Supplementary Information for

Photomodulated Tri-Color-Changing Artificial Flowers

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General Considerations. Platinum-divinyltetramethyldisiloxane complex and 4-dimethylaminopyridine (DMAP) were purchased from Aladdin Inc. Polymethylhydrosiloxanes (HMS-993, M.W. 2200-2400) were purchased from Gelest Inc. Organic dyestuffs (Green 575, Blue 623, Red 306, Yellow 110) were commercially available products bought from Kelly Chemical Corporation. 1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran (compound **11**, Supplementary Figure 14) was bought from Heowns Biochem LLC. Toluene and CH_2Cl_2 were redistilled from sodium benzophenone ketyl under nitrogen. Other chemical reagents were used without further purification. All non-aqueous reactions were conducted in oven-dried glasswares, under a dry nitrogen atmosphere.

Ultraviolet and visible spectra (UV-vis) were recorded with a UV-2600 ultraviolet-visible spectrophotometer (UV/VIS spectrometer) (Shimadzu Co., LTD). The scanning electron microscope (SEM) images were recorded on an Inspect F50 S3 field emission scanning electron microscope (FEI-SEM, America). A TA Q100 instrument (New Castle, DE) was used to record differential scanning calorimetry (DSC) spectra under nitrogen purge at a heating rate of 10 °C/min, to measure the phase transition temperatures of the samples. New chemical compounds routinely characterized by NMR spectroscopy. ^{1}H NMR spectra were recorded at a Bruker HW500 MHz spectrometer (AVANCE AV-500), using $CDCl_3$ (internal reference 7.26 ppm) as solvent. The mass spectra were obtained from Waters Micromass Q-TOF micro system mass spectrometer. Polarized optical microscopy (POM) observations of the LCE samples were performed

on an Olympus BX53P microscope with a Mettler PF82HT hot stage. The images were captured by using a Microvision MV-DC200 digital camera with a Phenix Phmias 2008 Cs Ver2.2 software. All the UV-responsive, NIR-responsive and visible light-responsive experiments were performed by using either a LP-20A UV lamp (5 $mW \cdot cm^{-2}$, λ = 365 nm; LUYOR Corporation), a 808 nm semiconductor laser source (0.83 $W.cm^{-2}$, Center wavelength: 808 ± 3 nm, Nanjing Latron Laser Company, China) or a 520 nm laser source (44 $mW.cm^{-2}$, Output power: 500 mW, Center wavelength: 520 ± 5 nm, Changchun Laser Optoelectronics Technology Co., Ltd., China).

Synthesis of (±)-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline]-5',8-diol (compound 8).

The synthetic intermediates of each step were prepared according to the literature procedures and the compound **8** (a dark powder) was used directly without further purification as described in the literature.[S1]

Synthesis of SP1 (compound 10, Figure S8).

To a 100 mL round-bottom Schlenk flask was added compound **8** (1.42 g, 4.01 mmol, 1.0 equiv.) and dimethylaminopyridine (1.47 g, 12.03 mmol, 3.0 equiv.). After purging the airtight system with nitrogen gas, 50 mL of dichloromethane was added into the Schlenk flask, followed by a dropwise addition of 10-undecylenoyl chloride (1.87 g, 9.22 mmol, 2.3 equiv.) in 5.0 mL dichloromethane at 0 ^{o}C. The reaction mixture was stirred at 0 ^{o}C

for 16 h, concentrated *via* rotovap, diluted by 100 mL of diethyl ether and further filtered off the precipitates. The organic solution was concentrated and purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1:15 v/v) to provide a yellow solid product (0.81 g, 1.18 mmol, 29.4 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.81 (d, □ = 5.0 Hz, 1H), 6.97 (d, □ = 10.0 Hz, 1H), 6.84 (m, 1H), 6.79 (s, 1H), 6.47 (d, □ = 5.0 Hz, 1H), 5.91 (d, □ = 10.0 Hz, 1H), 5.81 (m, 2H), 5.02 (s, 1H), 4.98 (s, 1H), 4.95 (d, □ = 10.0 Hz, 2H), 2.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.59, 171.04, 151.02, 145.09, 144.42, 140.15, 139.09, 137.69, 137.17, 128.44, 120.96, 120.12, 119.90, 119.33, 119.14, 115.36, 114.19, 114.16, 107.58, 107.26, 51.82.

Synthesis of SP2 (compound 12, Figure S12).

