

Electronic Supplementary Information (ESI)

Liquid Crystal Elastomer Actuator with Serpentine Locomotion

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Supplementary Figures

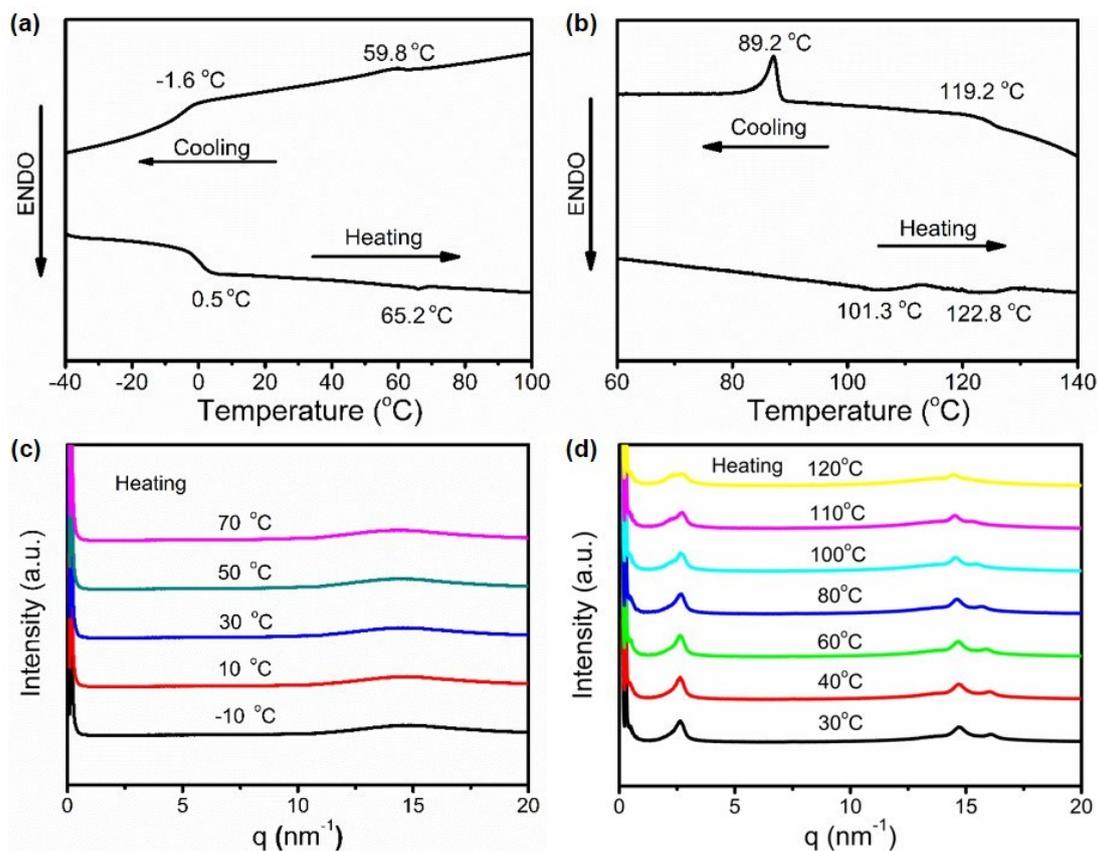


Fig. S1. Differential scanning calorimetry (DSC) diagrams of LCE1 (a) and LCE2 (b). One-dimensional wide-angle X-ray diffraction patterns of LCE1 (c) and LCE2 (d).

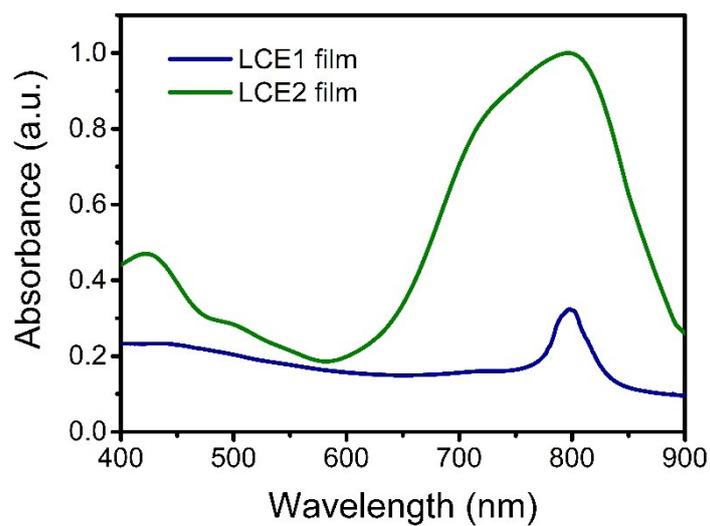


Fig. S2. UV-vis spectra of the LCE1 and LCE2 films.

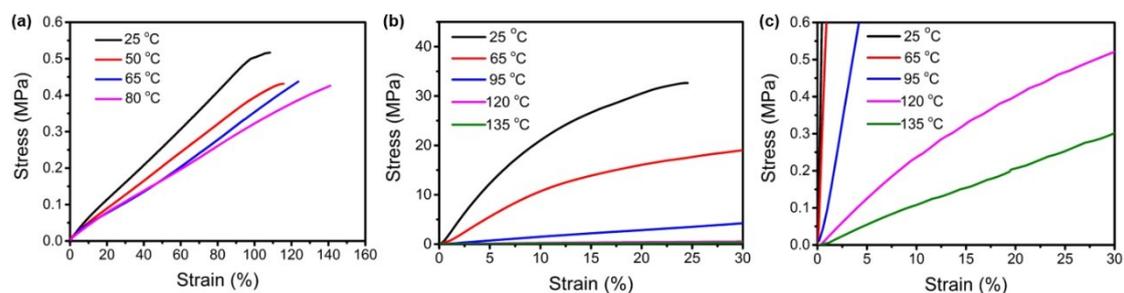


Fig. S3. Stress-strain diagrams of (a) LCE1 and (b,c) LCE2 ribbons measured at varied temperatures.

