Supporting Information

Biomimetic Inspired Liquid Crystal Elastomers with Dual-Mode Actuation Featuring Vapor Self-Oscillation and Photothermal Bending

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Experimental Section

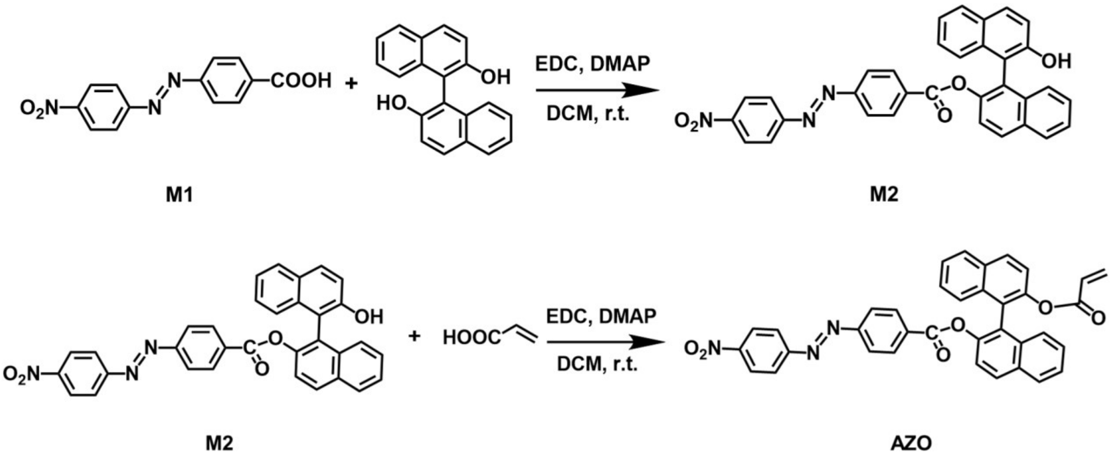
Materials: RM23, RM82 was purchased from KINDCHEM (Nanjing, China). photoinitiator 819 was obtained from Sigma-Aldrich (Merck, USA). 1,1'-bi-2-naphthol, 4-amino-3,5-difluorobenzoic acid, 2,6-difluoroaniline, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC), 4-dimethylaminopyridine (DMAP), acrylic acid were purchased from Bide Pharmatech Ltd (Shanghai, China).

UniPS® spacer plastic balls were purchased from KB spheres (Suzhou, China). All reagents and solvents have a purity of over 98% and can be used directly without further purification.

Characterizations： ^{1}H NMR spectra were measured on a Bruker 400 (400 MHz ^{1}H, ^{13}C) spectrometer at room temperature. UV-Vis spectroscopic studies were performed on a spectrometer (UV-2600). Fourier transform infrared (FT-IR) spectra were taken using a Thermo Nicolet Nexus FT-IR devise with the Smart Golden Gate ATR attachment in the range of 4000-500 cm^{-1} with 2 cm^{-1} resolution. The surface morphology was investigated by field emission scanning electron microscopy (FESEM, JSM-7500F, JEOL, Japan).

Synthesis

The synthetic protocols of **AZO** are outlined below.



Scheme S1. Synthesis routes for the compound **AZO**.

The synthesis method of **M1** was conducted as described in the previous literature.[1] The procedures of **AZO** are described below.

Synthesis of compound M2: M1 (271 mg, 1 mmol), EDC (215 mg, 1.2 mmol) and

DMAP (20 mg, 0.16 mmol) were dissolved in 20 mL of anhydrous DCM with stirring at room temperature, followed by the addition of binaphthol (572 mg, 2 mmol). After stirring for 24 hours, the solvent was removed under reduced pressure. The residue was purified by chromatography (using DCM) to afford **M2** in the form of an orange powder (302 mg, yield 56%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.68 (s, 1H), 8.47 (d, *J* = 9.0 Hz, 2H), 8.18 (d, *J* = 8.9 Hz, 1H), 8.15-8.05 (m, 3H), 7.91-7.79 (m, 4H), 7.74 (dd, *J* = 8.7, 2.9 Hz, 3H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 8.9 Hz, 1H), 7.27-7.19 (m, 3H), 7.02-6.95 (m, 1H).

