Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Mechanochemically Assisted Morphing of Shape Shifting Polymers

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Contents

I. General methods

All solvents and reagents used for synthesis were purchased from either Aladdin, Energy-Chemical, or Sinopharm Chemical Reagent Cooperation and used as received, unless otherwise noted. ^{1}H and ^{13}C NMR spectroscopy were conducted on a 400 MHz (or 600 MHz) Bruker spectrometer in chloroform-*d* ($\delta = 7.26$), acetone-d_6 ($\delta = 2.05$) or methanol-d_4 ($\delta = 3.31$) at 25 °C. Mass spectra were collected on a FTICR-MS Apex Ultra 7.0T. Mechanical tests were performed on an Instron 3343 instrument equipped with an Instron AVE2 video extender at room temperature (~ 25 °C). Electron spin resonance (ESR) measurements were carried out on a Bruker A30-10-12 equipped with nitrogen heating setup. Wide angle X-ray diffraction (WXRD) measurements were carried out on a Rigaku IV XRD at a rate of 10°/min.

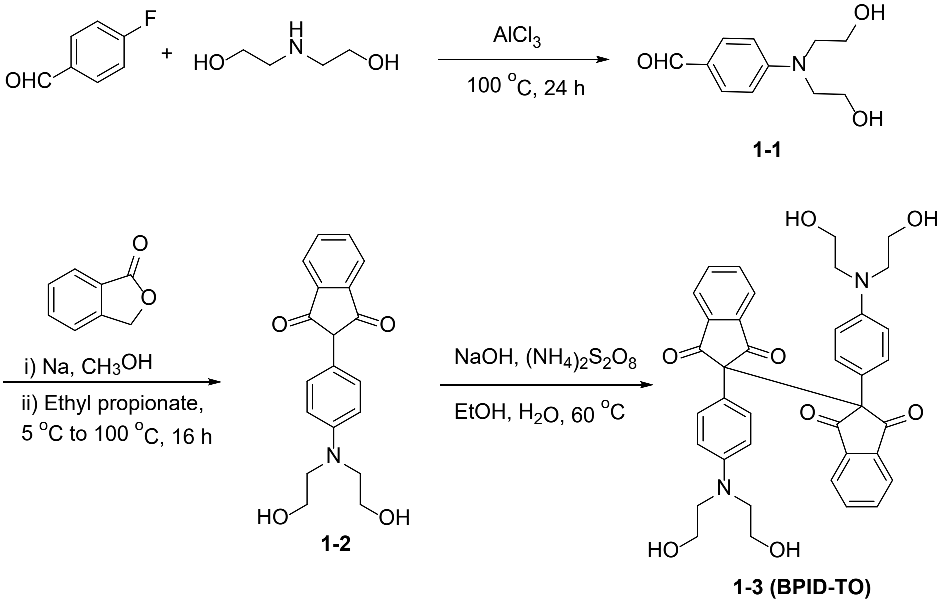
II. Electron spin resonance (ESR) measurements

Variable temperature ESR measurements were carried out on a Bruker A30-10-12 spectrometer (or EMXplus-9.5/12) equipped with nitrogen heating setup. DMF (*N*, *N*-dimethylformamide) solution of BPID-TO (1.5×10^{-3} mM) was transferred into 0.5 mm glass capillaries, which was filled up to more than 43.5 mm height. Polymer specimens (2 mm × 2 mm) were contained in 3 mm quartz tube. ESR spectra were measured using a microwave power of 2.04 mW and a field modulation 0.1 mT with a time constant of 40.96 ms. In the range from 25 °C to 80 °C, the spectra were recorded after sample was equilibrated at each temperature for 5 min.

ESR measurements of polymer films under strain were carried out on an EMXplus-9.5/12 spectrometer with a homemade strain-control device. The polymer films were cut into dumbbell-shape for tests.

III. Synthesis and properties of small molecules

1. Synthesis of BIPD-TO



Scheme S1. Synthetic route of BIPD-To.