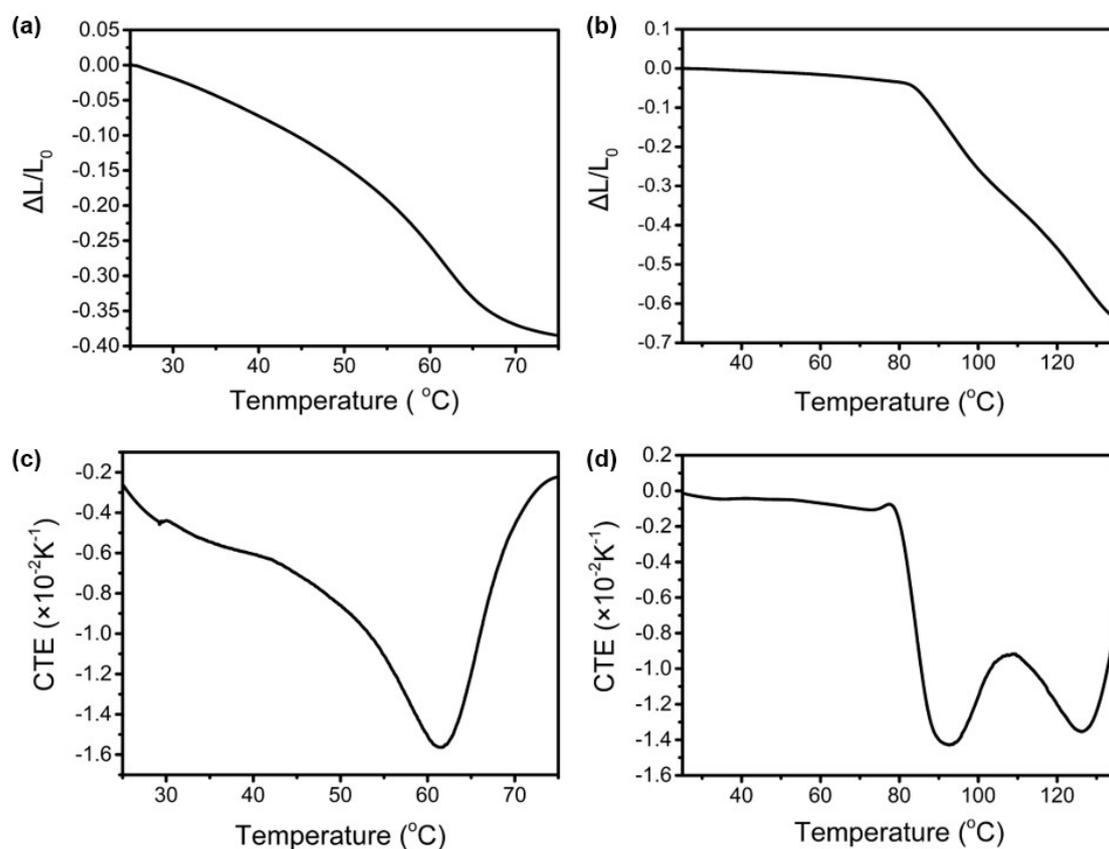


Fig. S4. Relationship between linear expansion and temperature of (a) LCE1 and (b) LCE2 ribbons. The coefficient of thermal expansion (CTE)-temperature diagrams of (c) LCE1 and (d) LCE2 ribbons.

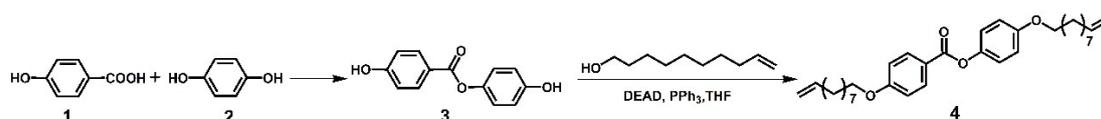


Fig. S5. The synthetic route of mesogenic monomer Y1709.

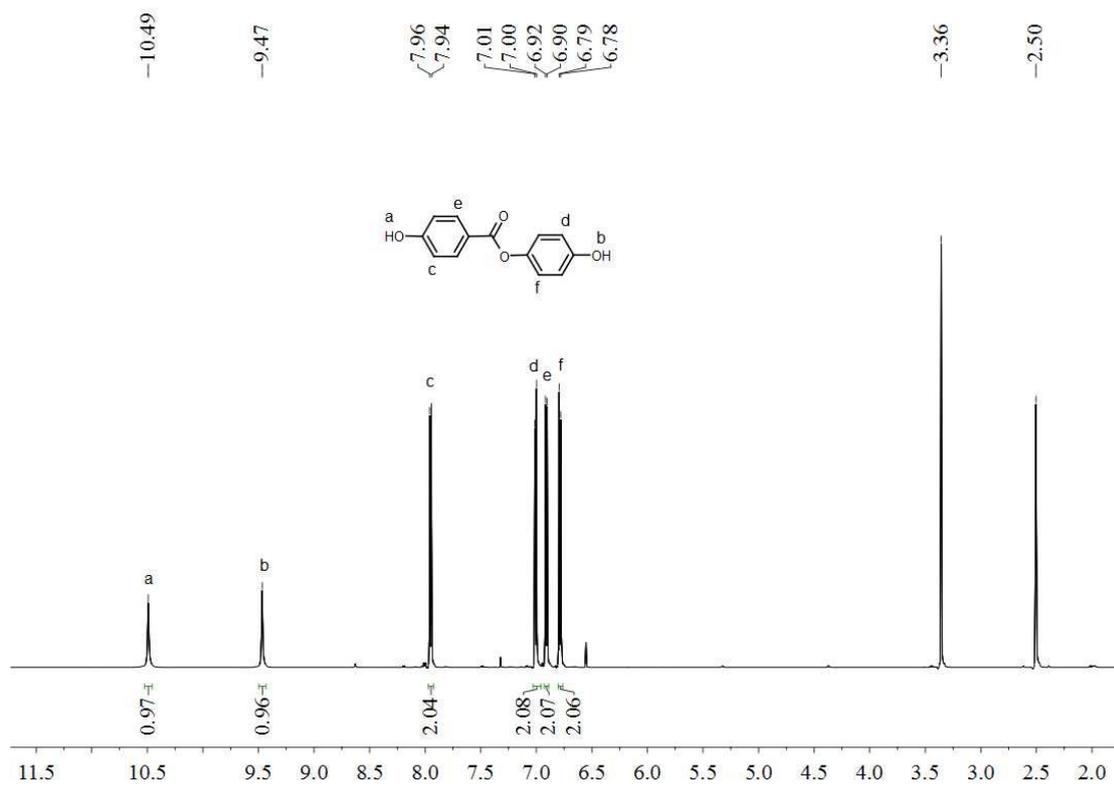


Fig. S6. ^1H NMR spectrum of compound **3**.

