Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Synchronous Differential Orientation of Liquid Crystal Elastomers Based on Dual Dynamic Covalent Bonds

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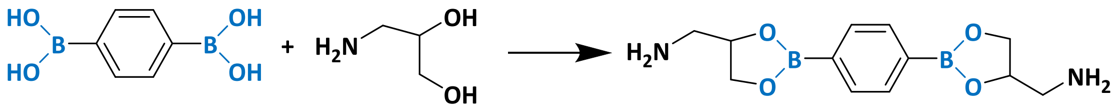
Materials and methods

1.1 Materials

Liquid crystal mesogen 1,4-bis-[4-(6-acryloyloxyhexyloxy) benzoyloxy]-2-methylbenzene (RM82, 97%) was purchased from Shijiazhuang Yesheng Chemical Technology Co. Ltd. (China). 2,2′-(Ethylenedioxy) diethanethiol (EDDET, 98%), 1,3-bis (aminopropyl) tetramethyldisiloxane (BATS, 97%), 3-amino-1,2-propanediol (98%), 1,4-phenylenebisboronic acid (98%), 4-aminophenol (96%), triethylamine (99.5%), 6-chlorohexanol (98%), acryloyl chloride (98%), potassium iodide (98%), phenol (98%), and hydroquinone (99%) were purchased from Energy Chemicals (China). Magnesium sulfate, tetrahydrofuran, sodium hydroxide, sodium nitrite, hydrochloric acid, potassium carbonate, chloroform, N, N-Dimethylformamide, methanol, ethanol, toluene and dichloromethane were purchased from Sinopharm (China). Dichloromethane was distilled from CaH_2 under nitrogen. Other chemical reagents were used without purification.

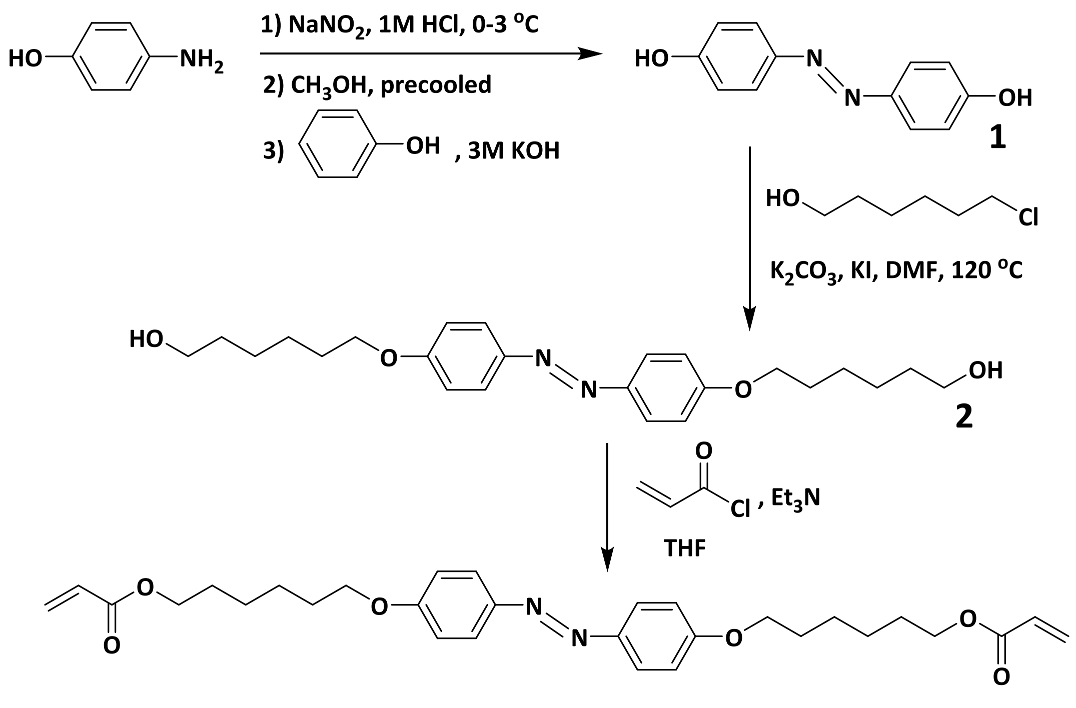
1.2 Synthesis of diamino-functionalized boronic ester DAB



Scheme S1. Synthetic route of DAB.