1.1 Synthesis of 4-(N, N-bis (2-hydroxyethyl)amino) benzaldehyde (**1-1**)

In an oven-dried round bottom flask, *p*-fluorobenzaldehyde (80 g, 0.645 mol), diethanolamine (270 g, 2.571 mol) and $AlCl_3$ (4 g, 0.030 mol) were added. The mixture was then heated to 100 °C under nitrogen atmosphere. After 24 h, the reaction was stopped and cooled to room temperature. The reaction mixture was neutralized to pH = 7 with 10% hydrochloric acid solution. Water was then added to this mixture followed by extraction with ethyl acetate at 65 °C. The organic layer was dried over magnesium sulfate. After filtration, organic solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography and dried under vacuum to give compound **1-1** as a tangerine solid (70 g, 52% yield). ^{1}H NMR (600 MHz, CDCl3): δ (ppm) = 9.503 (s, 1H), 7.562-7.548 (d, J = 8.4 Hz, 2H), 6.632-6.618 (d, J = 8.4 Hz, 2H), 4.663 (s, 2H), 3.804-3.789 (t, J = 4.8 Hz, 4H), 3.600-3.584 (t, J = 4.8 Hz, 4H); ^{13}C NMR (150 MHz, CDCl3): δ (ppm) = 190.595, 152.826, 132.081, 124.980, 111.473, 59.872, 54.743. FT-MS: m/z = 210.1126 [M + H$^+$] (Calculated 210.1125 for [$C_{11}H_{16}NO_3$]$^+$).

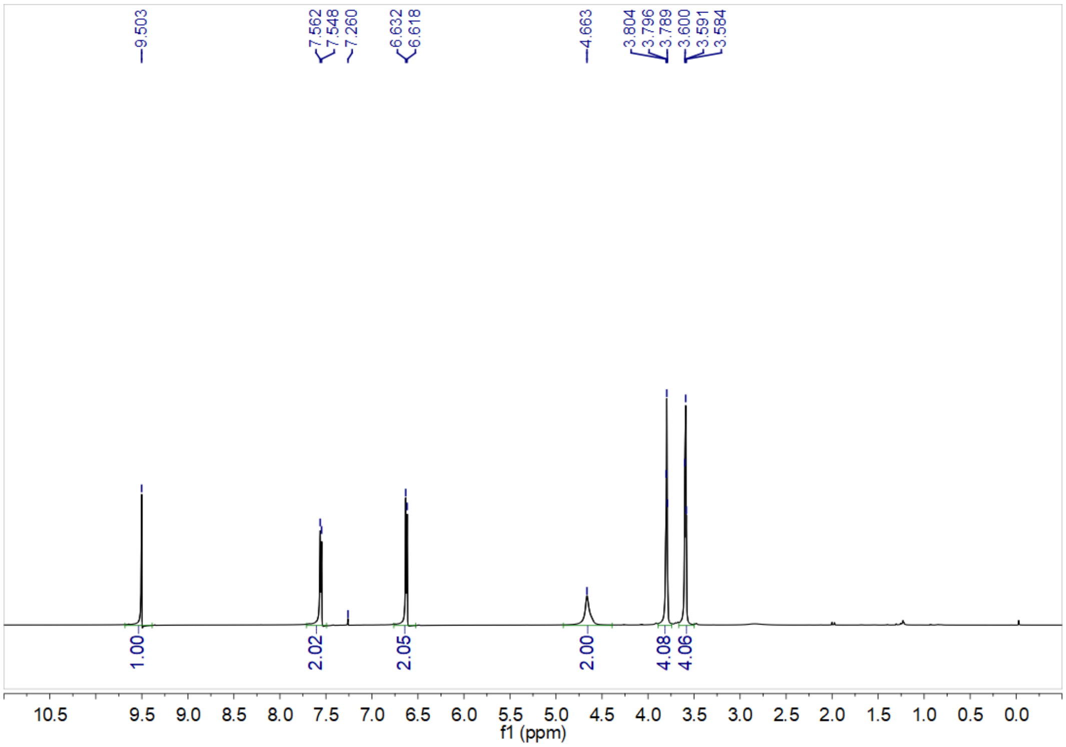


Figure S1. ^{1}H NMR spectrum of compound **1-1** in $CDCl_3$.