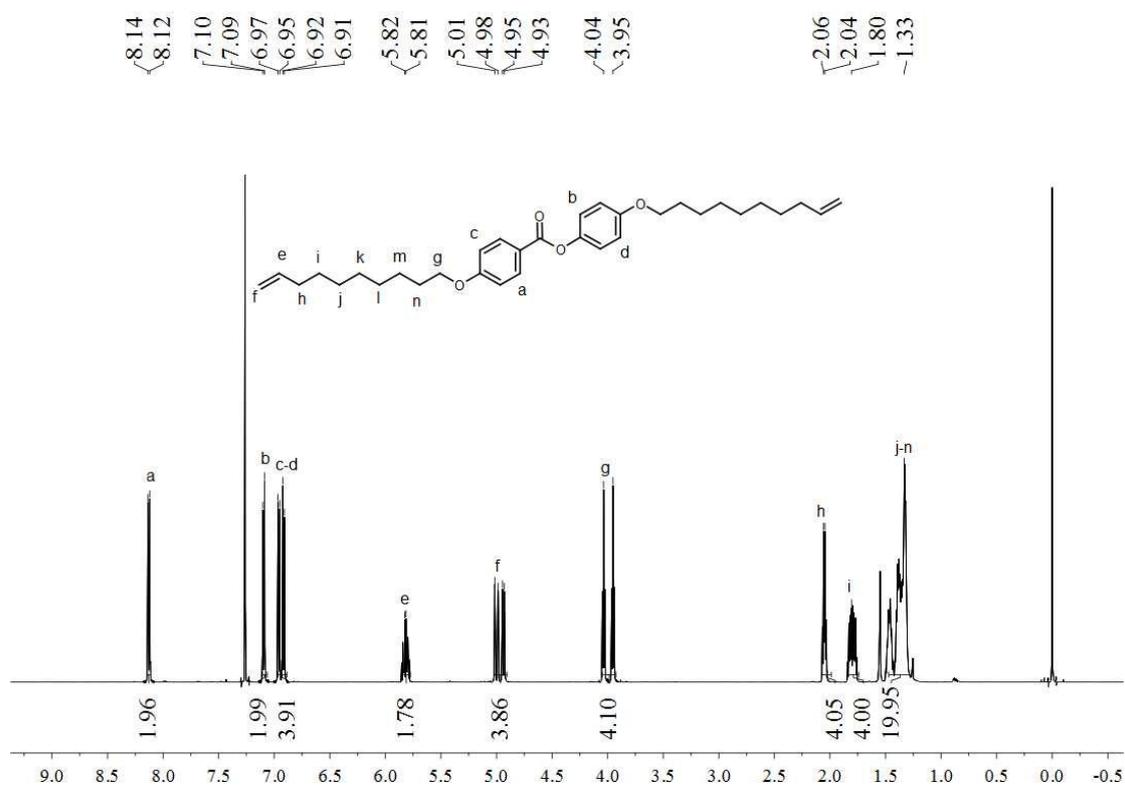


Fig. S7. ^1H NMR spectrum of monomer **Y1709 (4)**.

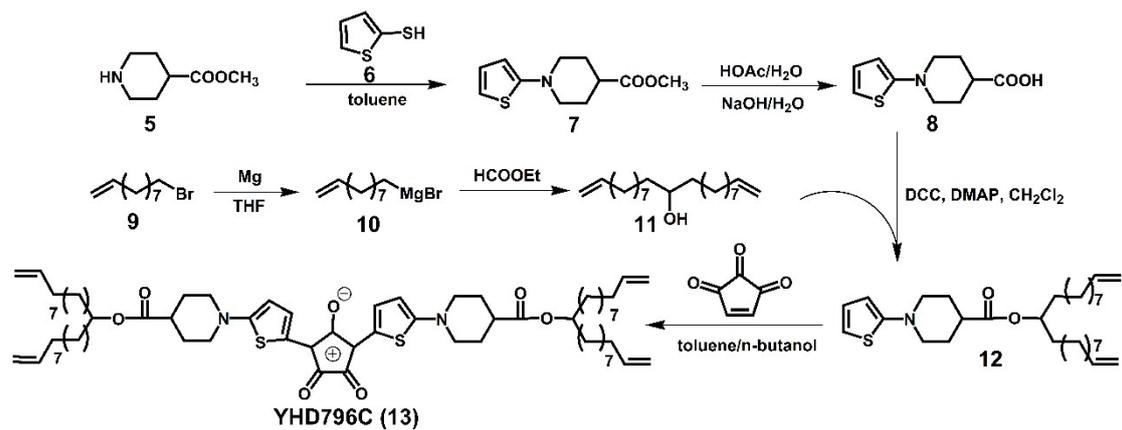


Fig. S8. The synthetic route of **YHD796C**.

