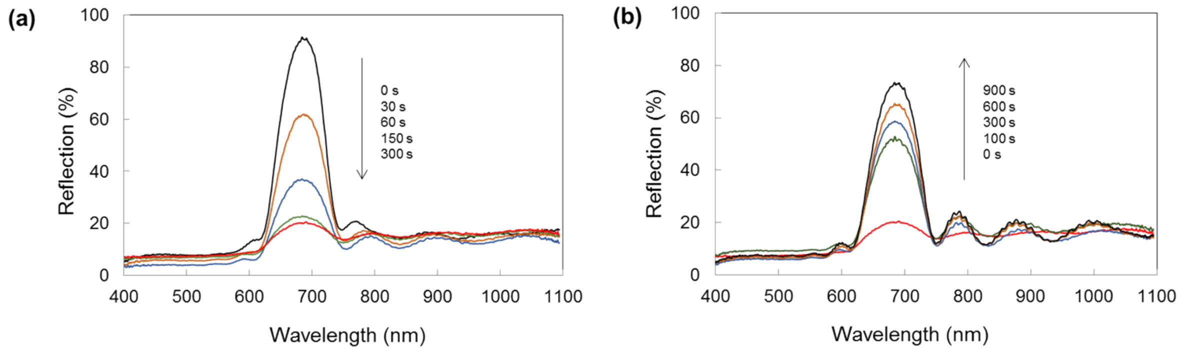


Fig. S4 The reflection spectra of the azobenzene CLCP inverse opal film under (a) the UV light irradiation (365 nm, 50 mW cm^{-2}) and (b) the visible light irradiation (530 nm, 20 mW cm^{-2}).

4. Photoinduced deformation of the CLCP film

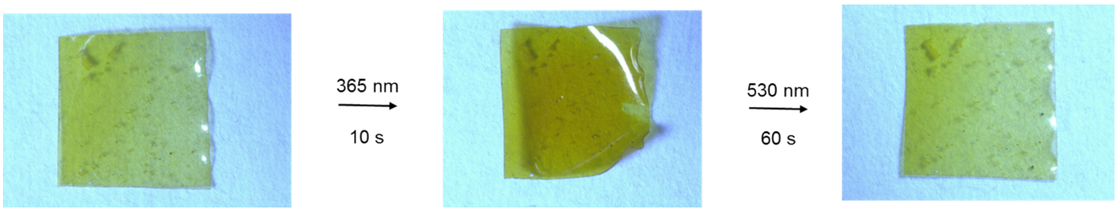


Fig. S5 Photographs of the film bending toward the light source in response to 365-nm light (30 mW cm^{-2}) and retaining the bent state after switching off the laser, and then the bent film reverted to the flat state after irradiation with 530-nm visible light (50 mW cm^{-2}). The bending direction of the CLCP film is random due to its inhomogeneous alignment of the mesogens in the macroscopic scale. The size of the CLCP film is 3 mm × 4 mm × 20 µm.

5. Photochemical changes of azobenzene moieties in the CLCP film

The POM images of the polydomain CLCP film are shown in Fig. S6. We can see that there is almost no difference between the two images, because the CLCP film is a polydomain film and the photochemical change only occurs in the surface region of the film.

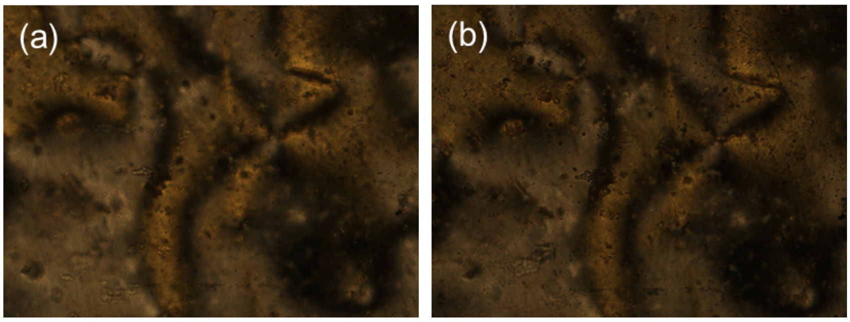
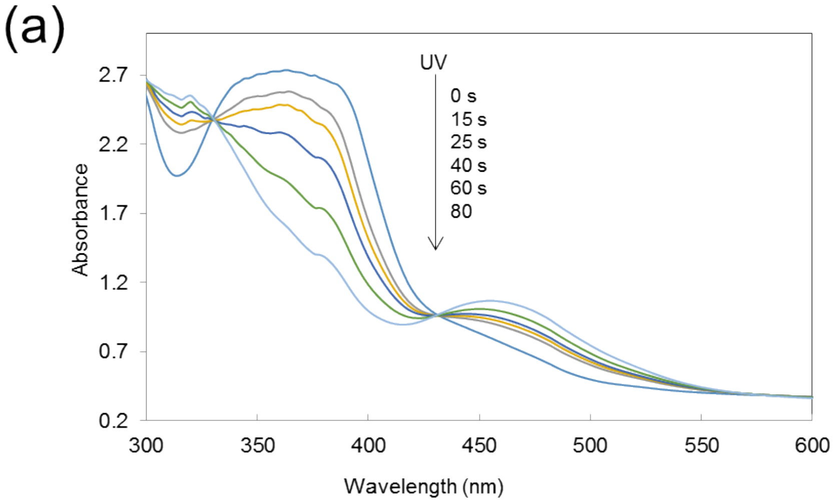