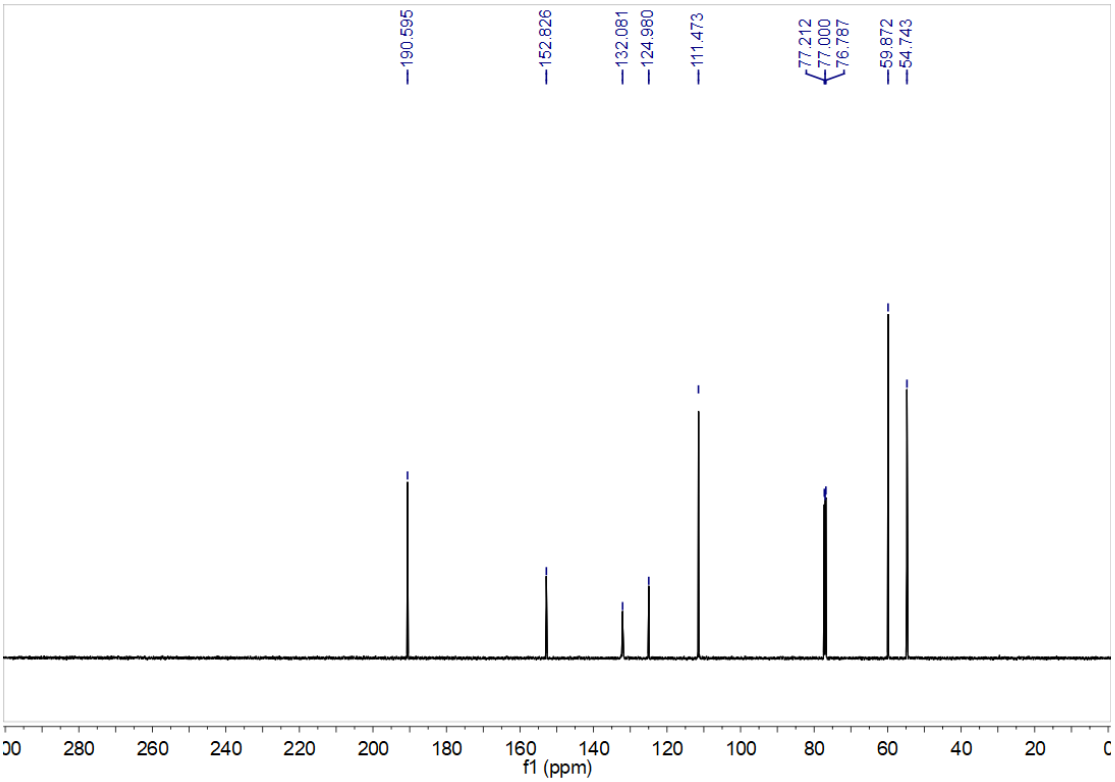


Figure S2. ^{13}C NMR spectrum of compound **1-1** in $CDCl_3$.