To a 50 mL round-bottom Schlenk flask was added compound **11** (0.20 g, 0.57 mmol, 1.0 equiv.) and dimethylaminopyridine (0.21 g, 1.70 mmol, 3.0 equiv.). After purging the airtight system with nitrogen gas, 30 mL of dichloromethane was added into the Schlenk flask, followed by a dropwise addition of 10-undecylenoyl chloride (0.26 g, 1.31 mmol, 2.3 equiv.) in 5.0 mL dichloromethane at 0 ^{o}C. The reaction mixture was stirred at 0 ^{o}C for 16 h, concentrated *via* rotovap, diluted by 50 mL of diethyl ether and further filtered off the precipitates. The organic solution was concentrated and purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1:15 v/v) to provide a yellow solid product (0.13 g, 0.25 mmol, 44.2 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (m, 2H), 7.24 (t, □ = 5.0 Hz, 1H), 7.12 (d, □ = 10.0 Hz, 1H), 6.95 (m, 2H), 6.81 (d, □ = 10.0

Hz, 1H), 6.74 (d, □ = 10.0 Hz, 1H), 5.92 (d, □ = 15.0 Hz, 1H), 5.85 (m, 1H), 5.05 (d, □ = 15.0 Hz, 1H), 4.99 (d, □ = 10.0 Hz, 1H), 4.28 (m, 2H), 3.51 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.57, 159.42, 146.70, 141.16, 139.13, 135.69, 128.27, 127.83, 125.95, 122.74, 121.84, 121.79, 119.92, 118.46, 115.55, 114.15, 106.76, 106.51, 62.28, 52.85, 42.45, 34.18.

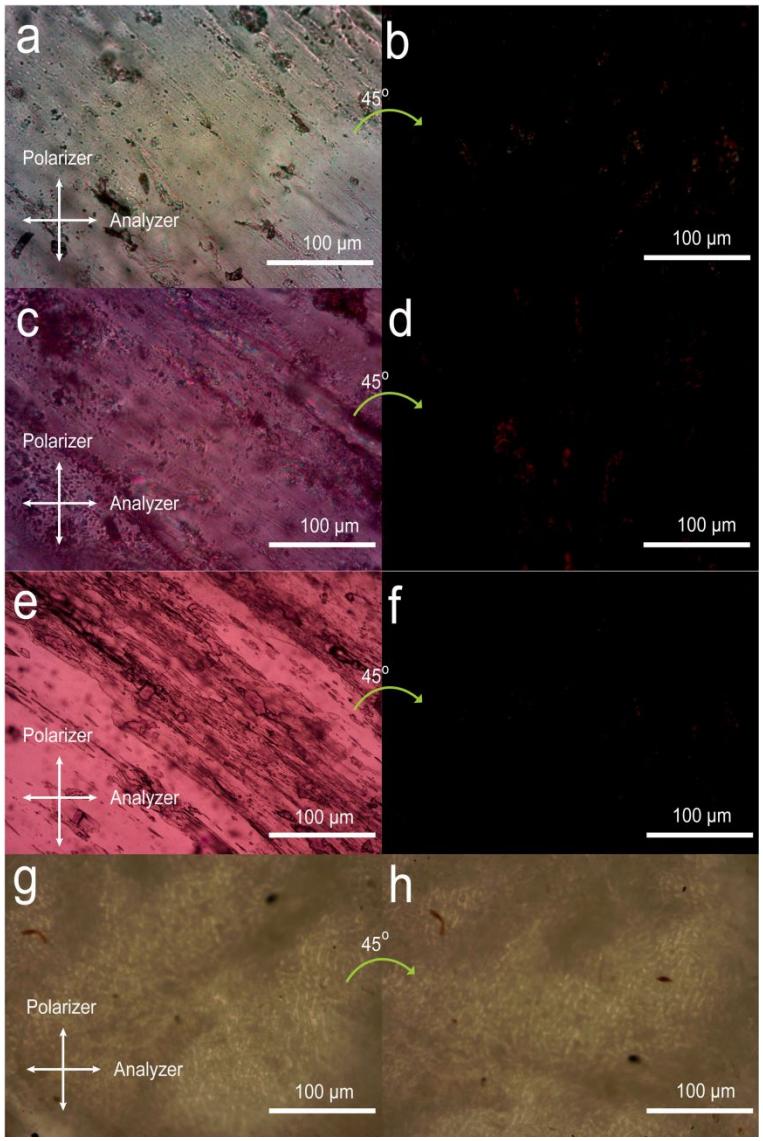

Figure S1. POM images of (a,b) LCE1 and (c,d) LCE2 and (e,f) LCE3 and (g,h) LCE0 recorded at room temperature.

