

Support information

Thermal- and Light-responsive Programmable Shape-memory Behavior of Liquid Crystalline Polyurethane with Pendant Photosensitive Group

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Materials.

N-methyldiethanolamine (MDEA, 98%), hexamethylene diisocyanate (HDI, 98%), and dibutyltin dilaurate (DBTDL, 95%) were all purchased from Sigma-Aldrich. *N,N*-dimethylformamide (DMF, >99%), dichloromethane (99%), anhydrous magnesium sulfate (>97%), Butane-1,4-diol (BDO, 99%), 3-bromo-1-propanol (BPO, 99%), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI, 97%), and 4-dimethylaminopyridine (DMAP, 98%) were provided by Aladdin (Shanghai, China). All materials were used as received without further purification.

Materials synthesis.

Synthesis of conventional polyurethane (PU): A solution of MDEA (0.96 g, 0.008 mol) in DMF (10 mL) was heated at 80 °C under a nitrogen atmosphere. HDI (1.68 g, 0.01 mol) and the catalyst DBTDL (0.2 wt% to MDEA) were then added to the solution. After mechanical stirring at 80 °C for 4 h, BDO (0.18 g, 0.002 mol) was added and the mixture was stirred for another 12 h. The resulting mixture was poured into a Teflon mold and dried in a vacuum oven at 80 °C for two days to yield PU.

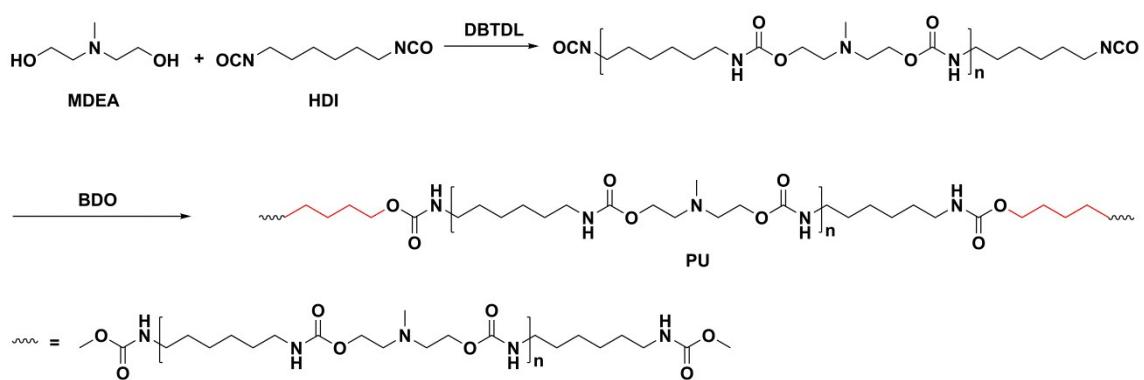


Figure S1. Synthetic route of PU.

Synthesis of 3-bromopropyl 4-((4-(octyloxy)phenyl)diazenyl)benzoate (Azo-Br):

Azo-COOH was prepared according to the literature¹. Azo-Br was synthesized by first dissolving Azo-COOH (3.5 g, 0.1 mol), BPO (1.4 g, 0.1 mol), EDCI (2.0 g, 0.1 mol), and a small amount of DMAP in dichloromethane (50 mL). The obtained mixture was

then stirred for 48 h at room temperature followed by washing with deionized water.

Next, the organic layer was dried with MgSO_4 and the solvent was removed under reduced pressure. Finally, the crude product was purified by the silica-gel column chromatography (eluent: dichloromethane/petroleum ether=1/1, v/v) to form a yellow powder with a 90 % yield.



Figure S2. Synthetic route of Azo-Br.