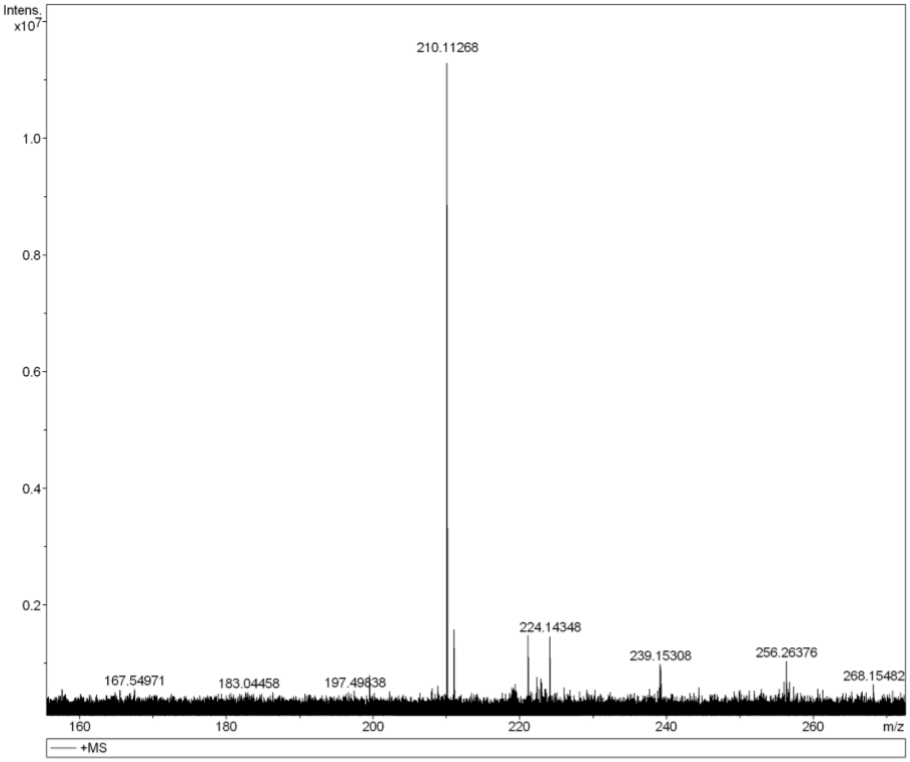


Figure S3. FT-MS spectrum of compound **1-1**.

1.2 Synthesis of 2-(4'- (N, N-bis (2-hydroxyethyl)amino)benzaldehyde)indan-1,3-dione (**1-2**)

A solution of sodium methoxide, freshly prepared from sodium (8.556 g, 0.372 mol) and methanol (140 mL) was added to a suspension of compound **1-1** (20 g, 0.096 mol) and phthalide (4.84 mg, 0.115 mol) in ethyl propionate (80 mL) at 5 °C. After heated under reflux for 16 h, the reaction mixture was concentrated under reduced pressure. Then, water (500 mL) was added, and the mixture was washed with dichloromethane (3 × 500 mL). The aqueous phase was acidified with acetic acid, and the suspension was stirred for 30 min, until a sticky black precipitate was formed. Water was poured off and the precipitate was dried under vacuum to give compound **1-2** (16 g, 51%) as dark red solid. ^{1}H NMR (600 MHz, CDCl3): δ (ppm) = 8.041-8.020 (m, 2H), 7.885-7.871 (dd, J = 3 Hz, 5.4 Hz, 2H), 6.990-6.976 (d, J = 8.4 Hz, 2H), 6.637-6.623 (d, J = 8.4 Hz, 2H), 4.138 (s, 1H), 3.780-3.764 (t, J = 4.8 Hz, 4H), 3.518-3.502 (t, J = 4.8 Hz, 4H); ^{13}C NMR (150 MHz, CDCl3): δ (ppm) = 199.185, 147.381, 142.571, 135.882, 129.583, 123.645, 121.023, 112.872, 60.572, 59.169, 55.153. FT-MS: m/z = 348.1208 [M + Na$^{+]}$ (Calculated 348.1206 for $[C_{19}H_{19}NO_4Na]^+$).