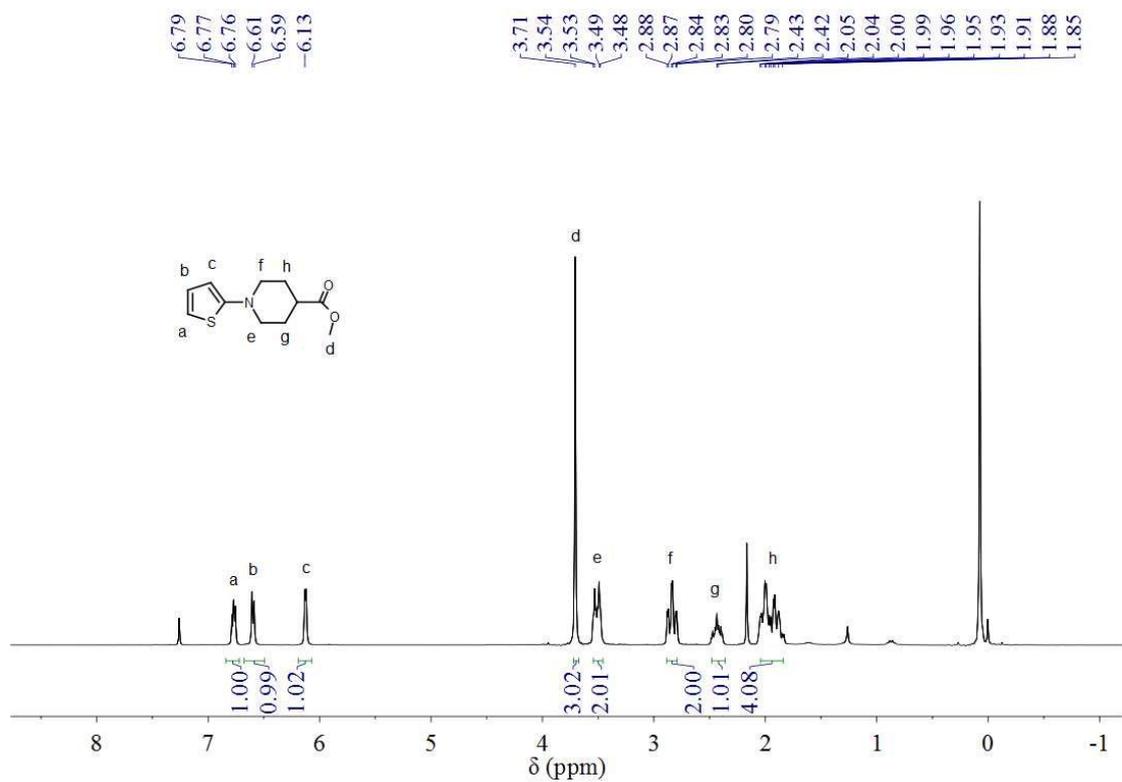


Fig. S9. ^1H NMR spectrum of compound **7**.

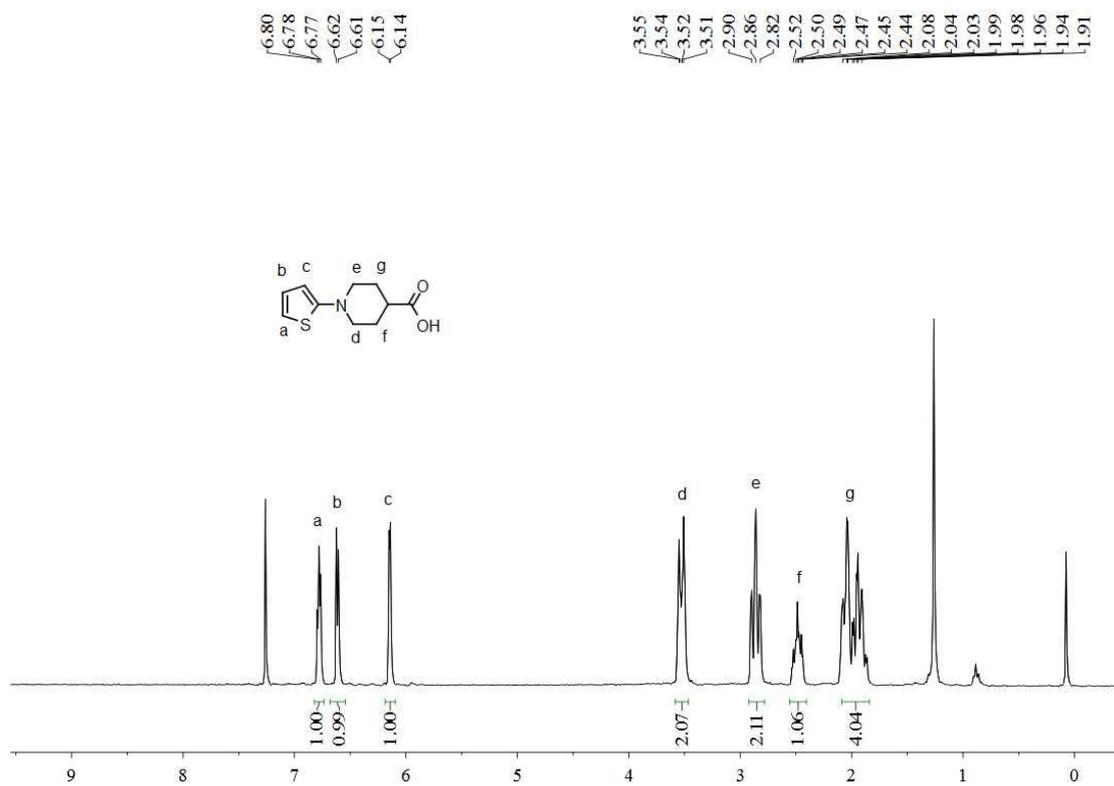


Fig. S10. ¹H NMR spectrum of compound 8.