Synthesis of compound AZO: M2 (269 mg, 0.5 mmol), acrylic acid (72 mg, 2 mmol), EDC (117 mg, 0.6 mmol) and DMAP (20 mg, 0.16 mmol) were dissolved in 20 mL of anhydrous DCM with stirring at room temperature. After stirring for 24 hours, the solvent was removed under reduced pressure. The residue was purified by chromatography (using DCM) to afford **AZO** in the form of an orange powder (121 mg, yield 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.4 Hz, 2H), 8.12-7.97 (m, 5H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.82 (q, *J* = 8.5 Hz, 4H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.58-7.45 (m, 3H), 7.38 (t, *J* = 6.3 Hz, 4H), 6.08 (d, *J* = 17.3 Hz, 1H), 5.93 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.69 (d, *J* = 10.4 Hz, 1H). ESI-MS: m/z calcd for $C_{36}H_{23}N_3O_6$, 593.16; found, 594.1690 ($M+H^+$).

Preparation of the glass cell. To prepare a parallel arrangement of LCE films on one side, the inner surfaces of glass substrates were coated with 10wt% of polyvinyl alcohol (PVA) aqueous solution (M_w = 89000) and dried at 100 °C for 40 min. The coated glasses were then rubbed in a parallel direction after drying. To prepare a perpendicular arrangement of LCE films, the substrate glasses were immersed in 1.5 wt% dimethyl octadecyl (3-trimethoxysilylpropyl) ammonium chloride (DMOAP) solution and shaken with an ultrasonic oscillator for 20 min. After taking out from the DMOAP solution, the treated glasses were shaken in water for 5 min. The treated glasses were taken out and placed in an oven (100 °C) for 1 h.

Preparation of the liquid crystal film. RM23, RM82, azobenzene (AZO), and the photoinitiator were weighed in the specified stoichiometric ratios and transferred to a brown glass vial, with strict protection from light throughout. These components were dissolved in 1 mL of DCM, after which the vial was sealed with a parafilm, pierced with a single pinhole to facilitate DCM evaporation, and placed on a hot plate set to 90 °C. Upon heating to a molten state, the mixture was drawn up with a syringe and injected into a glass cell. Polymerization was then conducted under light irradiation at 62 °C for 25 minutes, yielding an orange-yellow film.

Theoretical Calculation: Theoretical calculation was performed for AZO, 1,1′-binaphthyl, azobenzene. Conformational optimization of the three representative molecules.

Thermal conversion properties characterization: The 405 nm laser was irradiated at a film density at 54 mW cm^{-2}. The changes of temperature and photothermal images were recoded with an IR thermal camera (FOTRIC 226), when the 405 nm illumination was turned on and off in water and air.

LCE-2/LCE-3 Preparation： The preparation procedures of LCE-2 and LCE-3 were similar to that of LCE-1, except that the azobenzene-based monomer (AZO) was replaced by the corresponding control chromophores. Specifically, 1,1′-binaphthyl was used for LCE-2, and azobenzene was used for LCE-3, while all other components, including RM23, RM82, and photoinitiator 819, were kept at the same molar ratios. The mixtures were first heated to 100 °C to ensure complete dissolution and homogenization, and subsequently injected into alignment-treated glass cells in the isotropic state. The filled cells were then cooled at a controlled rate of 3 °C min⁻¹. Photopolymerization was carried out at 58 °C for LCE-2 and 62 °C for LCE-3, respectively, for 25 min under identical irradiation conditions. After polymerization, the glass substrates were removed to obtain the corresponding LCE films.