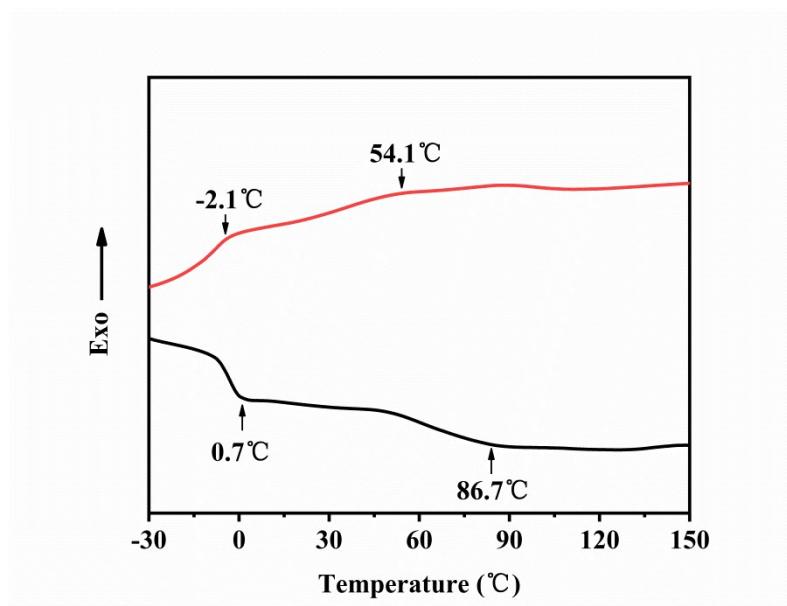


Figure S3. DSC thermogram of PU.

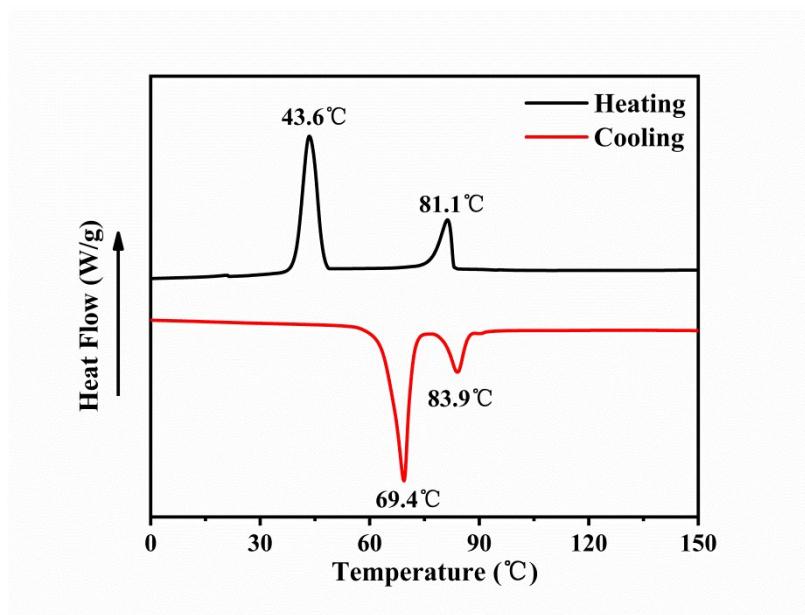
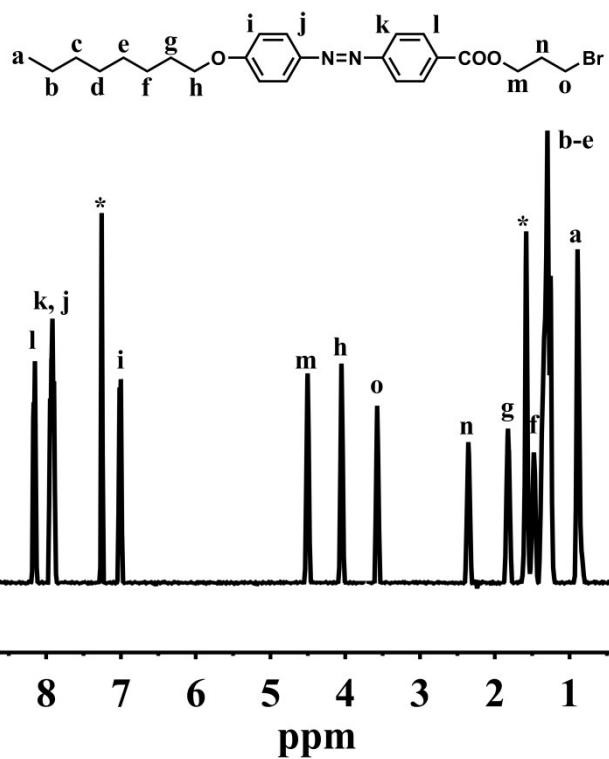


Figure S5. DSC thermogram of Azo-Br.