Fig. S6 POM images of the CLCP film (a) before and (b) after irradiation with UV light. (365 nm, 50 mW cm^{-2}, 120 s)

6. Photoisomerization of the azobenzene moieties in the CLCP film

The absorption spectrum in the initial state exhibited a distinct bands, which corresponds to the π-π* transitions of the azobenzene chromophore. When the film was irradiated with UV light (365 nm, 20 mW cm^{-2}), the photoisomerization process was monitored by absorption spectroscopy. The absorption band of the π-π* transitions gradually decreased with a concomitant increase in the band around 460 nm (n-π* transition), indicating the occurance of the trans-cis isomerization of the azobenzene moieties in the CLCP film (Fig. S7a). The reversible absorption change can be achieved by visible light irradiation at 530 nm (Fig. S7b).



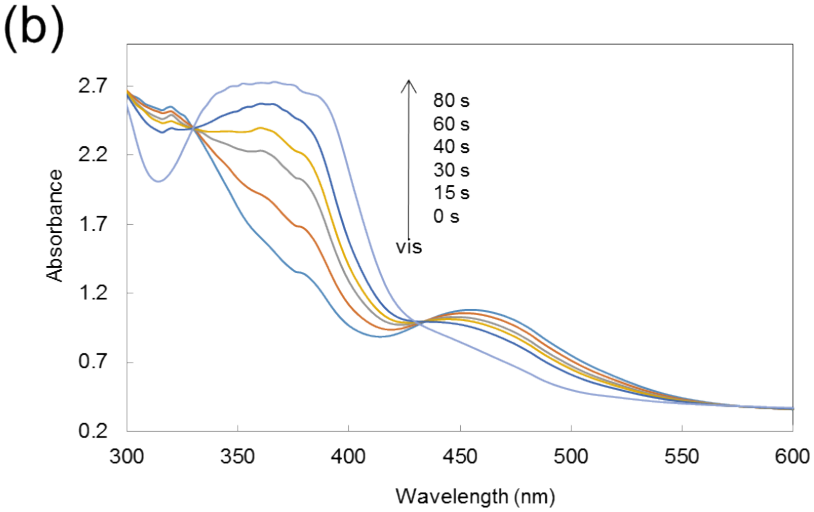


Fig. S7 Changes in the absorption spectra of the polydomain CLCP film upon the irradiation with (a) UV light (365 nm, 20 mW cm^{-2}) and (b) visible light (530 nm, 20 mW cm^{-2}), in which the arrow shows the increment of the irradiation time. (The film thickness is 2 μm)

7. The amount of energy for light induced vs. heat induced

As shown in Fig. S9, the inverse opal film with a thickness about 17 μm can be heated to 90 ºC in 3 s. The heat capacity of the inverse opal film was measured by DSC (about 1.614 J/(g ºC) at 60 ºC. We can estimate the amount of energy required for heat induced as follows:

$E = c\,m\,(T-T_0)$ (1)

Where c is heat capacity; m is the mass of the inverse opal film; T is the end temperature and T_0 is the initial temperature. In the work, mass is 9.25 mg; the end temperature is 90 ºC; the initial temperature is 30 ºC. So the amount of energy for heat induced is about 0.90 J.

The intensity of UV light is 50 mW cm^{-2}; irradiation time is 5 min and irradiation area is 0.07 cm^{-2}.

$$E = I\,A\,t \qquad (2)$$

Where I is the intensity of light; A is the area of irradiation and t is the irradiation time. According to formula 2, we can estimate on the amount of energy for light induced about 1.06 J.