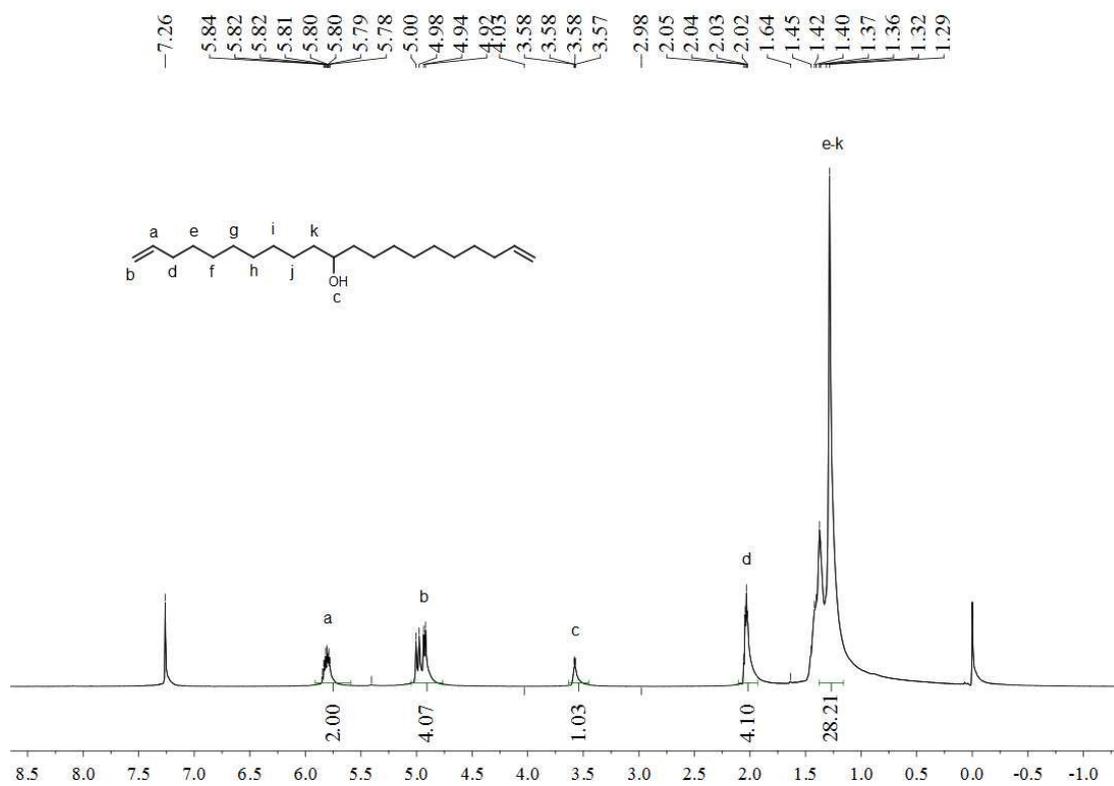


Fig. S11. ¹H NMR spectrum of compound 11.

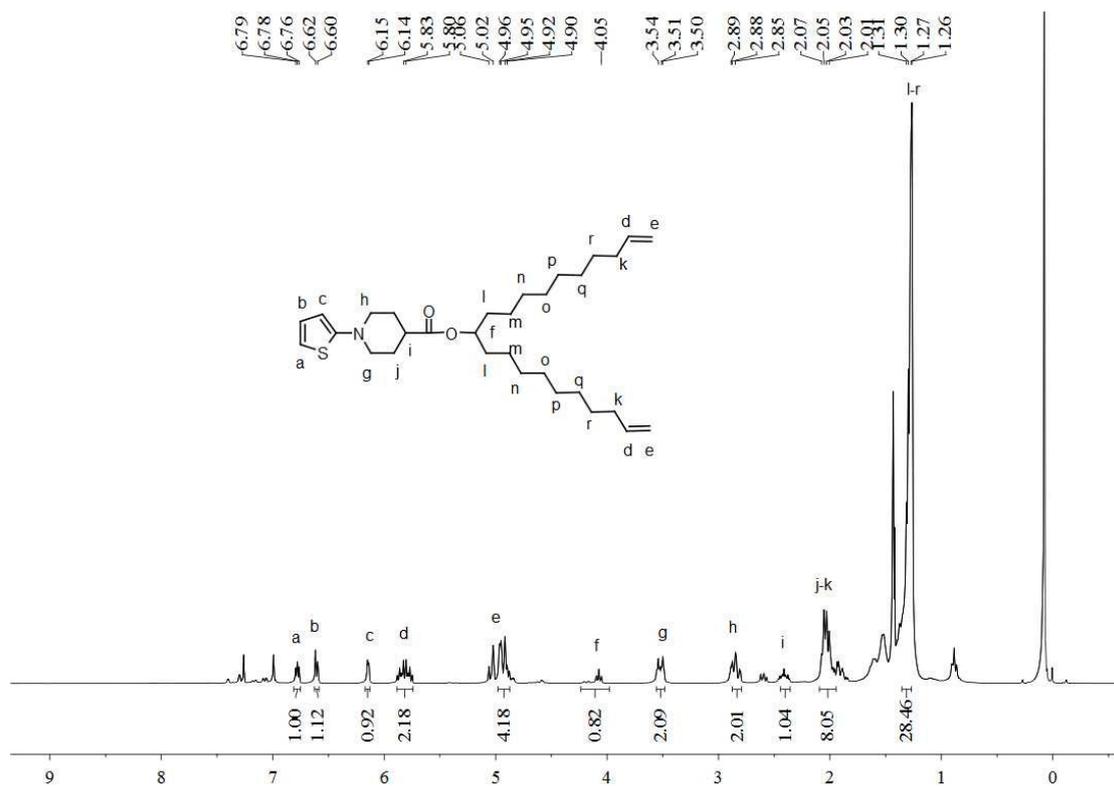


Fig. S12. ^1H NMR spectrum of compound 12.