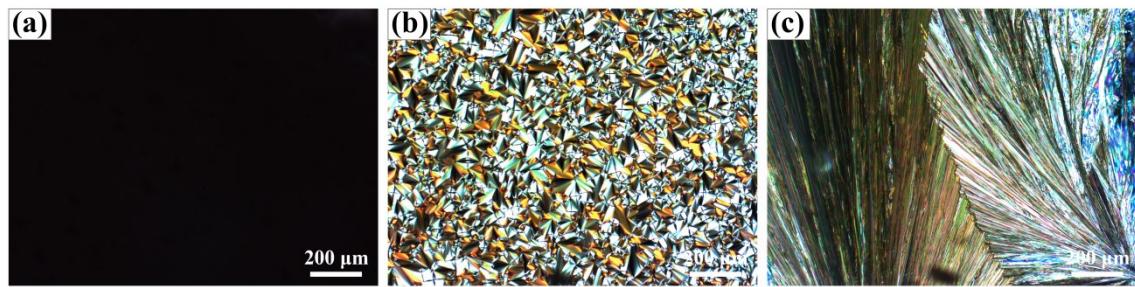


Figure S6. POM images of Azo-Br upon cooling at (a) 90 °C, (b) 75 °C, and (c) room temperature.

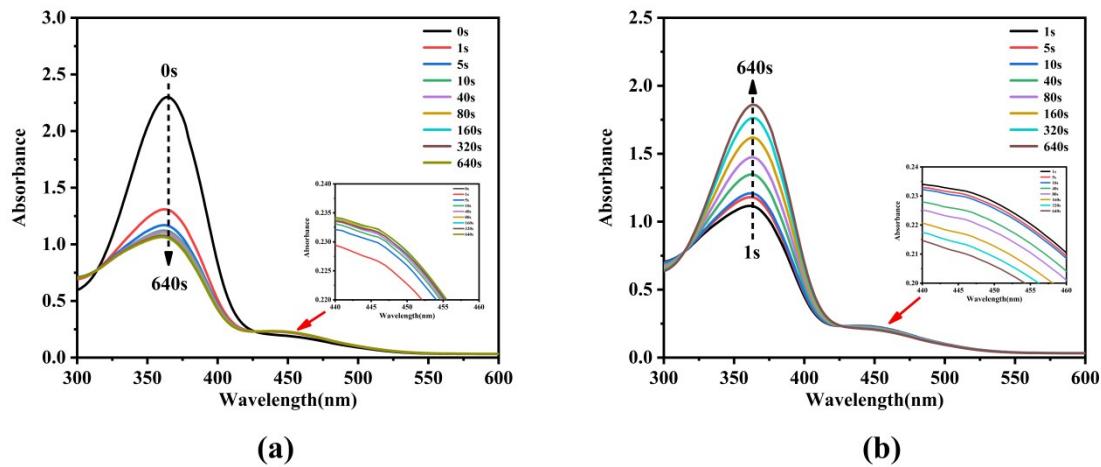


Figure S7. UV-vis absorption spectra of Azo-Br in DMF solution (2.0×10^{-6} mol/L) upon irradiation with (a) UV light (365nm) and (b) visible light (450 nm). The arrows show the increment in irradiation time.