The synthetic procedure of the diamino-functionalized boronic ester (DAB) is presented in **Scheme S1**. Firstly, 3-amino-1,2-propanediol (2.19 g, 24 mmol) was dissolved in ethanol (40 mL), and then 1,4-phenylene diboronic acid (2 g, 12 mmol) was slowly added to the solution. The reaction mixture was stirred at room temperature for 24 h, followed by filtration and washing, resulting in the formation of DAB (white solid).^{1}H NMR (*d*-DMSO, 400 MHz) δ: 7.48 (m, 2H), 4.19 (m, 1H), 4.04 (m, 1H), 3.92 (m, 1H), 3.8 (m, 1H), 3.65 (m, 1H) (**Figure S1**). HRMS m/z: 276.1537 [m+H]$^+$(**Figure S3**).

1.3 Synthesis of diacrylate-functionalized monomer DAHAB



Scheme S2. Synthetic route of DAHAB.

The synthetic route of diacrylate-functionalized monomer (DAHAB) is presented in **Scheme S2**. 4-Hydroxyaniline (5 g, 45.82 mmol) was dissolved in dilute hydrochloric acid (100 mL, 1M) and cooled to 0-3 °C. An aqueous solution of sodium nitrite (4.67 g, 54.9 mmol in 75 mL water) was added dropwise under continuous stirring. Next, the obtained diazonium salt was diluted with 100 mL ethanol. Separately, phenol (4.31 g, 45.82 mmol) was dissolved in NaOH solution (32.5 mL, 3M) and stirred 2 h at room temperature. Afterwards the resulting mixture was concentrated using a vacuum rotary evaporator, and then the solution was neutralized with dilute hydrochloric acid. The red precipitate was then filtered, washed with water and dried. The crude material was recrystallized from ethanol/water twice, yielding dark-red solid 1.

Compound 1 (4 g, 18.67 mmol), 6-chlorohexan-1-ol (7.64 g, 56 mmol), and K_2CO_3 (7.74 g, 56 mmol) were dissolved in 100 mL dimethylformamide. A catalytic amount of KI was added and the mixture was refluxed at 100 ^{o}C for 6 h. After the reaction mixture was cooled to room temperature, 800 mL water were added. The precipitate was collected, dried, and then extracted with a solvent mixture of tetrahydrofuran (THF) and chloroform (1:1 volume ratio). The organic layer was dried with anhydrous $MgSO_4$. After evaporation of the solvent, the crude product was purified through recrystallization in chloroform to give Compound 2.

Compound 2 (2 g, 4.82 mmol), triethylamine (0.53 g, 5.23 mmol), and acryloyl chloride (1.44 g, 15.9 mmol) were dissolved in dehydrated THF (100 mL). A trace amount hydroquinone was dissolved to stabilize the self-polymerization. The solution was mixed at 0 °C for 4 h and then at 40 °C for 24 h. The reaction was quenched by pouring 500 mL of deionized water into the mixture, after which it was extracted with chloroform for several times. The organic phase was then dried with $MgSO_4$. After filtration, the extracted solution was condensed and purified by silica gel column chromatography (eluent/chloroform: ethyl acetate = 1:1, v: v). The resulting material was recrystallized in methanol to yield pure DAHAB. ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 7.84 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 6.38 (d, J = 16.8 Hz, 1H), 6.11 (dd, J = 9.6, 10.4 Hz, 1H), 5.8 (d, J = 10.4 Hz, 1H), 4.17 (t, J = 14 Hz, 2H), 4.02 (t, J = 12.2 Hz, 2H),1.81 (t, J = 12.8 Hz, 2H), 1.71 (t, J = 14 Hz, 2H), 1.24-1.27 (m, 4H) (**Figure S2).** HRMS m/z: 523.2803 [m+H]$^+$ (**Figure S4**).