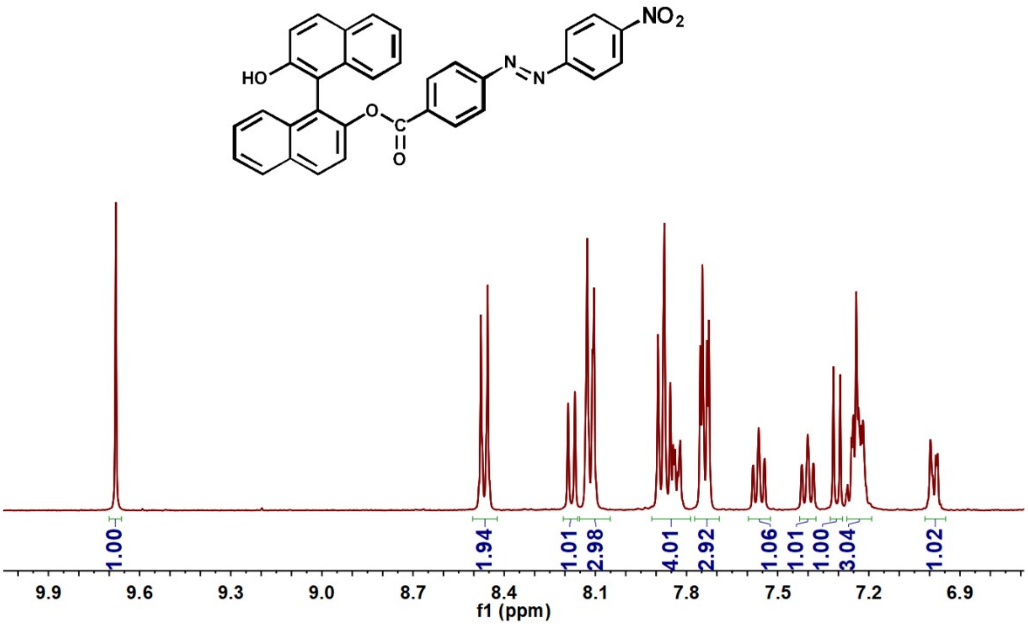


Figure S1. ^{1}H NMR spectrum of compound **M2** in DMSO-d$_6$.

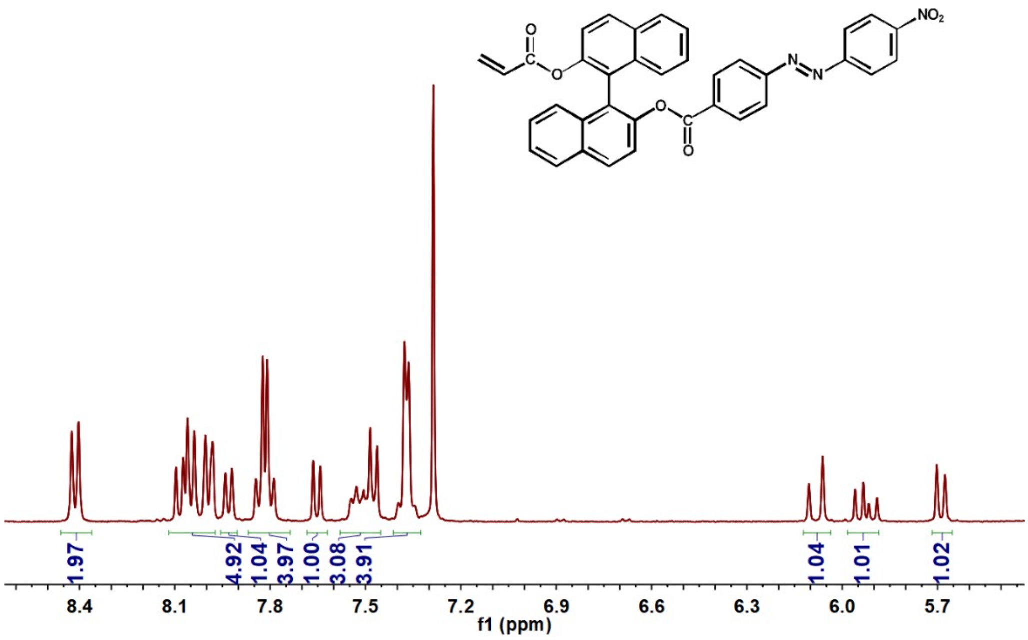


Figure S2. ^{1}H NMR of compound **AZO** in CDCl$_3$.