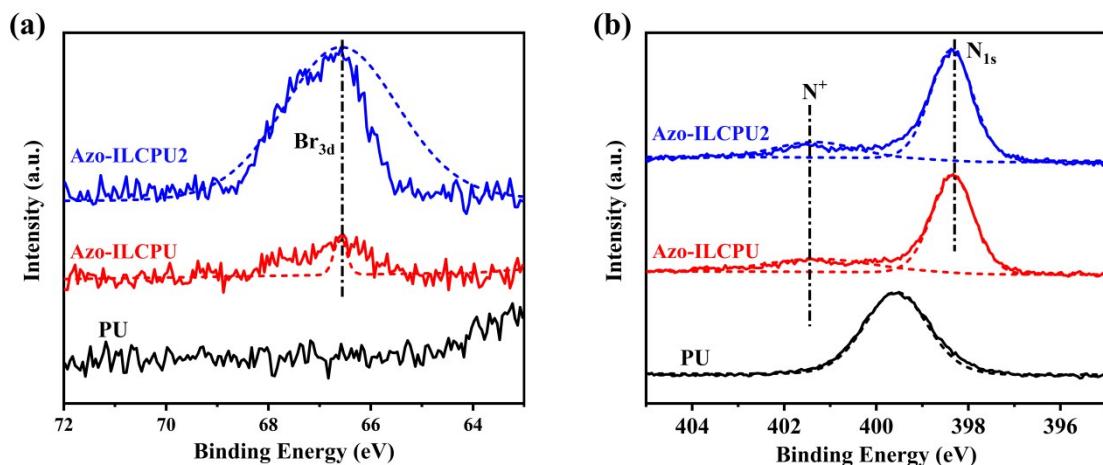


Figure S8. (a) Br_{3d} and (b) N_{1s} spectra of PU, Azo-ILCPU, and Azo-ILCPU2. To observe the change in XPS spectra for the polyurethane before and after grafting the mesogenic units, Azo-ILCPU2 with a larger grafting ratio was synthesized via the quaternarization reaction between PU (2g) and Azo-Br (2.48 g), and the detailed process was in the same way as Azo-ILCPU. The appearance of Br_{3d} peak at about 67.6 eV and quaternary-ammonium (N⁺) peak at 402.5 eV in the XPS spectra of Azo-LCPU in comparison with that of PU confirms the formation of quaternary ammonium.