1.4 Preparation of polydomain and monodomain Si-LCE, Si-LCE-B, LCE-Azo

A one-pot method was used to prepare LCEs by Micheal addition reaction with thiol-acrylate and amine-acrylate simultaneously occurred. Typically, certain amounts of RM82 and DAHAB were dissolved in DMF and heated to 80 °C until completely dissolved. Then BATS, DAB, and EDDET were successively added and mixed to obtain a homogeneous precursor solution with the assistance of a heat gun. The solution was ultrasonicated for 5 min to remove air bubbles and then poured into a PTFE mold of 6 cm×3 cm×2 cm. The mold was heated at 90 ºC to allow the reaction to proceed for 3 h. The polydomain LCE film was obtained afterwards. To prepare the monodomain LCE, the fully cured polydomain LCE film was stretched to 140% of its original length to align the mesogens and further cured at 120 °C for 1 h.

1.5 Instruments and Characterization

The Nuclear Magnetic Resonance (NMR) spectrum was recorded in *d*-DMSO or CDCl$_3$ on a Bruker Advance 400 NMR Spectrometer. Chemical shifts were reported in ppm downfield from tetramethyl silane (TMS) reference using the residual protonated solvent as an internal standard. High-resolution mass spectrum was obtained through Bruker ESI-Q-TOF mass spectrometer in positive ion mode. Polarized optical microscopy (POM) observations of the samples were performed on an Olympus BX53P microscope equipped with a Mettler PF82HT hot stage. The images were captured using a Microvision MVDC200 digital camera with a Phenix Phmias 2008 Cs Ver2.2 software. Small-angle X-ray scattering (SAXS) experiments were conducted by a Bruker Nanostar U instrument. The wavelength of X-ray source was 1.54 Å and the detector was Vantec 2000 with the sample-to-detector distance of 1048 mm. The exposure time was set as 600 s for each scan. Differential scanning calorimetry (DSC) was used to record the transition temperatures by using DSC4000 from PerkinElmer under nitrogen purge with a heating or cooling rate of 10 °C/min. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer TGA 7 instrument for thermal analysis at a heating rate of 10 °C/min under nitrogen. Dynamic mechanical analyzer (TA instruments, DMA Q850) was used to characterize the stress relaxation and stress-strain curves of LCE films with rectangular samples mounted on the tensile clamp. The self-healed samples and the cross sections of bilayer LCE films were observed by scanning electron microscope (SEM) (JEOL, JSM-7900F). Deformation velocity and bending angle vs time were measured using open-source software (Tracker 5.1.0).

Supplementary figures and results

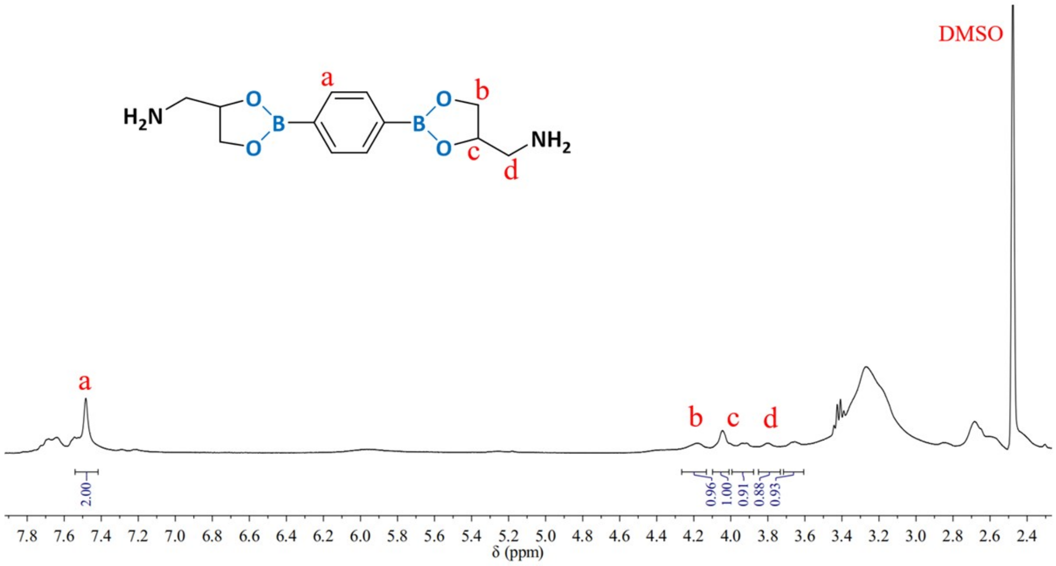


Figure S1. ^{1}H NMR spectrum of DAB monomer.