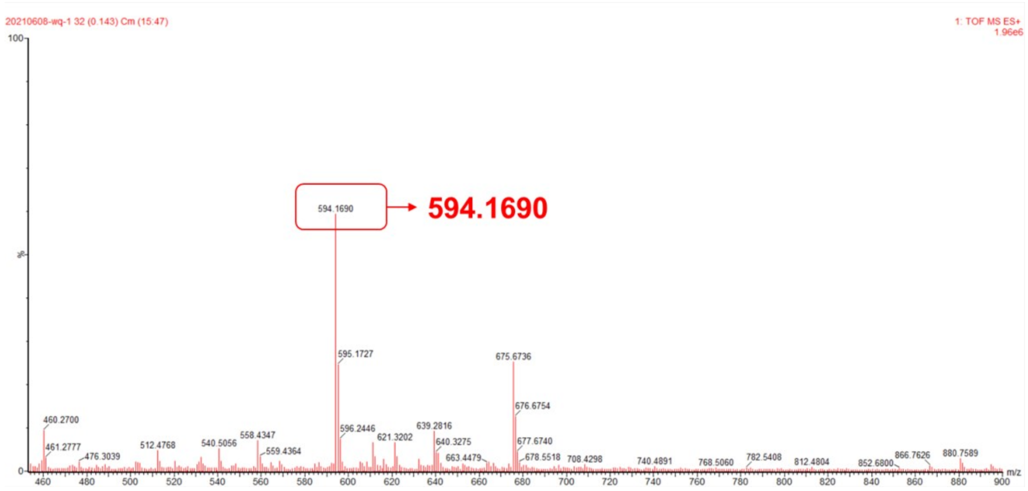
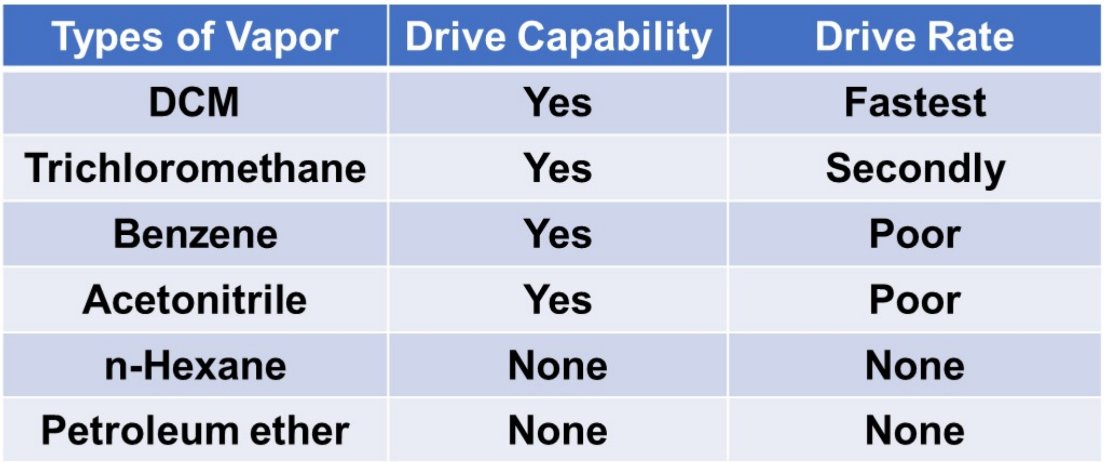


Figure S3. ESI-MS of compound **AZO**.



Types of Vapor	Drive Capability	Drive Rate
DCM	Yes	Fastest
Trichloromethane	Yes	Secondly
Benzene	Yes	Poor
Acetonitrile	Yes	Poor
n-Hexane	None	None
Petroleum ether	None	None

Table S1. Vapor-dependent self-oscillation behavior of LCE-1 films under different organic solvents.

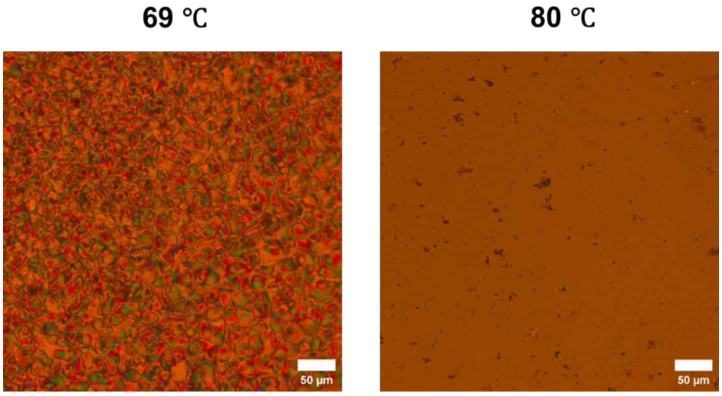


Figure S4. State of the **LCE-1** at different temperatures from 69 to 80 °C under a polarizing microscope.