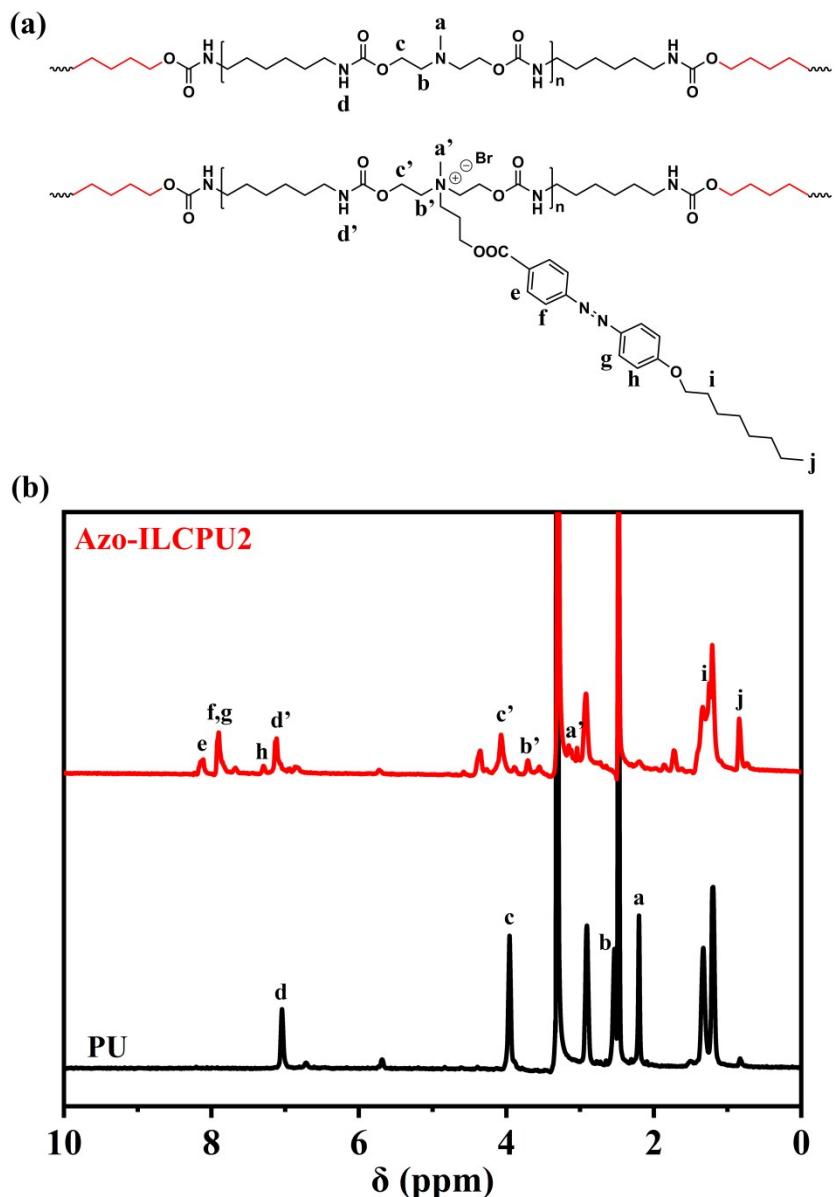


Figure S9. ^1H -NMR spectra of PU and Azo-ILCPU2, showing the successful grafting of the mesogenic units onto the PU chain after the quaternarization reaction.

The number-average molecular weight of polymers was evaluated by Gel permeation chromatography (GPC). The model of the GPC is Beijing Wenfen LC98IIRI equipped with two gel columns (Shodex, KD-803 and KD-806), and the refractive index detector is RI-201H, using DMF as the mobile phase. The test temperature is 40 °C and the standard sample is polystyrene.

Table S1. The GPC results of PU and Azo-ILCPU.

Sample	M_n (g/mol)	M_w (g/mol)	Polymer Dispersity Index
PU	1.53×10^4	3.88×10^4	2.53
Azo-ILCPU	2.04×10^4	4.59×10^4	2.25

The calculus of the grafting ratio of the mesogenic azobenzene moieties:

$$G = 100 \times \frac{\frac{M_{n,Azo-ILCPU} - M_{n,PU}}{M_{Azo-Br}}}{\frac{M_{n,PU} \times \omega}{M_{MDEA}}}$$

where, G denotes the grafting ratio of the liquid crystalline units of the sample;

$M_{n,Azo-ILCPU}$ and $M_{n,PU}$ denote the number-average molecular weight of Azo-ILCPU and PU, respectively; M_{Azo-Br} and M_{MDEA} denote the molecular weight of Azo-Br and MDEA, respectively; ω denotes the mass fraction of MDEA in the materials which were used to prepare PU.

The calculated grafting ratio (G) was about 24.7%.

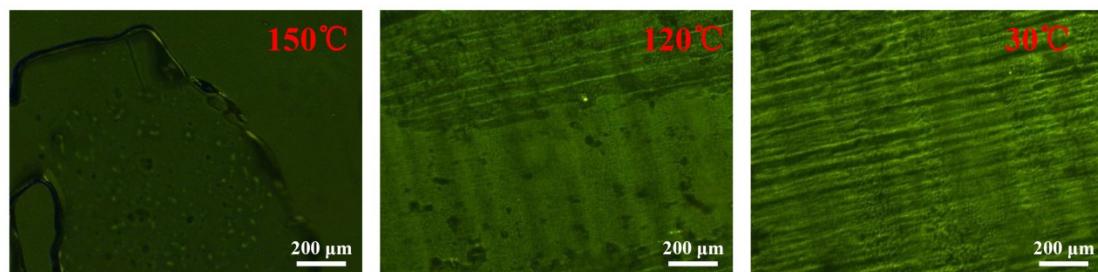


Figure S10. POM images of PU at different temperatures.