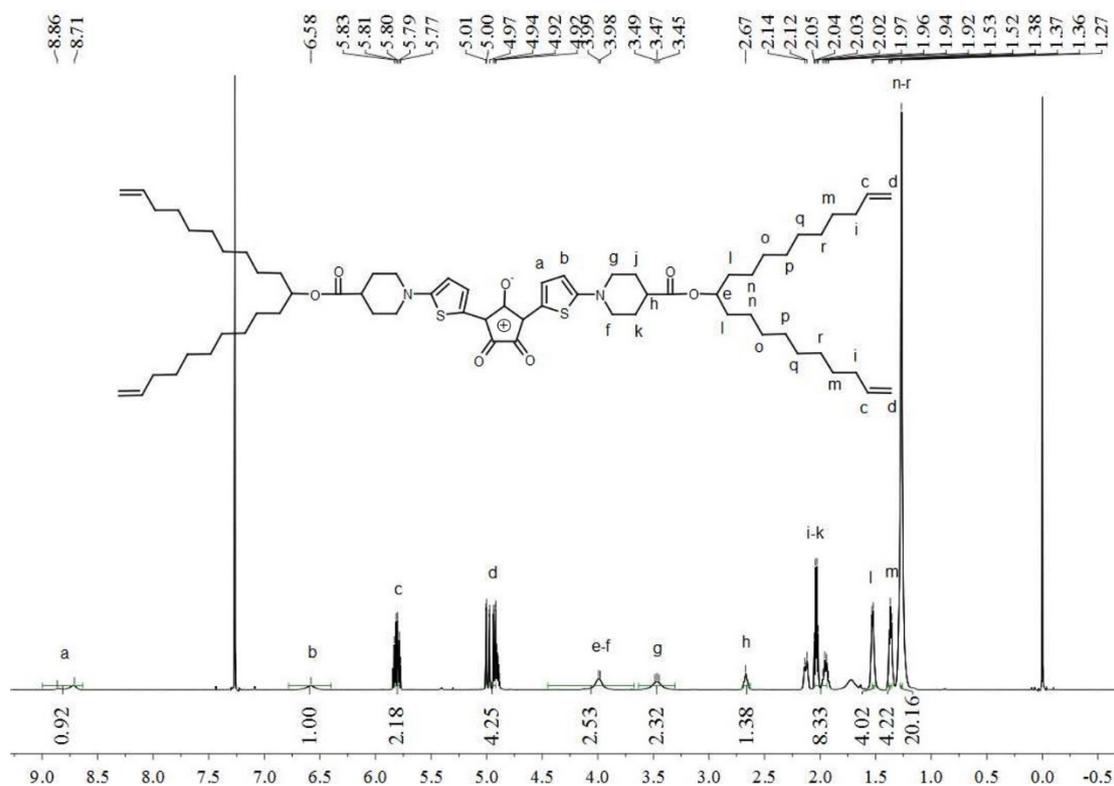


Fig. S13. ^1H NMR spectrum of compound YHD796C (13).

Supplementary Methods

General Considerations. Grubbs 2nd generation catalyst were purchased from Aldrich Inc. Croconic acid was purchased from Alfa Aesar Inc. 2-Thiophenethiol, 10-bromo-1-decene and dipropylamine (DPA) were purchased from TCI Inc. Methyl isonipecotate, diethyl azodicarboxylate (DEAD), 4-hydroxybenzoic acid, triphenylphosphine (PPh₃), dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), n-decyl alcohol, Irgacure 651, 1,2-bis(2-mercaptoethoxy)ethane (DODT) and pentaerythritol tetra(3-mercaptopropionate) (PETMP) were purchased from Aladdin (Shanghai) Inc. 1,4-Bis-[4-(3-acryloyloxypropyloxy)benzoyloxy]-2-methylbenzene (RM257) was purchased from Sdynano Fine Chemicals in Shijiazhuang. Toluene and dichloromethane (DCM) were distilled from CaH₂ under nitrogen. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl under nitrogen. All other chemical reagents were used without purification. Sylgard 184 polydimethylsiloxane (PDMS) pre-polymer was purchased from American Dow Corning Corporation. A repositionable adhesive 3M super 75 was purchased from 3M Inc. A commercial glue ERGO 6700 was purchased from Swiss Ergo Inc.

All ¹H NMR spectra were recorded on a Bruker HW600 MHz spectrometer (AVANCE AV-600), or a Bruker HW300 MHz spectrometer (AVANCE AV-300), using CDCl₃ or DMSO-d₆ as the solvent and CHCl₃ (δ 7.26), DMSO (δ 2.50) as the interior reference. Differential scanning calorimetry (DSC) spectra were measured on a TA Q100 instrument (New Castle, DE) under nitrogen purge at a heating/cooling rate of 10 °C/min. The second crosslinking process of LCE1 sample was performed by using a high-intensity ultraviolet (UV) lamp (LP-40, Shanghai Luyang Instrument Co. Ltd., emission spectral range: 365±5 nm). A TU-2700 ultraviolet-visible (UV-vis) spectrophotometer (Shimadzu Instruments Co., Ltd.) was used to obtain the UV-vis spectra of the samples. A high-flux small angle X-ray scattering instrument (SAXSess, Anton Paar), equipped with Kratky block-collimation system and an Anton Paar TCS300 temperature control unit, was used to perform the X-ray scattering experiments. All XRD Data were collected at a sample-to-detector distance (SDD) of

79 mm using an incident X-ray beam (50.047 keV, 0.999 mA, 1.542 Å wavelength). For each specimen, six frames of 900 s exposures were collected and averaged. Two-dimensional data was transformed to one-dimensional curves by using SAXS analysis software (Anton Paar). All mechanical properties tests of samples were performed on a dynamic mechanical analyzer (DMA Q850, TA Instrument). A thermo-mechanical analyzer (TMA 402 F3, NETZSCH) was used to measure the thermal expansion coefficients. All NIR-responsive experiments were performed using an 808 nm semiconductor laser source (Center wavelength: 808 ± 3 nm, Nanjing Latron Laser Company, China). The temperature variations of the film surfaces were measured by a thermal imager (FLUKE Ti95).

Synthesis of LC monomer Y1709 (Fig. S2)

4-Hydroxyphenyl-4-hydroxybenzoate (HPHB, 3).¹ A 100 mL three-neck round-bottom flask equipped with a refluxing condenser was charged with 4-hydroxybenzoic acid (1.26 g, 9.08 mmol) and hydroquinone (10.12 g, 91.86 mmol) under nitrogen. The mixture was heated at 260 °C for 3.5 h. After cooling to room temperature, 100 mL of water was added into the above mixture. The crude product was obtained by filtration and further recrystallized from ethanol/water (1/1, v/v) solution to give compound **3** as a white solid (1.24 g, yield 59.05%). ¹H NMR (600 MHz, DMSO) δ : 10.43 (s, 1H), 9.40 (s, 1H), 7.90 (d, $J = 8.8$ Hz, 2H), 6.95 (d, $J = 8.9$ Hz, 2H), 6.86 (d, $J = 8.8$ Hz, 2H), 6.73 (d, $J = 8.9$ Hz, 2H).