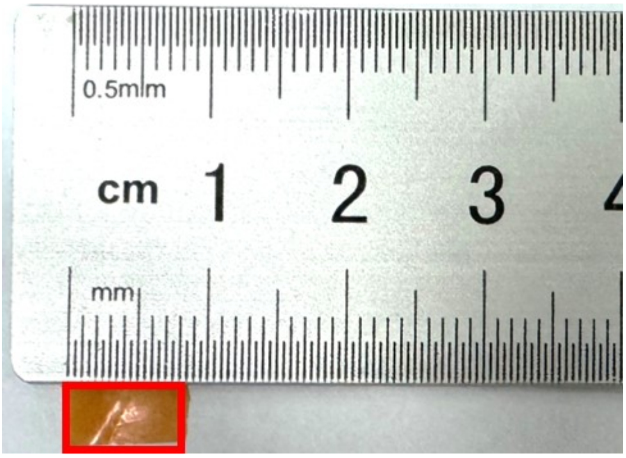


Figure S5. Image of prepared planar **LCE-1** films (8 mm× 2 mm) with thickness of 20 μm.

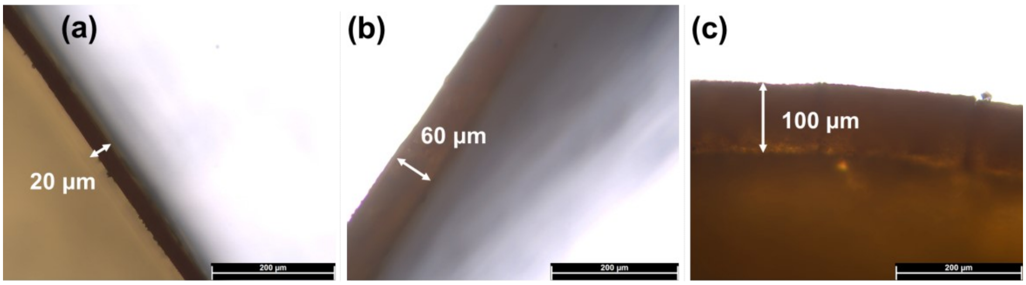


Figure S6. Prepared planar **LCE-1** films with thickness of (a) 20 μm, (b) 60 μm, and (c) 100 μm. Only a thin film with 20 μm thickness can exhibit the self-oscillation movement.

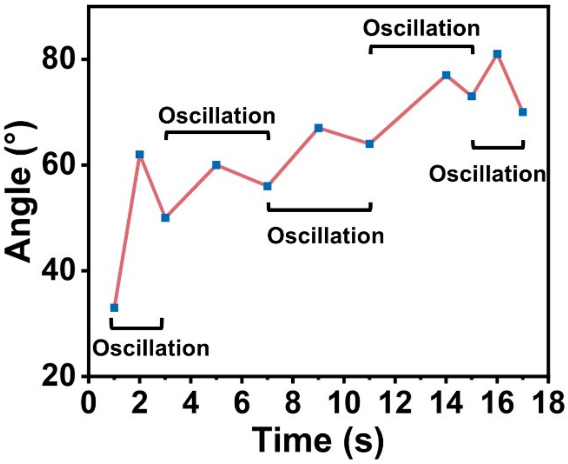


Figure S7. Summary of bending angles against time calculated from the screenshot of the oscillating video of the LCE films.

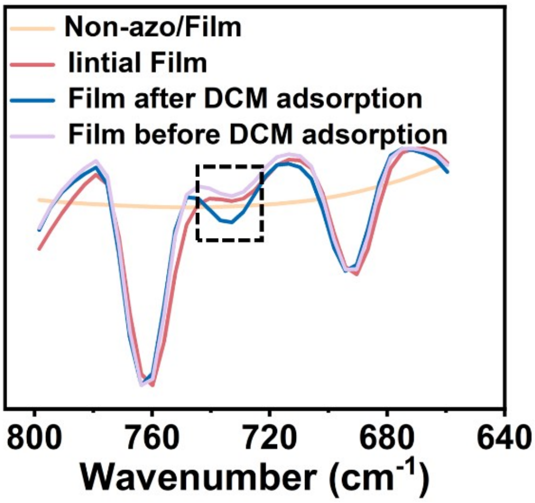


Figure S8. ATR-FTIR spectra of the planar LCE films before and after DCM treatments.