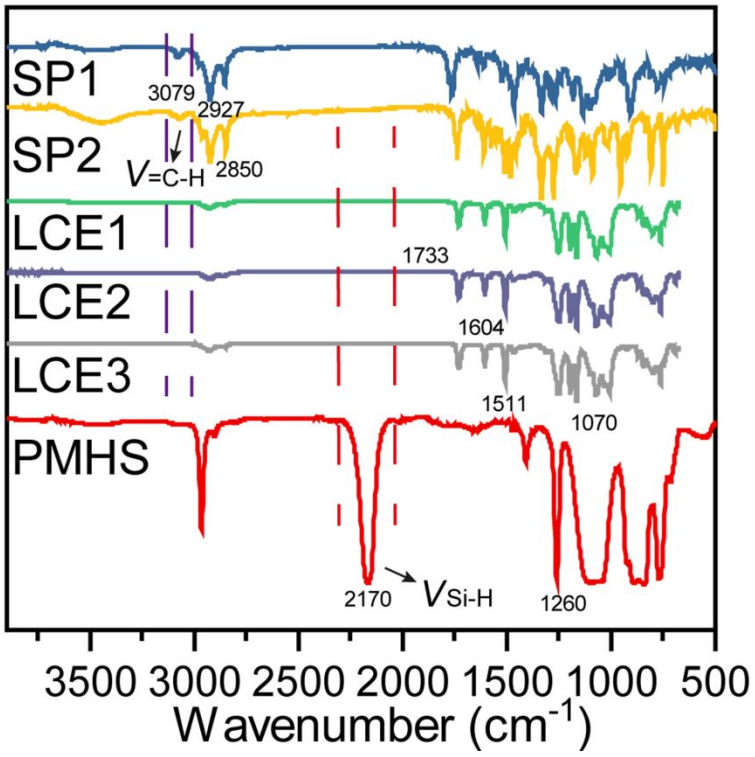

Figure S2. FT-IR spectra of monomers (SP1, SP2), LCE samples (LCE1, LCE2, LCE3) and the starting polymer PMHS.

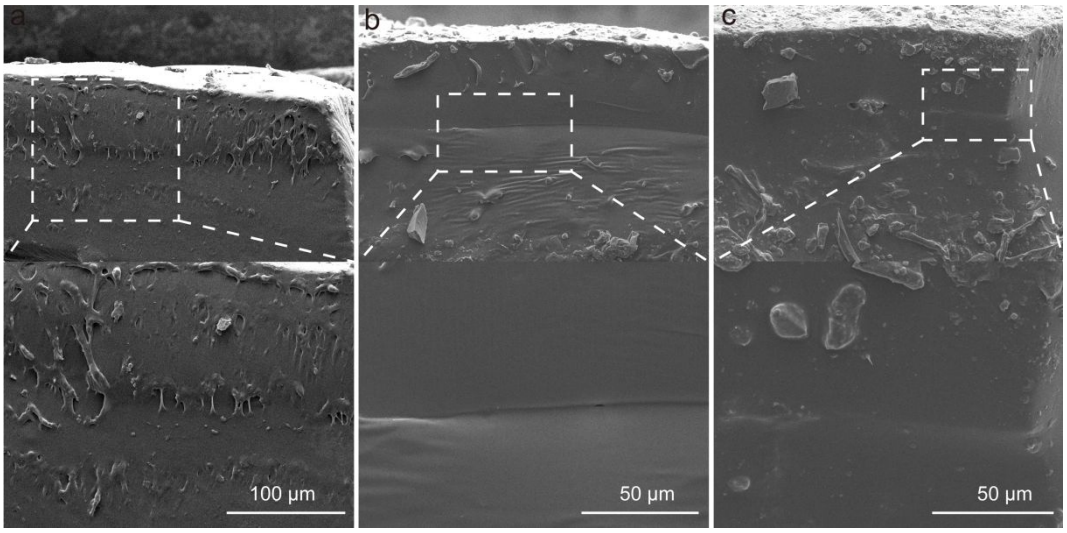

Figure S3. SEM images of the cross-sectional areas of the bilayered (a) LCE1B, (b) LCE2B and (c) LCE3B.

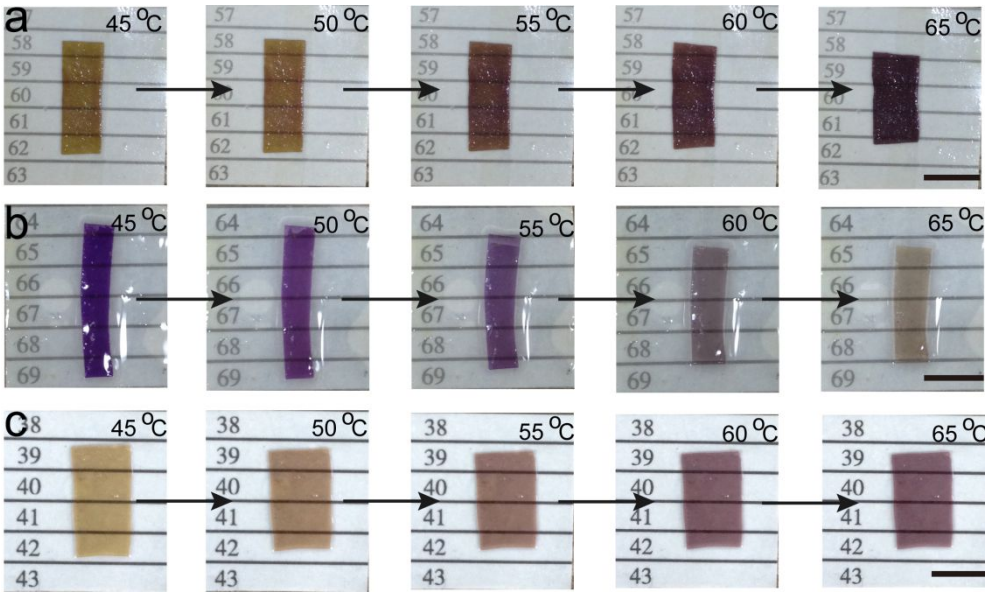

Figure S4. Thermo-chromic responses of (a) LCE1, (b) LCE2 and (c) LCE3 films at 45, 50, 55, 60 and 65 °C. Scale bar = 8 mm.