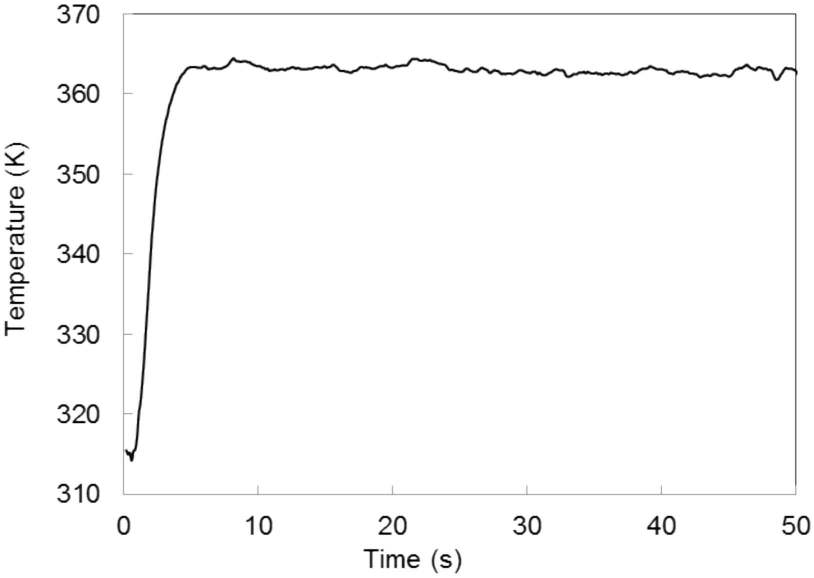


Fig. S8 Temperature changes data of the inverse opal film as a function of heating time on the hot stage. (Thickness of the inverse opal film 17μm)

8. Thermoinduced deformation of the CLCP film

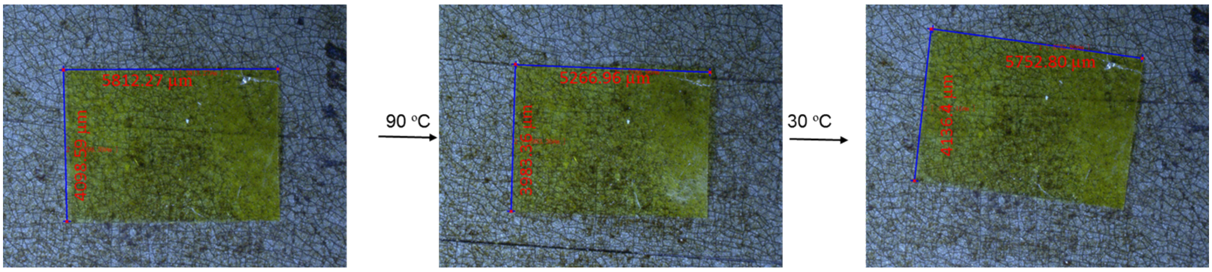


Fig. S9 Deformation of the CLCP film with the size of 4 mm × 6 mm × 20 μm.

9. Repeatable photoresponsive behavior of the CLCP inverse opal films with different crosslinking densities

The CLCP inverse opal films with different crosslinking densities were prepared by varying the feed concentration of crosslinker C3A from 0 to 90 mol% in the polymerizable mixture and their dual responsive properties were studied. As shown in Fig. S10, the change on the maximum intensity of the reflection spectra become smaller with the increase of feed concentrations of C3A. The nomenclature for polymerizable mixtures was summarized in Table S2.

Table S2 Nomenclature and composition of the polymerizable samples.

nomenclature	A6Bz1 (mol %)	A6BCN (mol %)	C3A (mol %)	DA11AB (mol %)
M7201	70	20	0	10
M4231	40	20	30	10
M1171	10	10	70	10
M0091	0	0	90	10