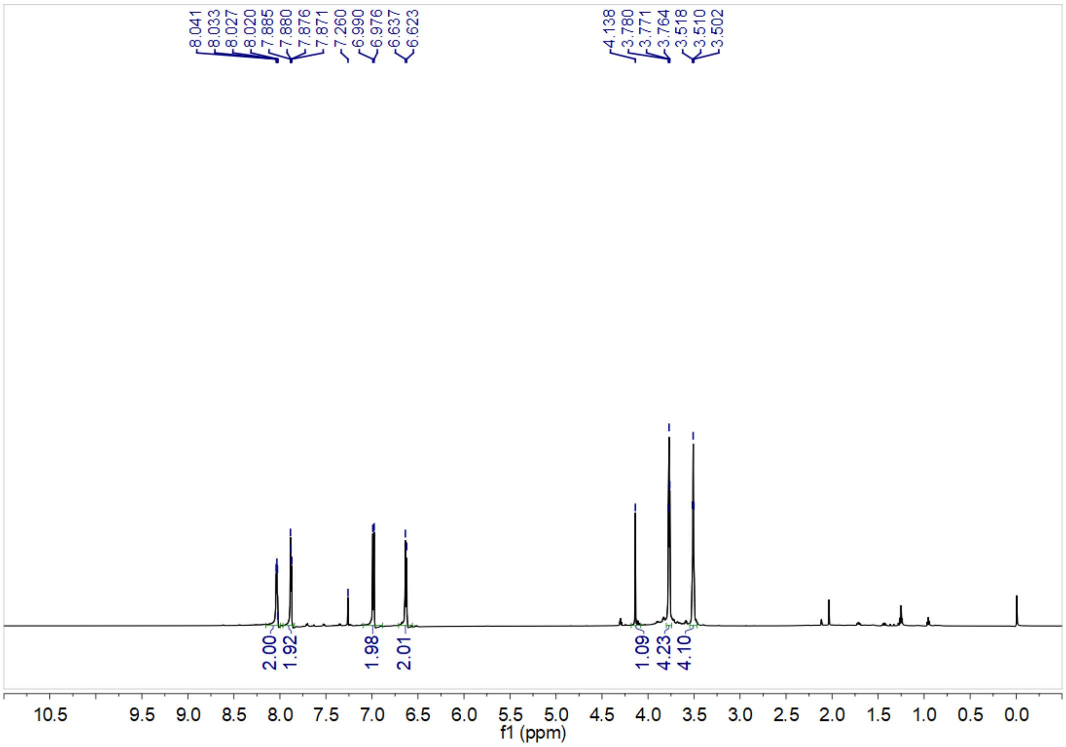


Figure S4. ^{1}H NMR spectrum of compound **1-2** in $CDCl_3$.

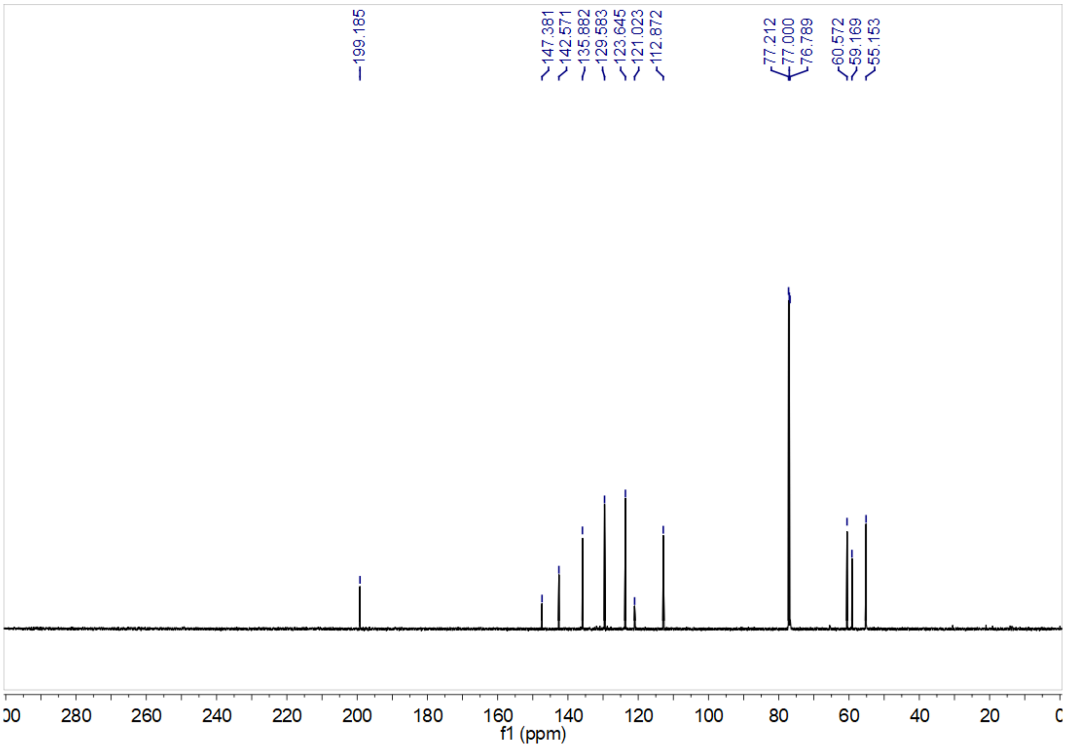


Figure S5. ^{13}C NMR spectrum of compound **1-2** in $CDCl_3$.