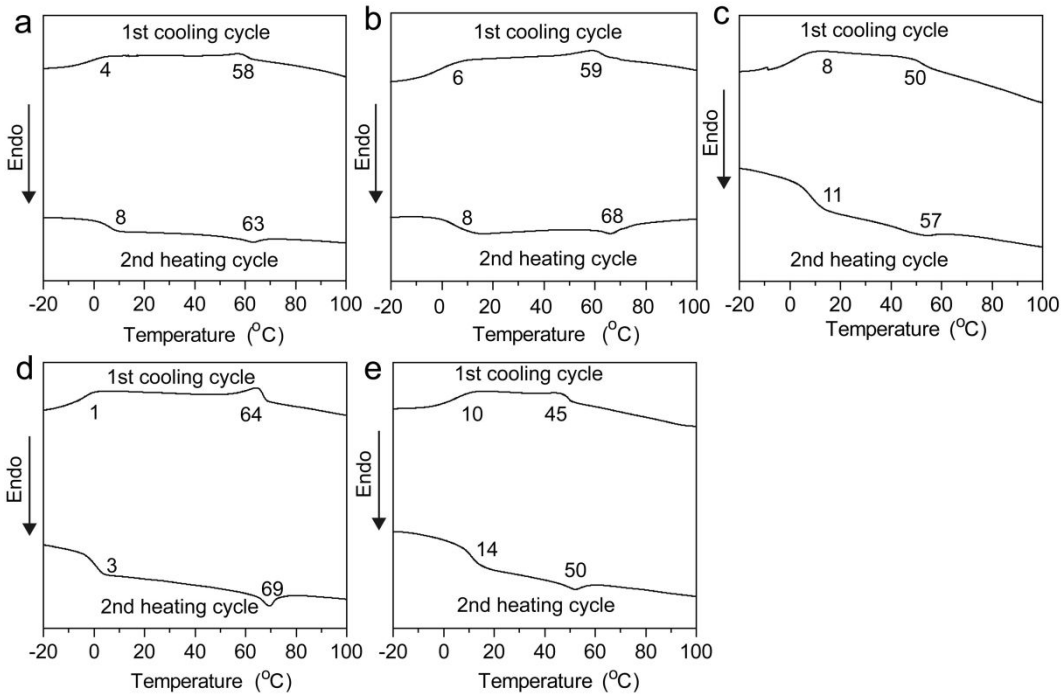

Figure S5. DSC curves of (a) LCE1, (b) LCE2, (c) LCE3, (d) LCE0 and (e) the LCE sample containing 10% SP1 crosslinker, during the first cooling and second heating scans at a rate of 10 °C/min under nitrogen atmosphere.

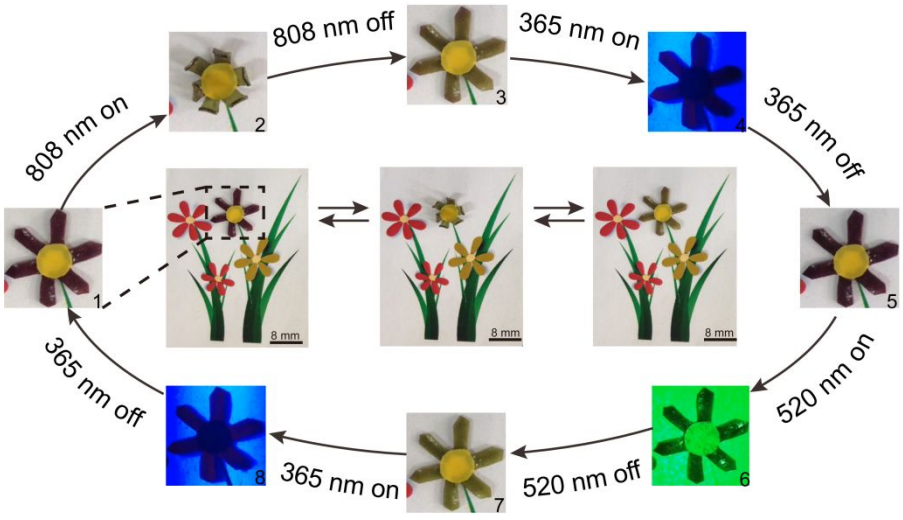

Figure S6. Bicolor-changing LCE2B "flower" doped with Green-575 (0.5 wt%) with its blossom blooming and unblooming modulated by light with different wavelengths.

