## Supplementary data

### Bio-inspired Design of Active Photo-Mechano-Chemically Dual-Responsive Photonic Film Based on Cholesteric Liquid Crystal Elastomers

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Figure S1. UV–Vis absorption spectra in CHCl<sub>3</sub> solvent of the (left) A11M and (right) D-AZO.



Figure S2. DSC thermogram of CLC mixture with a heating/cooling rate of 5 °C/min.



Figure S3. Effect of photo irradiation on the selective reflection band upon successive irradiation of 405 nm blue light and 532 nm green light.



Figure S4. Experimental setup to measure the changes of reflection band for the CLCE samples as a function of temperature and light irradiation.



Figure S5. Effect of heat on the selective reflection band of the CLCE.

# Dynamic UV-Vis absorption spectra of A11M under successive irradiation of UV and green light

Figure S6 shows the dependence of the UV-Vis absorption spectra of

A11M (dissolve in chloroform with  $10^{-4}$  mol%) on irradiation time under successive 365 nm (UV) and 532 nm (green) light irradiation. Apparently, the  $\pi$ - $\pi^*$  and n- $\pi^*$  transition peaks of the A11M at 330 and 425 nm decreases and increases, respectively, after UV irradiation induced the trans–cis isomerization of A11M. Upon green light irradiation, the absorption spectrum of A11M recovers back to its original state due to the photoinduced cis–trans back isomerization.



Figure S6. Dependence of the UV-Vis absorption spectra of A11M on the irradiation time under 365 nm irradiation and recovery by 532 nm irradiation.



Figure S7. Dependence of the UV-Vis absorption spectra of (a) A11M and (b) D-azo on the irradiation time under 405 nm blue light irradiation.



Figure S8. Thermal analysis of CLCE film was performed by DSC before and after exposure of 405 blue light. The measured glass transition temperature of the film is reduced by the light exposure.



Figure S9. Synthetic route of chiral AZO dopant D-AZO.

#### Synthesis of Isosorbide Bis(4-nitrobenzoate)

Isosorbide (3.65 g, 25 mmol) and triethylamine (5.77 g, 57 mmol) were dissolved in 20 mL of  $CHCl_3$ , and the mixture was stirred at 0 °C. A solution of 4-nitrobenzoyl chloride (9.28 g, 50 mmol) dissolved in 20 mL of  $CHCl_3$  was further added dropwise, and the mixture was stirred for 6 h at 30 °C. After completing the reaction, the resulting solution was poured in water and

extracted by CHCl<sub>3</sub>. The extracted solution was concentrated using a rotary evaporator under vacuum. The residue was recrystallized with ethanol to give the product in 29.9% yield. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 4.10-4.11 (m, 4H, CH<sub>2</sub>O), 4.71-4.72 (d, 1H, CH), 5.09-5.11 (m, 1H, CH), 5.46-5.53 (m, 2H, COOCH), 8.33-8.18 (d, 8H, Ar-H).

#### Synthesis of Isosorbide Bis(4-aminobenzoate)

The intermediate Isosorbide Bis(4-nitrobenzoate) compound (4.70 g, 11 mmol) and ammonium chloride (4.50 g, 84 mmol) were dissolved in 50 mL of H<sub>2</sub>O and 80 mL of ethanol. A solution of sodium sulfide hydrate (14.40 g, 60 mmol) was further added to the mixture and then heated at reflux for 6 h. After cooling to room temperature, the precipitated solid was collected. The solid was redissolved in an aqueous HCI (10 M) solution (100 mL) and filtered. After ammonium was added to the solution to give pH 8, the precipitated solid was collected and dried. The residue was recrystallized with ethanol to give the product in 48.4% yield. <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>,  $\delta$  in ppm): 3.82-3.94 (m, 4H, CH<sub>2</sub>O), 4.52-4.53 (d, 1H, CH), 4.86-4.88 (m, 1H, CH), 5.20-5.26 (m, 2H, COOCH), 5.99-6.02 (d, 4H, NH), 6.53-6.57 (d, 4H, Ar-H), 7.60-7.64 (d, 4H, Ar-H).