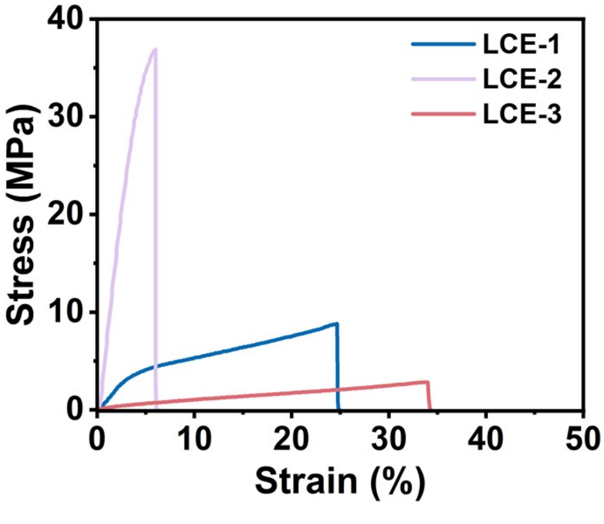


Figure S9. Stress–strain curves of LCE-1, LCE-2, and LCE-3 measured under tensile loading, illustrating the differences in mechanical strength and elongation behavior among the samples.

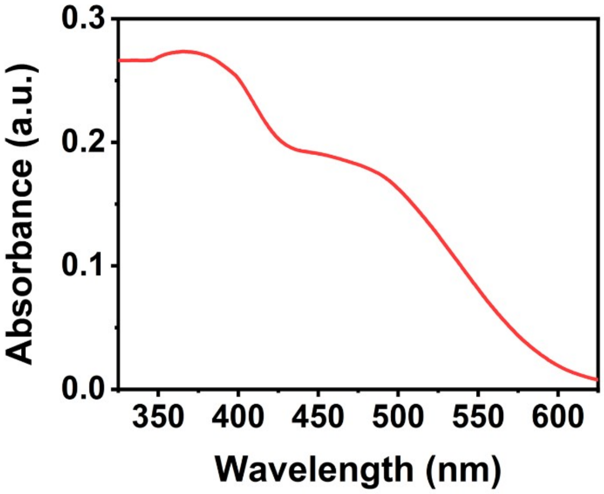


Figure S10. UV-vis absorption spectra of the splay LCE film. UV-vis absorption spectra of the splay **LCE-1** film.