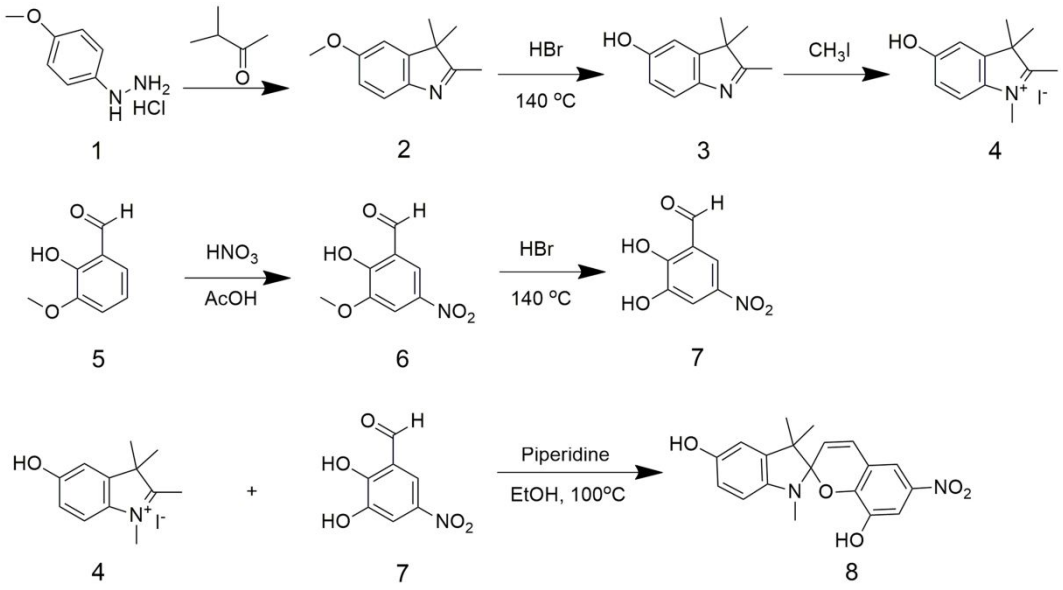

Figure S7. Synthetic route of compound **8**.

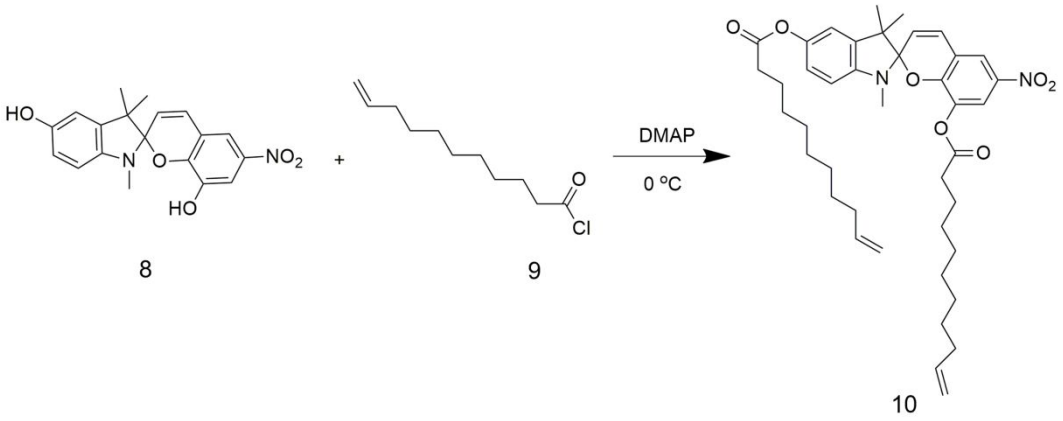

Figure S8. Synthetic route of compound **10** (SP1).