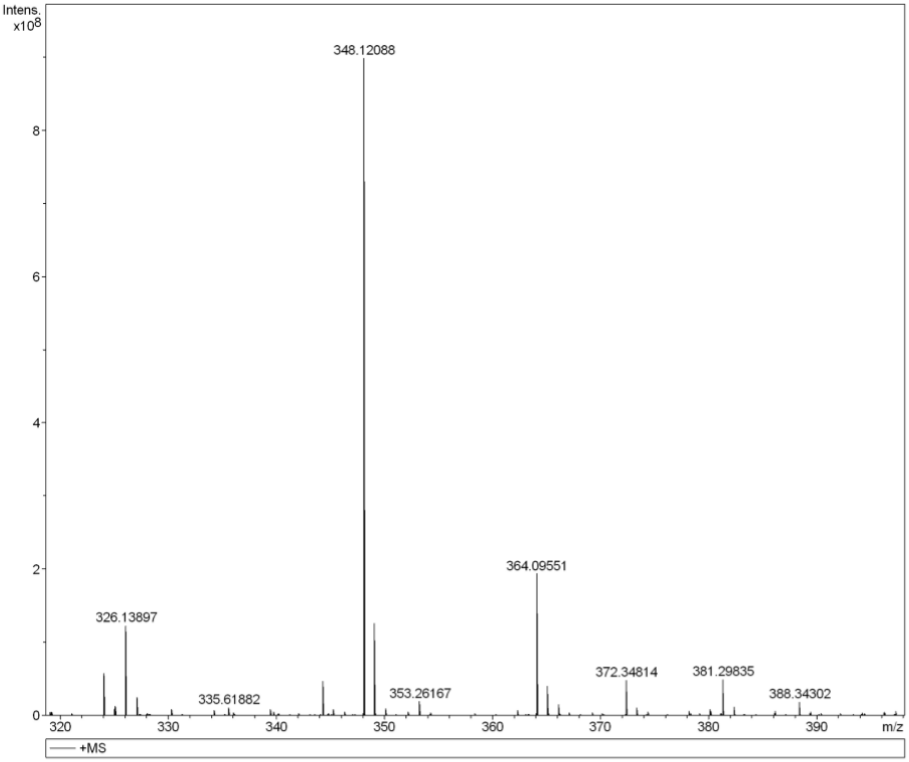


Figure S6. FT-MS spectrum of compound **1-2**.

1.3 Synthesis of 2,2'-bis[2-(4''-(N,N-bis(2-hydroxyethyl)amino)benzaldehyde)indan- 1,3-dione] (**1-3**)

A solution of compound **1-2** (5 g, 0.015 mol) in 70 mL ethanol was added to a solution of NaOH (4.57 g, 0.114 mol) in 100 mL water at 60 °C. Then, ammonium persulfate (6.8 g, 0.028 mol) in 100 mL water was added dropwise into the above mixture. Precipitation was observed almost instantly. The precipitate was collected, dried and further purified by silica gel column chromatography. Compound **1-3** was obtained as a yellow solid (1.5 g, 15% yield). ^{1} H NMR (600 MHz, (CD3)2CO): δ (ppm) = 7.893 (m, 8H), 6.949-6.935 (d, J = 8.4 Hz, 4H), 6.599-6.585 (d, J = 8.4 Hz, 4H), 4.193 (s, 4H), 3.713 (m, 8H), 3.530 (m, 8H); ^{13}C NMR (150 MHz, (CD3)2CO): δ (ppm) = 206.317, 205.991, 148.987, 141.767, 136.610, 132.038, 124.140, 117.505, 111.543, 64.952, 60.207, 55.043. FT-MS: m/z = 649.2549 [M + H $^+$] (Calculated 649.2544 for $[C_{38}H_{37}N_2O_8]^+$).