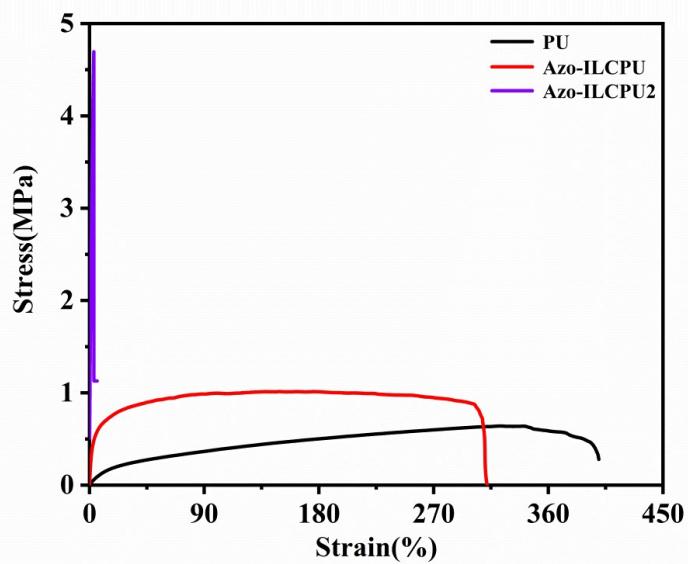


Figure S11. The stress-strain curves of PU film, Azo-ILCPU film, and Azo-ILCPU2 film. The graft of mesogenic moieties weakened the toughness of the materials. Therefore, Azo-ILCPU was chosen for photomechanical studies in comprehensive consideration of the mechanical properties and liquid crystalline properties of the materials.

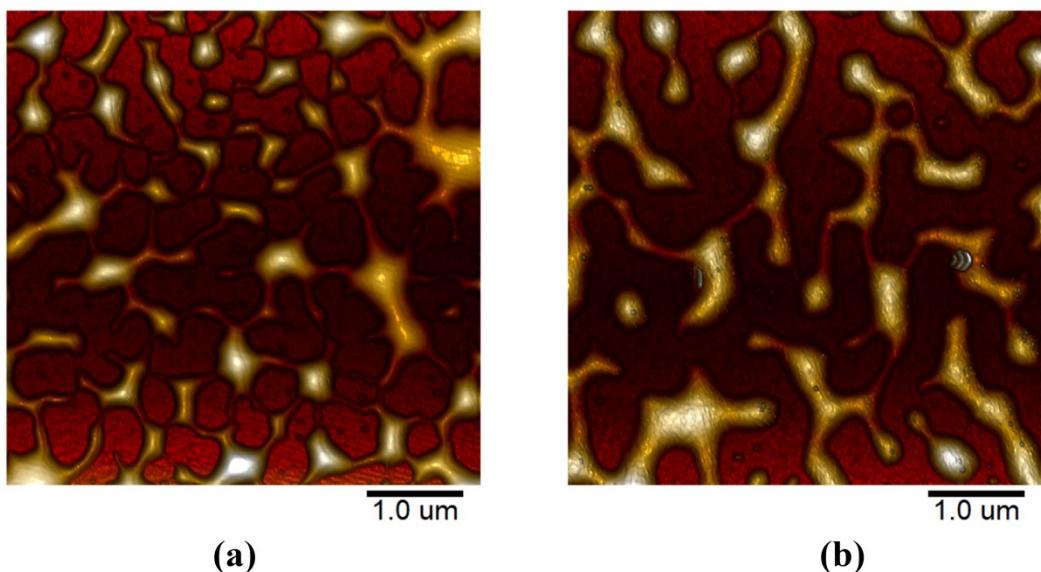


Figure S12. AFM images of (a) PU and (b) Azo-ILCPU. Granular hard domains (bright) and uniformly distributed soft domains (dark) were noticeable.



Figure S13. Photograph of temperature-induced shape memory effect cycle of PU film.



Figure S14. Photograph of temperature-induced shape memory effect cycle of Azo-ILCPU film.