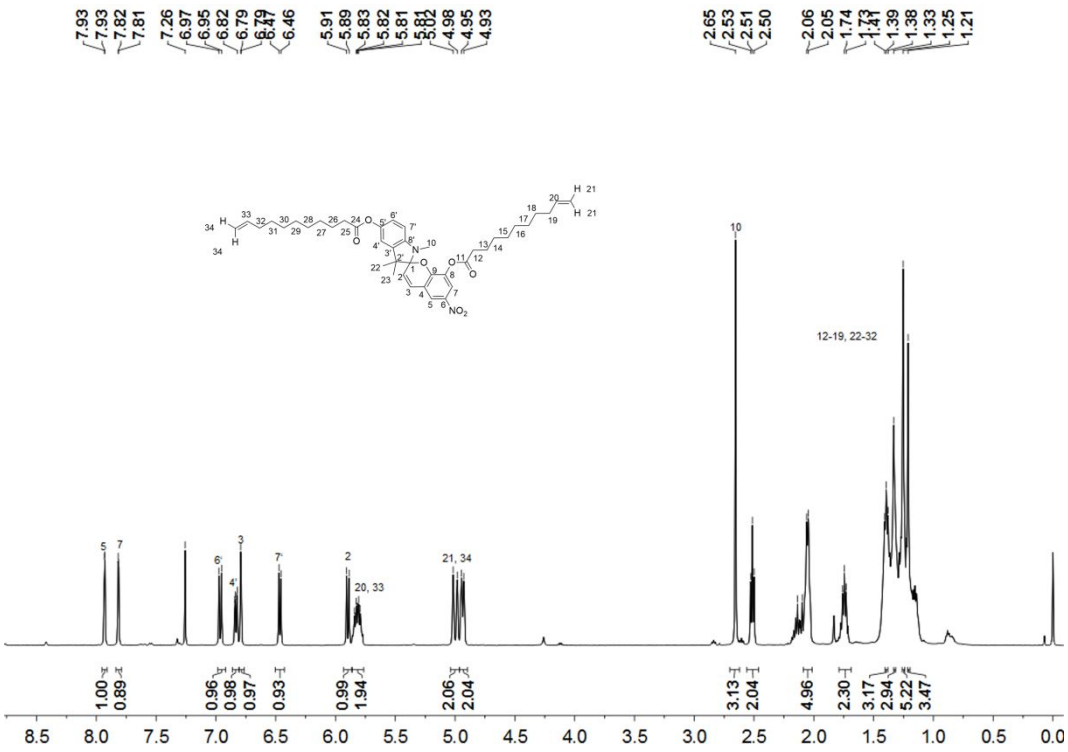

Figure S9. ^{1}H NMR spectrum of compound **10** (SP1).

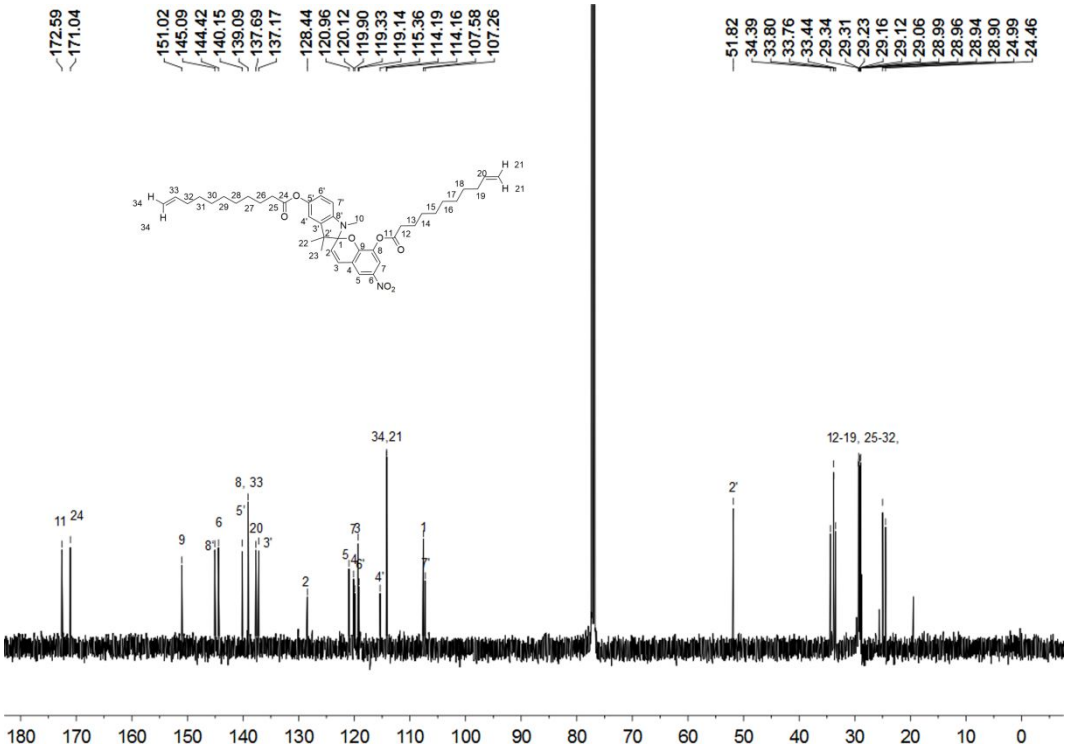

Figure S10. ^{13}C NMR spectrum of compound **10** (SP1).