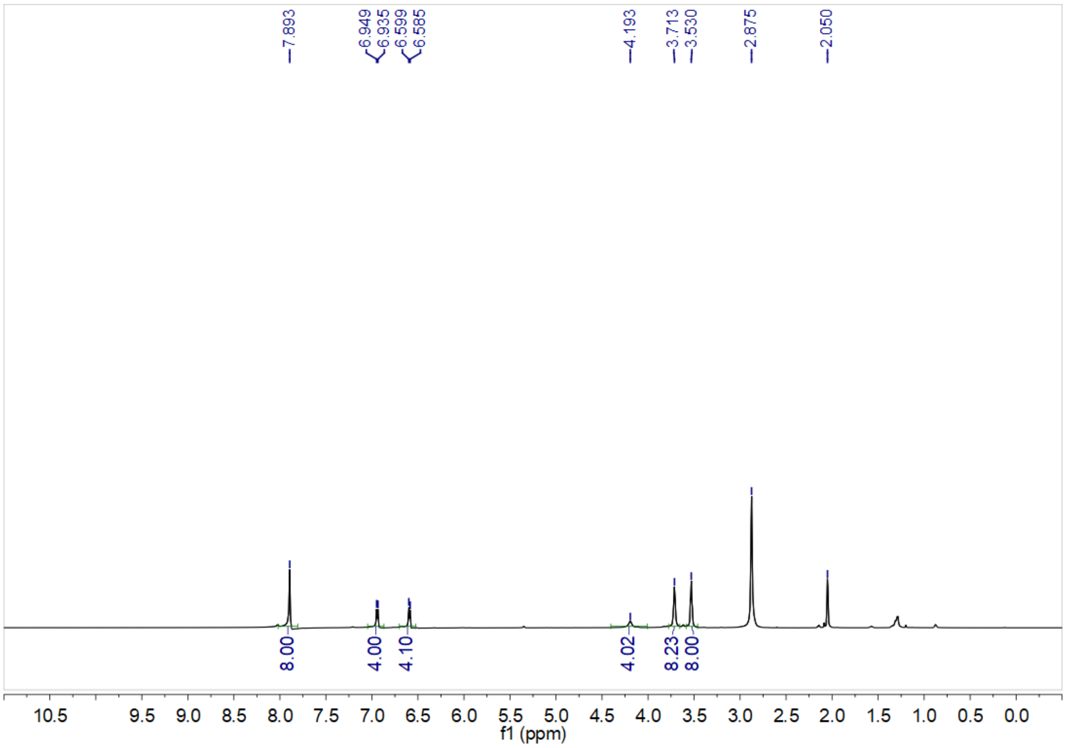


Figure **S7.** ^{1}H NMR spectrum of compound **1-3** (BPID-TO) in $(CD_3)_2CO$.