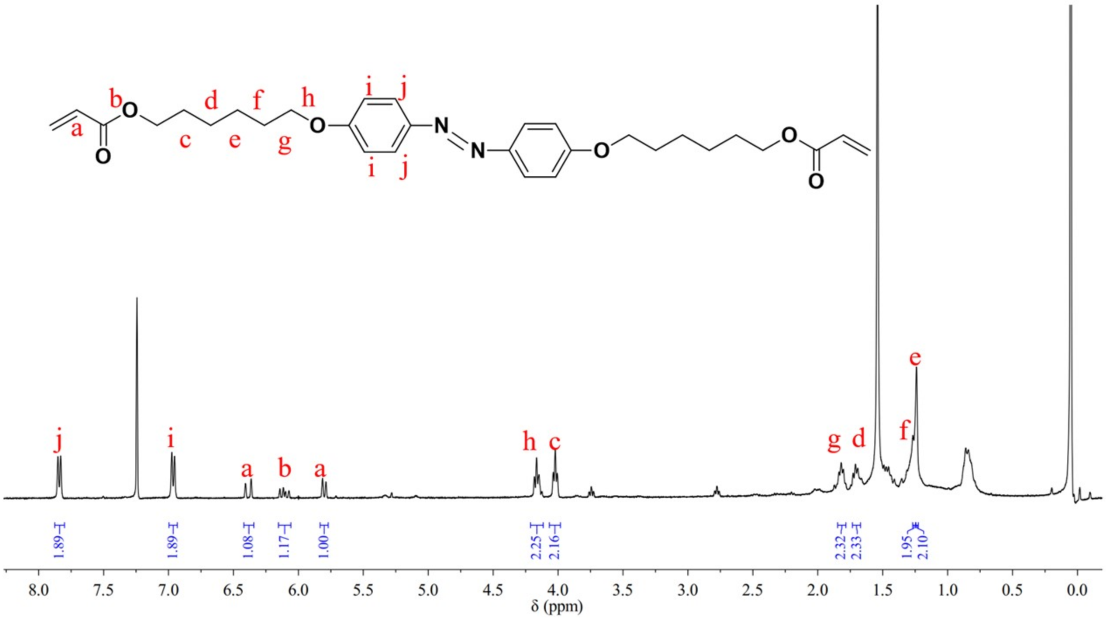


Figure S2. ^{1}H NMR spectrum of DAHAB monomer.