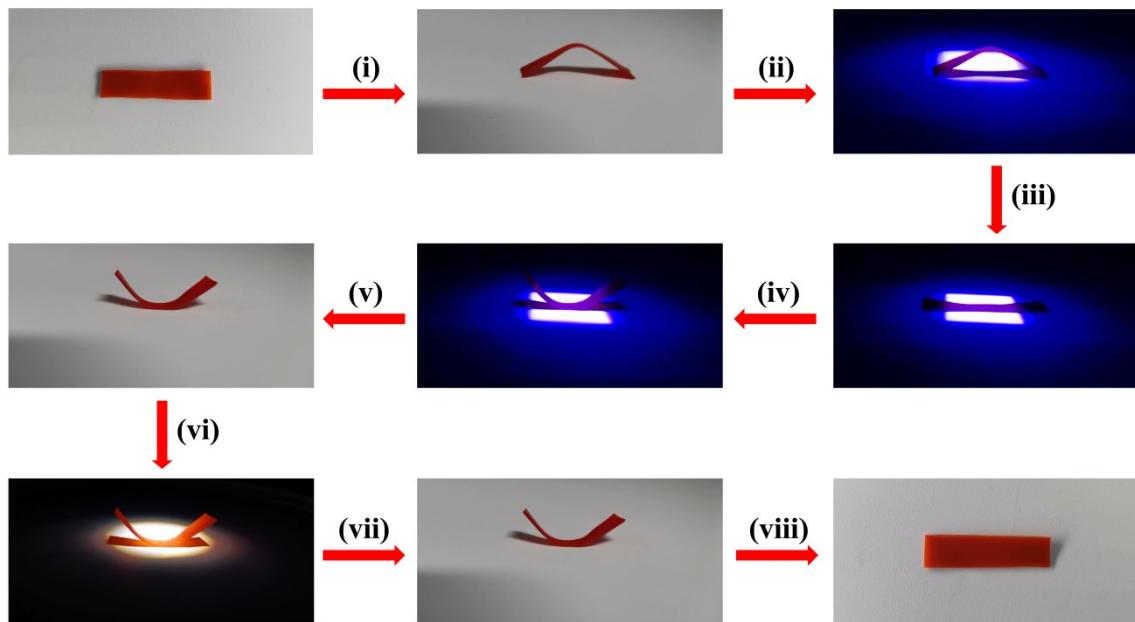


Figure S15. Photographs of the thermal- and light-responsive programmable shape-memory cycle for the Azo-ILCPU film under different conditions. (i) stretched and bent at 100 °C and then cooled to room temperature, irradiated with UV light (365 nm, 50 mW/cm²) for (ii) 0s, (iii) 3s, and (iv) 8s, (v) removed UV light, (vi) irradiated with visible light for ten minutes, (vii) removed visible light, and (viii) heated to 100 °C for some minutes. To further confirm the thermal- and light-responsive programmable shape-memory behavior, the Azo-ILCPU film was first stretched and bent to obtain a curved shape with a certain curvature. Once irradiated with UV light (365 nm, 50

mW/cm^2), the film bent toward the light source and deformed into another curved shape with the opposite curvature. The as-obtained curved shape with the opposite curvature was held in the absence of UV light or even under visible light exposure. After heating to 100 °C for some minutes, the film recovered to the original flat shape.



Figure S16. Photograph of the as-stretched PU film under UV light (365 nm, 50 mW/cm^2). The as-stretched PU film did not bend and still held the flat shape even under UV exposure for 60 s.