#### Synthesis of Isosorbide Bis(4-hydroxy-4'-azobenzoate)

The intermediate Isosorbide Bis(4-aminobenzoate) compound (0.7 g (1.8 mmol) was dissolved in a mixture of 6 mL of concentrated hydrochloric acid and water. With stirring at 0 °C, 0.4 g (5.8 mmol) of sodium nitrite in water (4 mL) was added to the solution to produce diazonium salt. After the resulting solution was stirred at 0 °C for 1 h, a mixture of phenol (0.55 g, 5.8 mmol) and sodium hydroxide (0.53 g, 13.3 mmol) in 10 mL of water cooled to 0 °C was slowly added. The reaction mixture was stirred at 0 °C for 2 h. After HCI (5%) was added to the reaction mixture to give pH 4, the precipitated solid was collected and dried. The residue was recrystallized with ethanol to give the product in 25% yield. <sup>1</sup>H-NMR (500 MHz, acetone-d<sub>6</sub>,  $\delta$  in ppm): 4.09-4.15 (m, 4H, CH<sub>2</sub>O), 4.76-4.77 (d, 1H, CH), 5.01 (s, 2H, OH), 5.11-5.13 (m, 1H, CH), 5.46-5.54 (m, 2H, COOCH), 7.02-7.05 (d, 4H, Ar-H), 7.89-7.98 (m, 8H, Ar-H), 8.17-8.25 (dd, 4H, Ar-H).

## Synthesis of Isosorbide Bis(4-octoxycarbonyloxy-4'-azobenzoate) (D-AZO)

Nonanoyl chloride (0.97 g, 5.5 mmol) was added dropwise to a solution of a mixture of the intermediate Isosorbide Bis(4-hydroxy-4'-azobenzoate) compound (1.5 g, 2.5 mmol) and triethylamine (0.58 g, 5.75 mmol) in anhydrous

THF (40 mL). The reaction mixture was stirred at room temperature for 24 h. After completing the reaction, the resulting solution was poured in distilled water and extracted by  $CHCl_3$ . The extracted solution was concentrated using a rotary evaporator under vacuum. The residue was recrystallized with THF to give the product in 78% yield.



Figure S11. Synthetic route of monomer A11M.

#### Synthesis of 4-Hydroxy-4'-methoxy-azobenzene

4-Methoxyaniline (4.46 g, 36.23 mmol) was dissolved in 1M aqueous HCI (100 ml) and kept in the ice bath at 0 °C. NaNO<sub>2</sub> (3.53 g, 51.16 mmol) in water (20 ml) was added dropwise to the former solution and stirred for 30 min. NaOH (4.4 g, 0.11 mol) and phenol (5.0 g, 53.19 mmol) were dissolved in water (100 ml) and stirred for 30 min at 0 °C. The former solution was added dropwise to the latter solution at 0 °C and then stirred for 1 h. The resulting mixture was poured into water and solution was neutralized with 5% aqueous HCI. The

crude product was filtered and recrystallized twice by EtOH. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 3.68 (s, 3H, OCH<sub>3</sub>), 5.12 (s, 1H, OH), 7.02-7.08 (d, 4H, Ar-H), 7.76-7.80 (m, 4H, Ar-H).

#### Synthesis of 1-Hydroxy-n-(4-methoxy-azobenzene-4'oxy)undecane

4-Hydroxy-4'-methoxy-azobenzene (3.76 g, 16.50 mmol) was dissolved in N,Ndimethylacetamide (150 ml). KOH (1.1 g. 19.8 mmol) dissolved in N,Ndimethylacetamide (30 ml) was then added dropwise to the former solution. 11-Bromo-1-undecanol (26.09 g, 103.9 mmol) and a trace of KI were then added, and the solution was heated at reflux for 2 days. The resulting mixture was poured into water and extracted with  $CH_2Cl_2$ . After drying, the crude product was recrystallized twice by EtOH. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 1.16-1.84 (m, 18H, CH<sub>2</sub>), 3.5 (m, 2H, *ortho* to OH), 4.12 (t, 2H, -CH<sub>2</sub>OPh-), 7.02-7.08 (d, 2H, Ar-H), 7.78-7.88 (d, 4H, Ar-H), 7.96 (d, 2H, Ar-H).

#### Synthesis of 11-(4-Methoxy-4'-oxy-azobenzene)undecyl acrylate (A11M)

1-Hydroxy-n-(4-methoxy-azobenzene-4'oxy)undecane (2.32 g, 5.83 mmol), N,N-dimethylaniline (2.0 g, 16.5 mmol) and a catalytic amount of 2,6-ditertbutyl-*p*-cresol were dissolved in distilled 1,4-dioxne (30 ml). The solution was cooled with an ice/salt bath and then acryloyl chloride (1.05 g, 11.7 mmol), dissolved in distilled 1,4-dioxane (20 ml), was added dropwise under vigorous stirring. The mixture was stirred for 8 h at room temperature. After completing the reaction, the solution was poured into cold water and the precipitate was filtered. The crude product was washed several times with water and recrystallized twice by EtOH.