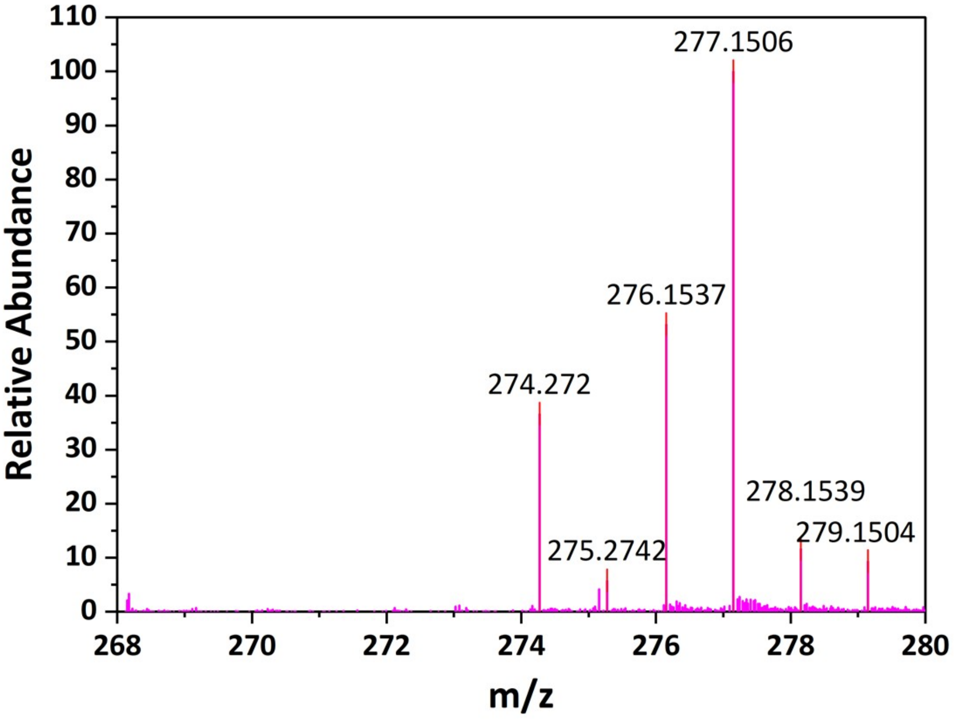


Figure S3. High-resolution mass spectrum of DAB monomer.

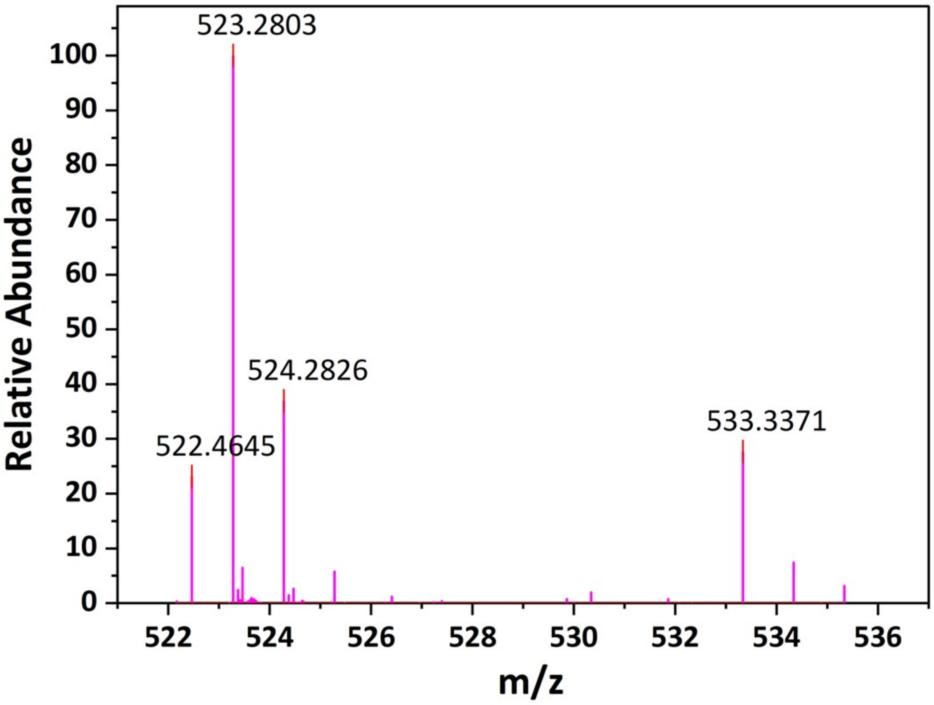


Figure S4. High-resolution mass spectrum of DAHAB monomer.

Table S1 Chemical formulations and molar ratio of monomers of Si-LCE-Bx systems.

Samples	Molar ratio of DAB	Mass of RM82	Mass of BATS	Mass of DAB	Mass of EDDET
Si-LCE	0	750 mg	90 mg	0 mg	100 mg
Si-LCE-B10	10	750 mg	81 mg	10 mg	100 mg
Si-LCE-B20	20	750 mg	72 mg	20 mg	100 mg
Si-LCE-B30	30	750 mg	63 mg	30 mg	100 mg
Si-LCE-B50	50	750 mg	45 mg	50 mg	100 mg