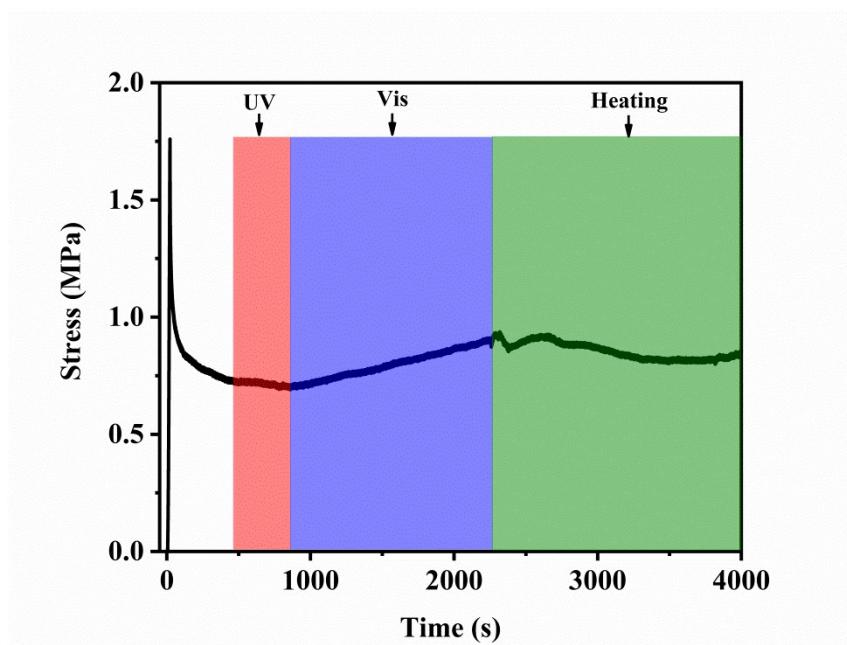


Figure S17. The measured tensile stress via Mode I in the PU film at different stimuli.

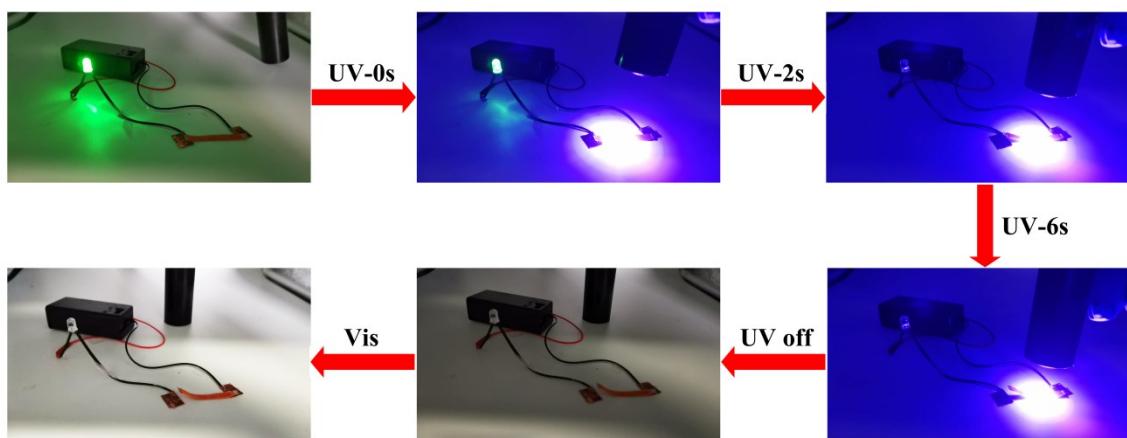


Figure S18. Photographs of the work processes of the intelligent circuit switch based on Azo-ILCPU. The Azo-ILCPU was also programmed into an intelligent circuit switch via adhering a copper foil to an as-stretched film. A simple circuit containing a power supply, a light bulb, and the as-fabricated intelligent circuit switch was constructed. The intelligent circuit switch was in a flat shape, and the circuit was closed and the light bulb was on. Once irradiated with UV light, the intelligent circuit switch transformed from the flat shape into a curved shape, and the circuit was disconnected and the light bulb was off. Owing to the shape memory performance of the Azo-ILCPU film, the intelligent circuit switch held the curved shape and the circuit remained disconnected state after the UV light was removed or under visible light exposure. Therefore, the liquid crystalline polyurethane in this work also may be applied in intelligent circuit fields.

1. I. Niezgoda, D. Pociecha and Z. Galewski, *Thermochimica Acta*, 2014, **587**, 59-66.