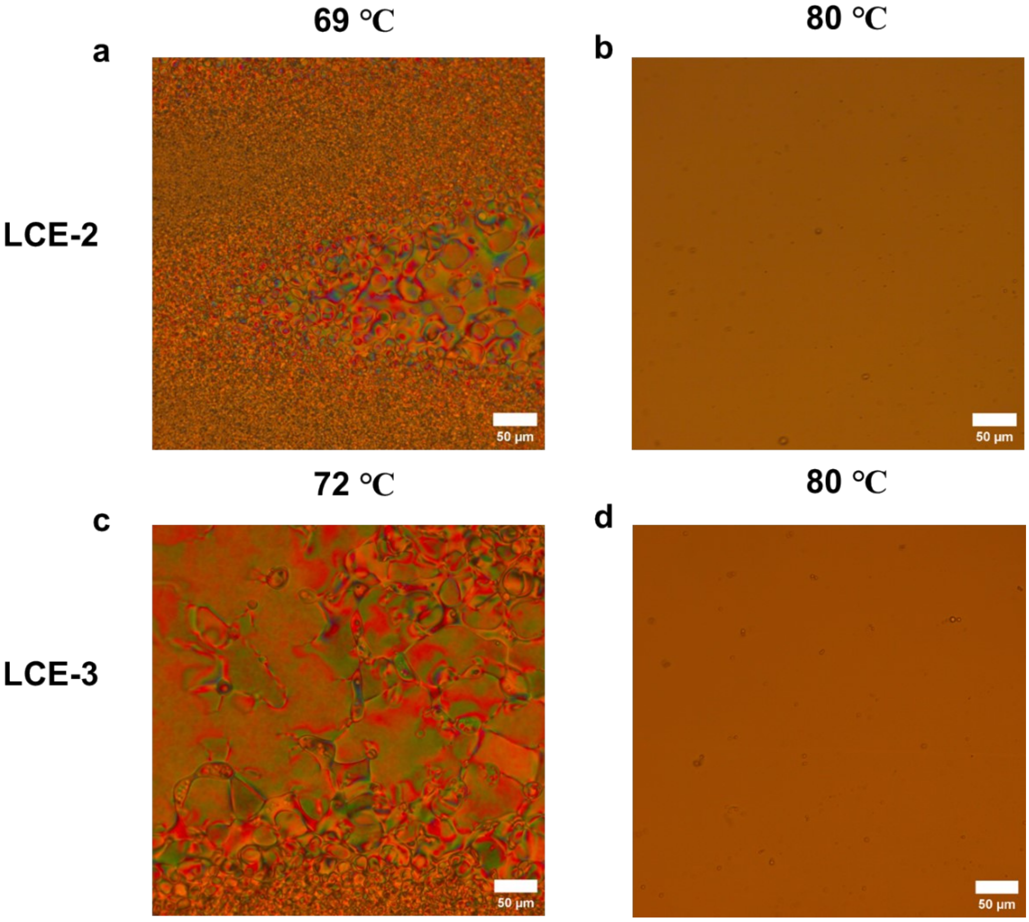


Figure S11. State of the **LCE-2** and **LCE-3** at different temperatures under a polarizing microscope.

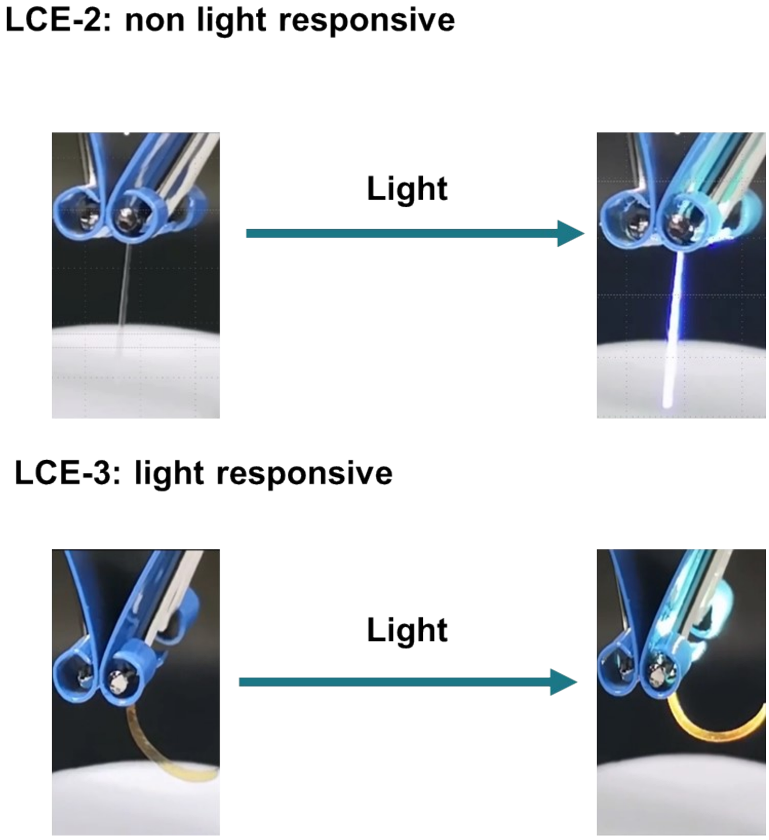


Figure S12. **LCE-2** and **LCE-3** were evaluated for their photoresponsive capabilities before and after light exposure.

Notably, **LCE-2** exhibited no photoresponsive, which further confirms that the photoresponsive properties are inherently conferred by the azobenzene moiety.

References

1. H. W. Zhou, C. G. Xue, P. Weis, Y. Suzuki, S. L. Huang, K. Koynov, G. K. Auernhammer, R. Berger, H. J. Butt and S. Wu, *Nat. Chem.*, 2017, **9**, 145-151.