4-Undec-10-enyloxy-benzoic acid 4-dec-9-enyloxy-phenyl ester (Y1709, 4).² A 100 mL Schlenk flask was charged with the mixture of 4-hydroxyphenyl-4-hydroxybenzoate (1.50 g, 6.51 mmol), triphenylphosphine (3.75 g, 14.28 mmol), 9-decen-1-ol (2.04 g, 13.02 mmol) and 30 mL of anhydrous THF. Under nitrogen atmosphere, DEAD (1.66 g, 14.28 mmol) was added to the above mixture. The reaction solution was stirred at room temperature overnight. After removing the solvent, the crude product was subsequently purified by column chromatography (petroleum ether/ethyl acetate = 20/1) to give compound **4** (1.78 g, yield 53.85 %) as a white solid. ¹H NMR (600 MHz, CDCl₃) δ : 8.13 (d, $J = 8.9$ Hz, 2H), 7.09 (d, $J = 9.0$ Hz, 2H), 6.94

(m, 4H), 5.82 (m, 2H), 4.97 (m, 4H), 3.99 (m, 4H), 2.05 (d, $J = 7.2$ Hz, 4H), 1.80 (s, 4H), 1.33 (s, 20H).

Synthesis of YHD796C (Fig. S5)

1-Thiophen-2-yl-piperidine-4-carboxylic acid methyl ester (7).³ A mixture of methyl isonipicotate (4.04 g, 28.35 mmol), thiophene-2-thiol (1.8 mL, 20.25 mmol) and anhydrous toluene (30 mL) were added into a 100 mL three-neck round-bottom flask. The reaction mixture was purged with nitrogen and stirred magnetically. After refluxed at 90 °C for 8 h, the solvent was removed by filtration, and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 30/1) to give the desired product **7** (2.51 g, yield 55.05 %) as a white solid. ¹H NMR (300 MHz, CDCl₃) δ : 6.76 (dd, $J = 5.4, 3.8$ Hz, 1H), 6.60 (t, $J = 3.0$ Hz, 1H), 6.17 – 6.08 (t, $J = 3.0$ Hz, 1H), 3.70 (s, 3H), 3.51 (m, 2H), 2.90 – 2.79 (m, 2H), 2.43 (m, 1H), 1.94 (m, 4H).

1-Thiophen-2-yl-piperidine-4-carboxylic acid (8).⁴ Compound **7** (3.62 g, 16.1 mmol) was added into a 250 mL three-neck round-bottom flask. Under nitrogen atmosphere, a sodium hydroxide solution (0.5 M, 106 mL) was added slowly into the above flask. The mixture was heated to reflux for 5 h. After cooling to the room temperature, the solution was acidified with aqueous acetic acid (conc. 10%) solution. The precipitate was obtained by filtration, to give compound **8** (3.04 g, yield 61.81 %) as a white solid. ¹H NMR (300 MHz, CDCl₃) δ : 6.78 (dd, $J = 5.3, 3.8$ Hz, 1H), 6.62 (d, $J = 5.4$ Hz, 1H), 6.15 (d, $J = 3.6$ Hz, 1H), 3.57 – 3.45 (m, 2H), 2.92 – 2.79 (m, 2H), 2.49 (m, 1H), 1.97 (m, 4H).

11-Hydroxy-1,20-heneicosadiene (11).⁴ A solution of 10-bromo-1-decene (16 mL) in 80 mL of dry THF was added dropwise into a mixture of freshly scoured Mg turnings (5.46 g, 227.54 mmol) and a small amount of iodine in 24 mL of dry THF. After heating under reflux for 2 h, the resulting Grignard solution was chilled to 0 °C, and methyl formate (3.60 g, 48.64 mmol) was added slowly *via* syringe. The reaction was heated at 35 °C and stirred for ca. 3 h. The reaction was quenched with saturated ammonium chloride solution. The organic layer was extracted with diethyl ether, washed with brine, dried over MgSO₄, and concentrated. The crude product was further purified by

column chromatography (petroleum ether/ethyl acetate = 20/1) to give compound **11** (7.06 g, yield 49.00 %) as a white solid. ¹H NMR (600 MHz, CDCl₃) δ: 5.80 (m, 2H), 5.03 – 4.91 (m, 4H), 3.58 (dd, J = 6.9, 4.2 Hz, 1H), 2.05 (q, J = 7.0 Hz, 4H), 1.40 – 1.26 (m, 28H).

1-Thiophen-2-yl-piperidine-4-carboxylic acid 1-dec-9-enyl-undec-10-neyl ester (12).² In a 150 mL Schlenk flask, a mixture of compound **8** (1.77 g, 8.36 mmol), compound **11** (3.09 g, 10.02 mmol), DMAP (105.00 mg, 0.84 mmol) and DCC (2.07 g, 10.02 mmol) were suspended in 75 mL of anhydrous dichloromethane under a nitrogen atmosphere. The mixture was stirred at room temperature for 24 h. The resulting suspension was filtered to remove the solid residue, and the filtrate was collected and concentrated by rotary evaporation. The raw product was further purified by column chromatography (petroleum ether/ethyl acetate = 20/1) to give compound **12** (2.24 g, 53.53 %) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 6.76 (dd, J = 5.4, 3.8 Hz, 1H), 6.60 (dd, J = 5.5, 1.1 Hz, 1H), 6.15 (d, J = 2.8 Hz, 1H), 5.88 5.75 (m, 2H), 5.02 – 4.91 (m, 4H), 4.22 – 4.00 (m, 1H), 3.52 (m, 2H), 2.84 (m, 2H), 2.46 – 2.36 (m, 1H), 2.04 (m, 8H), 1.32 (m, 29H).