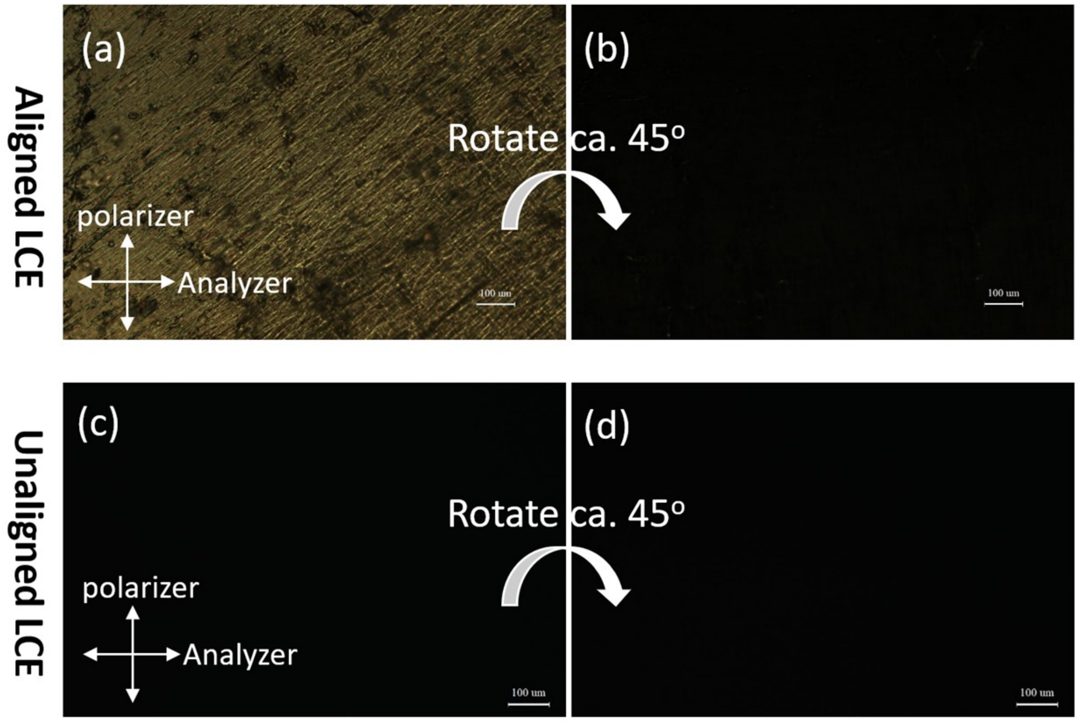


Figure S5. POM images of monodomain and polydomain Si-LCE-B30 samples oriented at the angle either (a, c) 45° or (b, d) 0° to the polarizer.

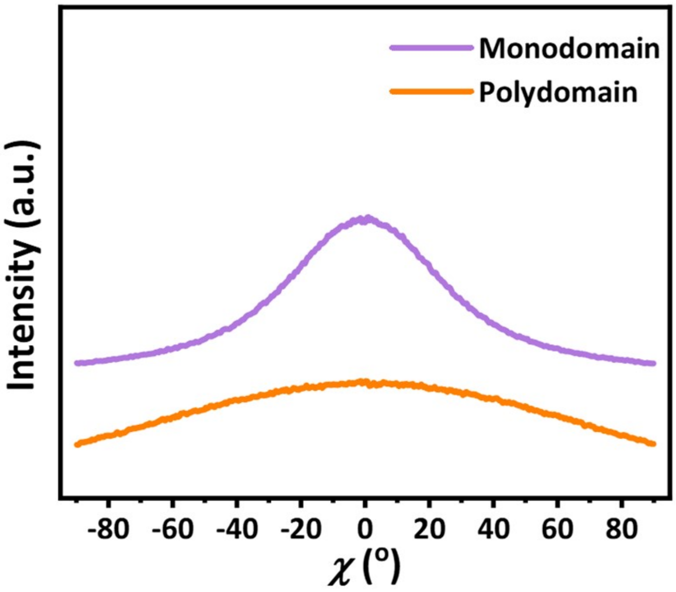


Figure S6. Azimuthal profiles of polydomain and monodomain Si-LCE-B30 films.