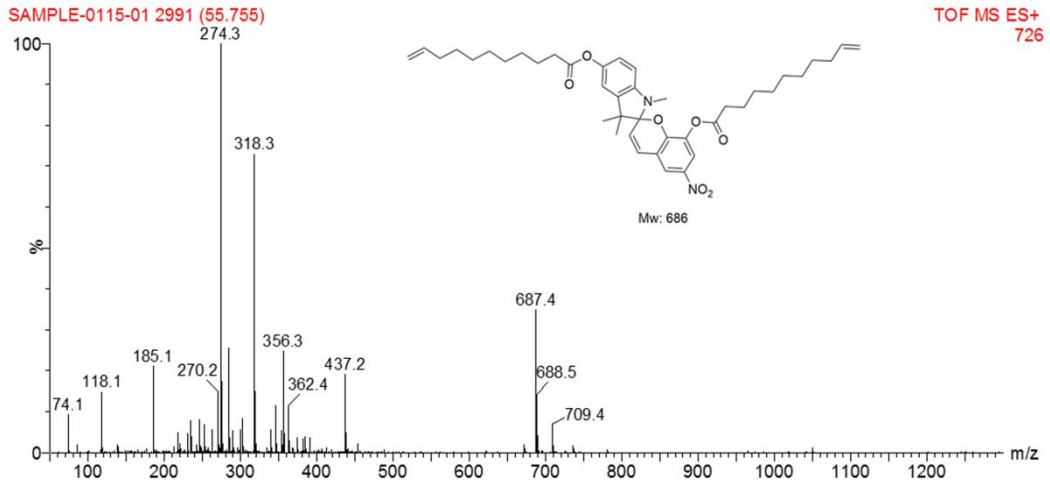

Figure S11. The mass spectra of compound **10** (SP1).

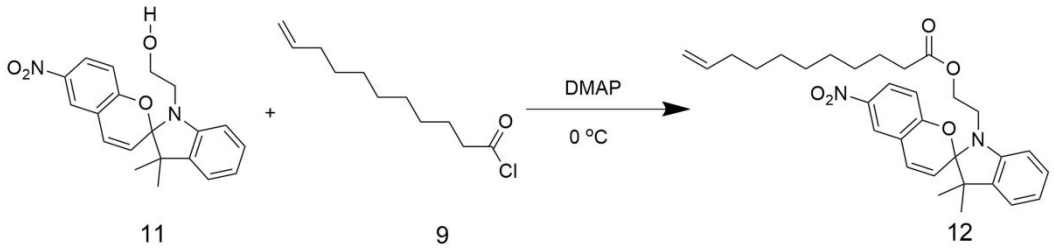

Figure S12. Synthetic route of compound **12** (SP2).

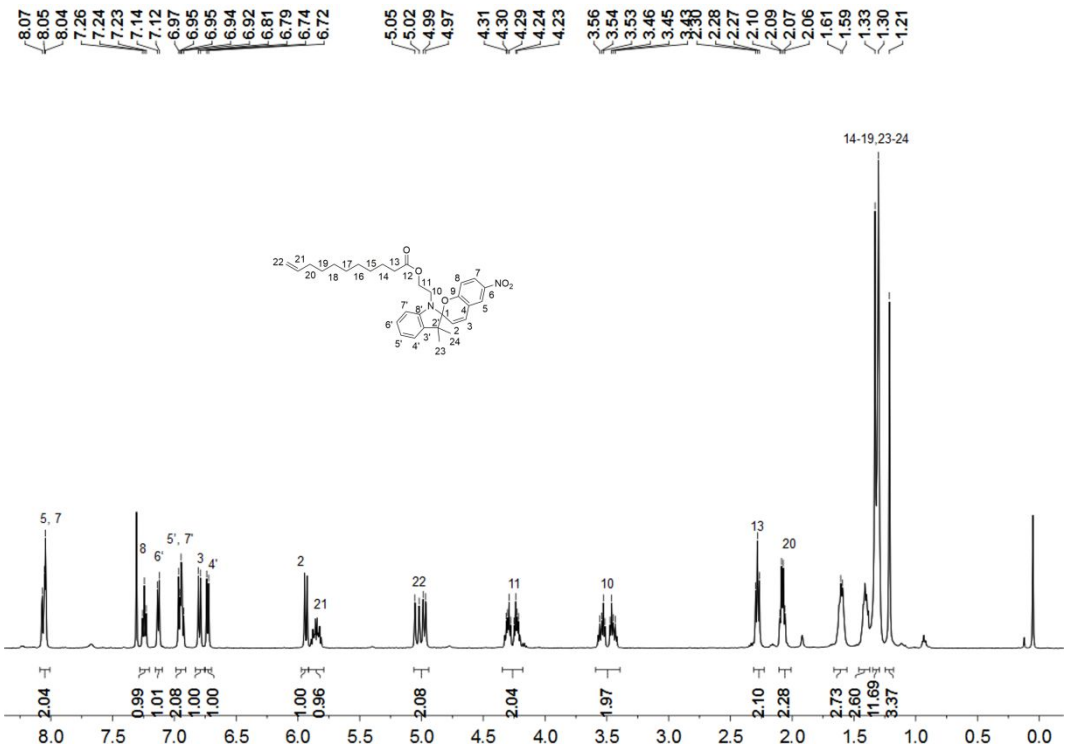

Figure S13. ^{1}H NMR spectrum of compound **12** (SP2).