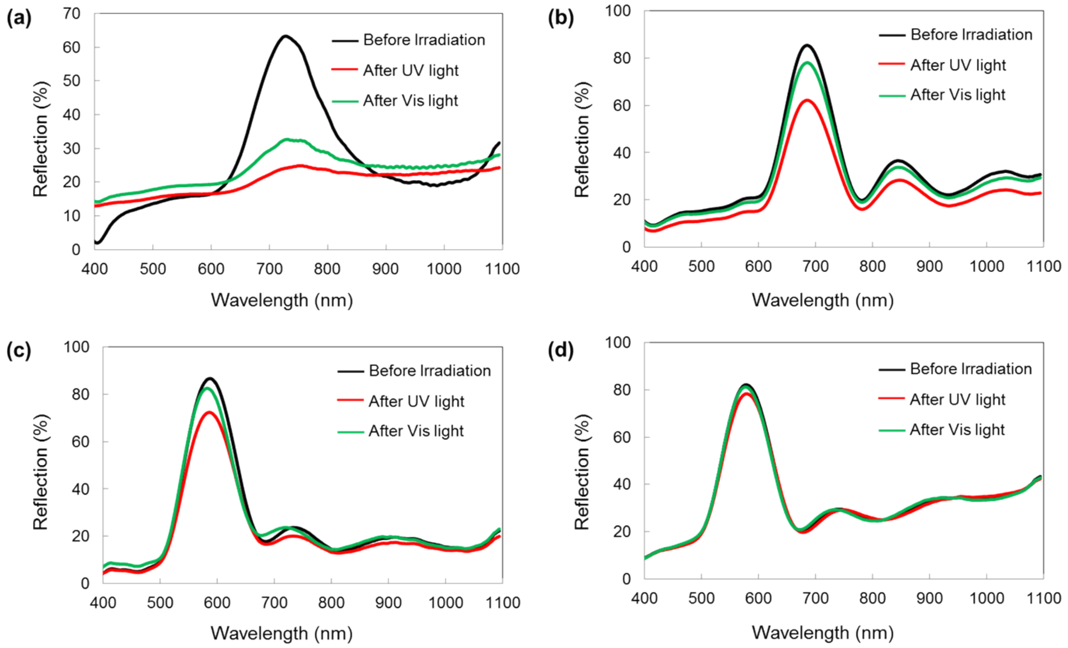


Fig. S10 The reflection spectra of the azobenzene CLCP inverse opal films polymerized by (a) M7201, (b) M4231, (c) M1171 and (d) M0091 under the UV light irradiation (365 nm, 50 mW cm^{-2}) and the visible light irradiation (530 nm, 20 mW cm^{-2}).

10. Temperature-induced responsive behavior of the CLCP inverse opal films with different crosslinking densities

As shown in Fig. S11, the change on the maximum intensity of the reflection spectra becomes smaller with the increase of the feed concentration of C3A during heating process. What's more, the switching behavior without the crosslinker C3A cannot be repeatable.

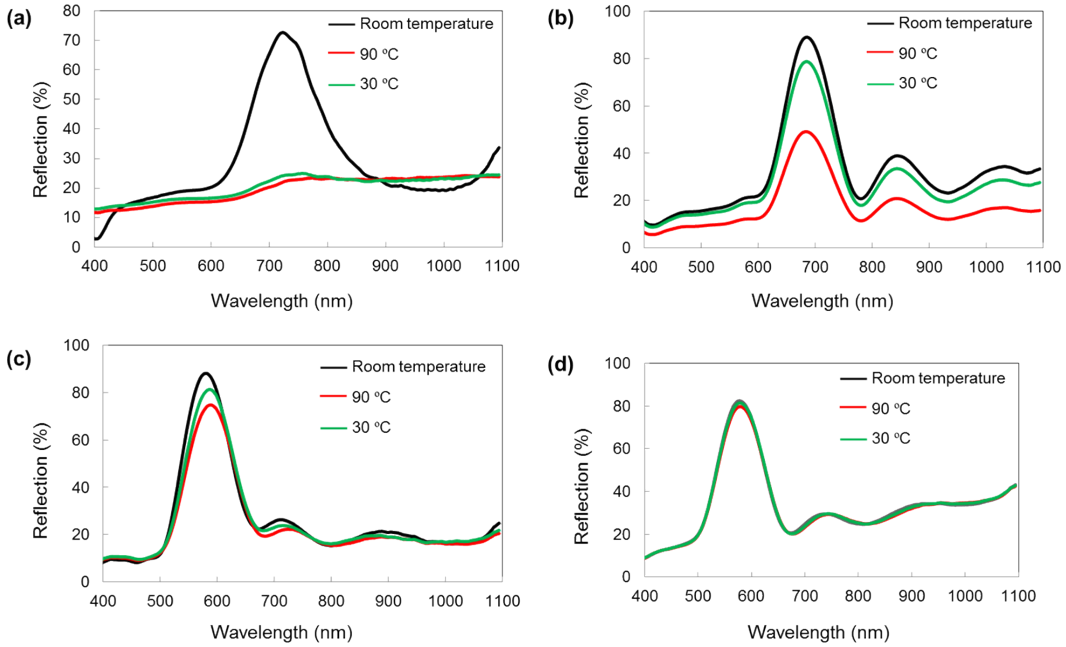


Fig. S11 The reflection spectra of the azobenzene CLCP inverse opal films polymerized by (a) M7201, (b) M4231, (c) M1171 and (d) M0091 as a function of temperature.

Reference:

1 Y. Y. Zhang, J. X. Xu, F. T. Cheng, R. Y. Yin, C. C. Yen and Y. L. Yu, *J. Mater. Chem.,* 2010, **20**, 7123-7130.

2 Z. Jiang, J. Lv, F. Cheng, J, Wei, Y. Yu, *Aust. J. Chem.,* 2014, **67**, 570-577.