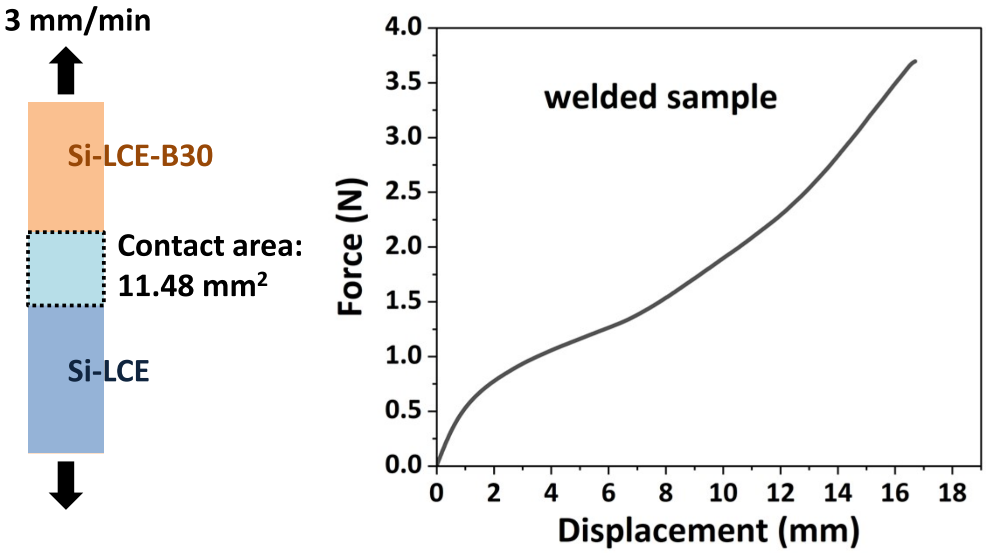


Figure S7. Bond shear strength of the welded sample by Si-LCE and Si-LCE-B30, measured using the tensile testing method.

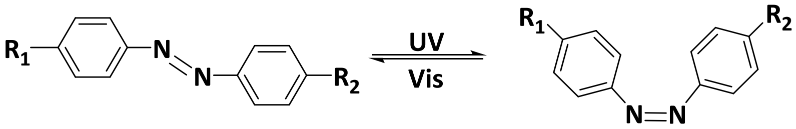


Figure S8. Reversible trans–cis photoisomerization of azobenzene.

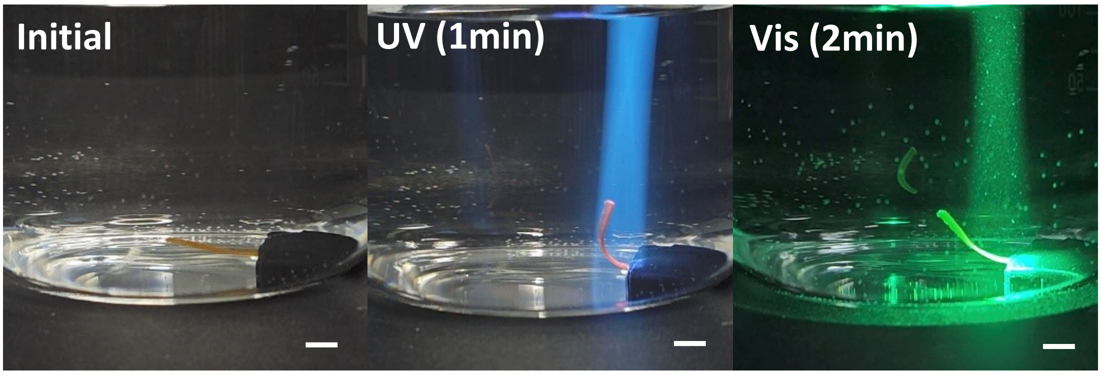


Figure S9. Images of reversible photoinduced bending deformation of LCE-Azo20 sample underwater (scale bar=1 cm).

Captions of supporting videos

Video S1: Bending deformation and recovery process of LCE samples with different azobenzene contents under UV and visible light irradiation.

Video S2: Bending angle stability of LCE-Azo10 sample for 13 irradiation cycles.

Video S3: Reversible photoinduced bending deformation of LCE-Azo20 sample underwater.