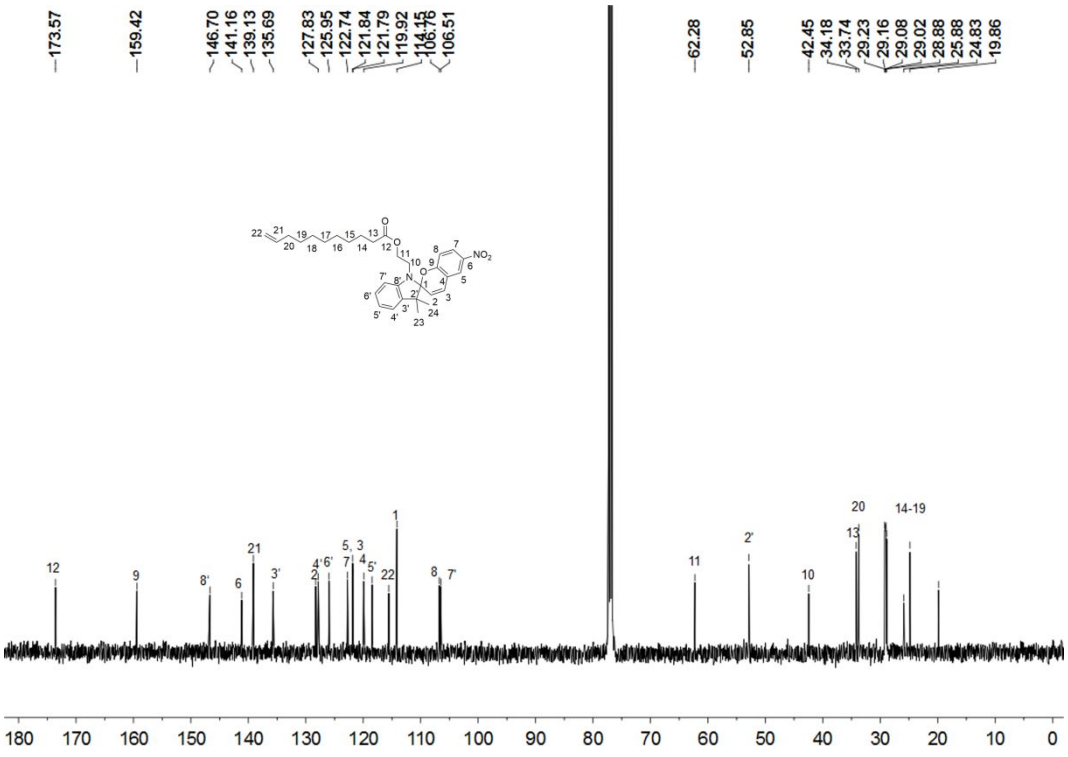

Figure S14. ^{13}C NMR spectrum of compound **12** (SP2).

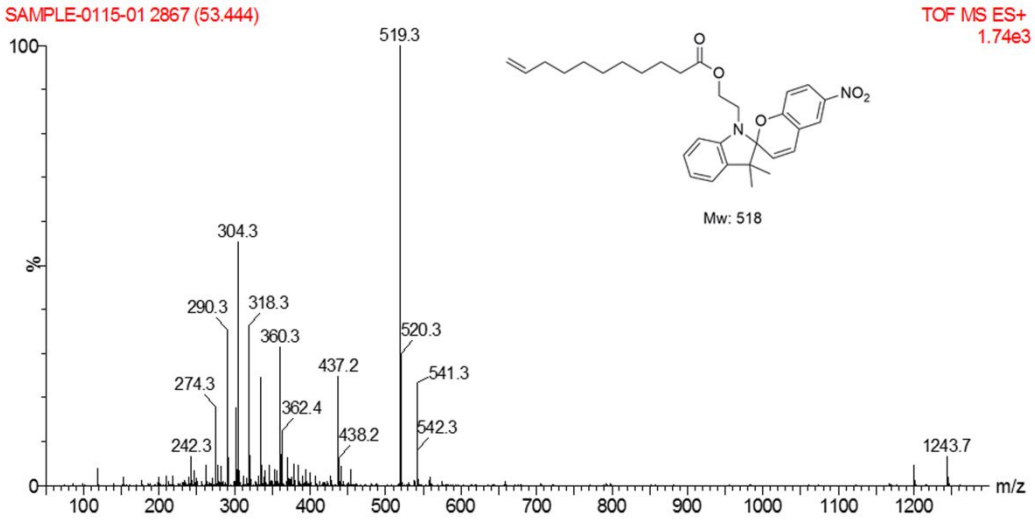

Figure S15. The mass spectra of compound **12** (SP2).

References

S1. Davis, D. A.; Hamilton, A.; Yang, J. L.; Cremar, L. D.; Gough, D. V.; Potisek, S. L.; Ong, M. T.; Braun, P. V.; Martinez, T. J.; White, S. R.; Moore, J. S.; Scottos, N. R. Force-induced Activation of Covalent Bonds in Mechanoresponsive Polymeric Materials. *Nature* **2009**, *459*, 68-72.