2,5-Bis[(1-dec-9-enyl-undec-10-neyl-4-carboxylate-piperidylamino)thiophenyl]-croconium (YHD796C, 13).² A 100 mL three-neck round-bottom flask was charged with precursor **12** (460 mg, 0.92 mmol), croconic acid (60 mg, 0.46 mmol) and a 20 mL solution of toluene/n-butanol (v/v, 1/1) under nitrogen atmosphere. The mixture was refluxed at 90 °C for 2 h. The solvent was evaporated and the crude product was purified by column chromatography (dichloromethane/methanol = 45/1) to provide the final product **YHD796C** (309 mg, yield 59.87 %). ¹H NMR (600 MHz, CDCl₃) δ: 8.92 – 8.62 (m, 1H), 6.61 (m, 1H), 5.80 (m, 2H), 5.00 – 4.91 (m, 4H), 4.00 (m, 3H), 3.44 (t, J = 10.5 Hz, 2H), 2.64 (d, J = 9.4 Hz, 1H), 2.10 – 1.91 (m, 8H), 1.52 (d, J = 6.0 Hz, 4H), 1.35 (dd, J = 13.8, 6.7 Hz, 4H), 1.25 (d, J = 8.2 Hz, 21H).

General procedure for the preparation of LCE0 ribbon

A polytetrafluoroethylene (PTFE) rectangular mould (4.0 cm long \times 2.0 cm wide \times 1.5 cm deep) with a wave-shaped bottom was charged with **Y1709** (142.2 mg, 0.28 mmol), **YHD796C** (30.0 mg, 2.71×10^{-2} mmol), Grubbs 2nd generation catalyst (3.4 mg, 2.14×10^{-3} mmol) and fresh distilled toluene (2.5 mL). The mixture was sonicated at room temperature for 2 min to achieve a homogeneous dispersion. The reaction solution was heated at 60 °C under nitrogen atmosphere for 3 h, during which the generated ethylene gas was removed *via* vacuum periodically. The resulting pre-crosslinked gel was removed from the mould and cut into wavy strips using a sharp knife. The wavy strip was then pressed into a reverse wave shape by using two intermeshing wave-shaped moulds and fixed with heavy weight. After heating at 100 °C for 48 h under nitrogen atmosphere, the second crosslinking process was completed and the obtained film was further cut into an S-shaped ribbon (1.3 cm long \times 0.27 cm wide, the thickness was ca. 180 μ m).

General procedure for the preparation of LCE1 ribbon

A mixture solution containing **RM257** (300.0 mg, 0.51 mmol), **PETMP** (13.2 mg, 2.6×10^{-2} mmol), **DODT** (84.6 mg 0.47 mmol), **Irgacure 651** (8.8 mg, 3.9×10^{-3} mmol), **YHD796C** (7.0 mg, 6.32×10^{-3} mmol), **DPA** (20 μ L) and DCM (3 mL) was poured into a PTFE rectangular mould (4.0 cm long \times 2.0 cm wide \times 1.5 cm deep). The mixture was sonicated at room temperature for 2 min to ensure a homogeneous dispersion and remove the air bubbles. After pre-crosslinking at room temperature for 5 h, a flat film was obtained and cut into thin strips. The flat strip was then pressed between two intermeshing wave-shaped transparent glass moulds to form a wavy structure. After polymerization under 365 nm ultraviolet (UV) light for 5 min, a wavy film was removed from the mould and cut into an S-shaped ribbon (1.3 cm long \times 0.27cm wide, the thickness was ca. 640 μ m).

General procedure for the preparation of LCE2 ribbon

A PTFE rectangular mould (4.0 cm long \times 2.0 cm wide \times 1.5 cm deep) was charged with LC monomer **Y1709** (132.9 mg, 0.26 mmol), crosslinker **YHD796C** (28.0 mg, 2.53×10^{-2} mmol), Grubbs 2nd generation catalyst (32.0 mg, 2.89×10^{-2} mmol) and fresh distilled toluene (2.5 mL). The mixture was sonicated at room temperature for 2 min to achieve a homogeneous dispersion. The reaction solution was heated at 60 °C under nitrogen atmosphere for 3 h, during which the generated ethylene gas was removed *via* vacuum periodically. The resulting pre-crosslinked gel was removed from the mould and sliced into strips using a sharp knife. The pre-crosslinked LCE strip was hung in a nitrogen-filled oven and burdened with a heavy load at 120 °C to achieve uniaxial stretching. The stretched film was fixed on a glass slide by binder clips and kept in a nitrogen-filled oven with the temperature set at 100 °C for 2 days. The monodomain LCE film was then pressed between two intermeshing wave-shaped moulds and fixed with heavy weight. After heated at 80 °C for 2 h, the wave-shaped film was obtained and cut into arc-shaped strips (0.65 cm long \times 0.27 cm wide, the thickness was ca. 120 μ m).

General procedure for the preparation of bilayered LCE ribbon

A commercial repositionable adhesive (3M super 75) was used to glue two arc-shaped **LCE2** strips on the two opposite ridge sides of the S-shaped **LEC1** film. The main layer was the S-shaped **LEC1** film and the outer layers were two arc-shaped **LCE2** strips. Then, the dual-layer LCE film was cut into strips (1.3 cm long \times 0.2 cm wide, the thickness was ca. 800 μ m).

General procedure for the preparation of support feet

A PTFE rectangular mould (8.0 cm long \times 4.0 cm wide \times 3.0 cm deep) with the 45° inclined serrations at the bottom was used as the template. The Sylgard 184 Silicone Elastomer pre-polymer (5 g, Base/Curing Agent =10/1, wt./wt.) was mixed uniformly and poured into the above mould. After heating at 60 °C for 24 h, a soft rubber model

with 45° inclined serrations was obtained from the template and further cut into pieces (5.0 mm long × 1.5 mm wide × 2.0 mm high) as the support feet. Finally, the two support feet was stuck on both ends of the bilayered LCE ribbon by a commercial adhesive (ERGO 6700).

References

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