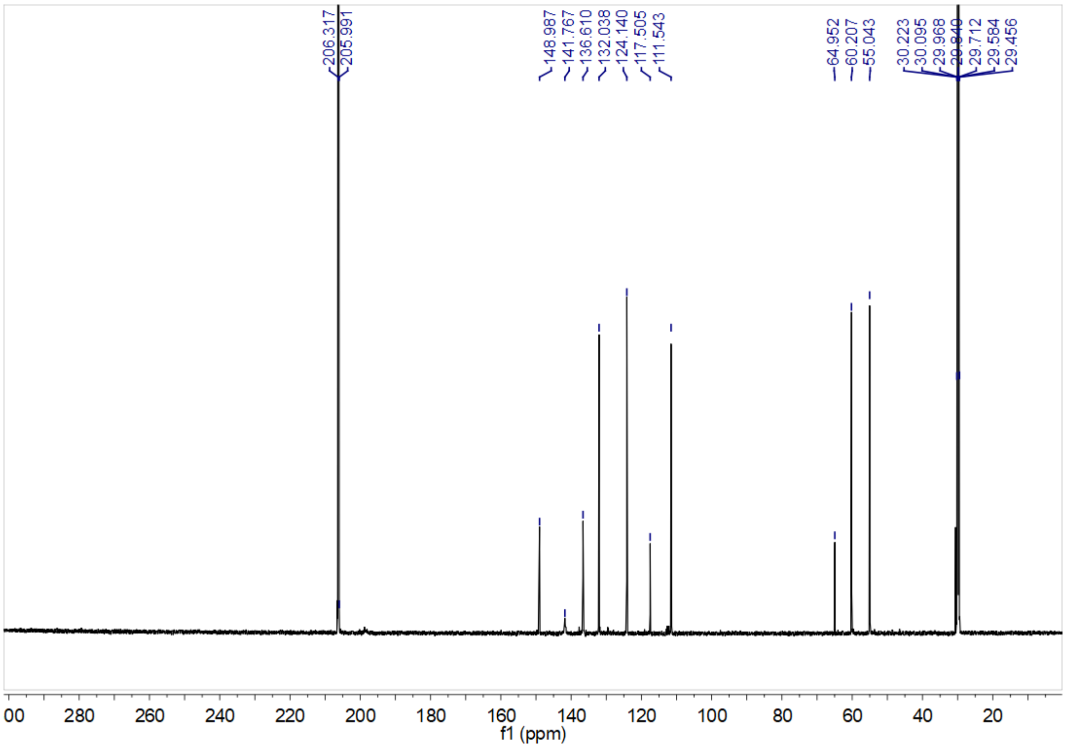


Figure **S8.** ^{13}C NMR spectrum of compound **1-3** (BPID-TO) in $(CD_3)_2CO$.

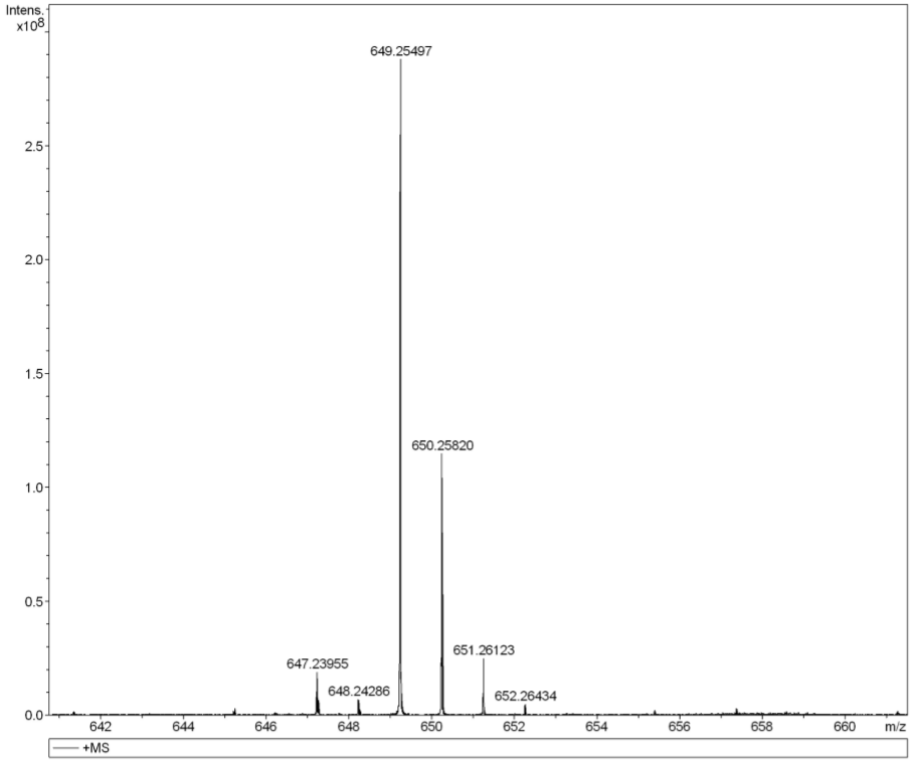


Figure S9. FT-MS spectrum of compound **1-3** (BPID-TO).

2. Responsive properties of BPID-TO

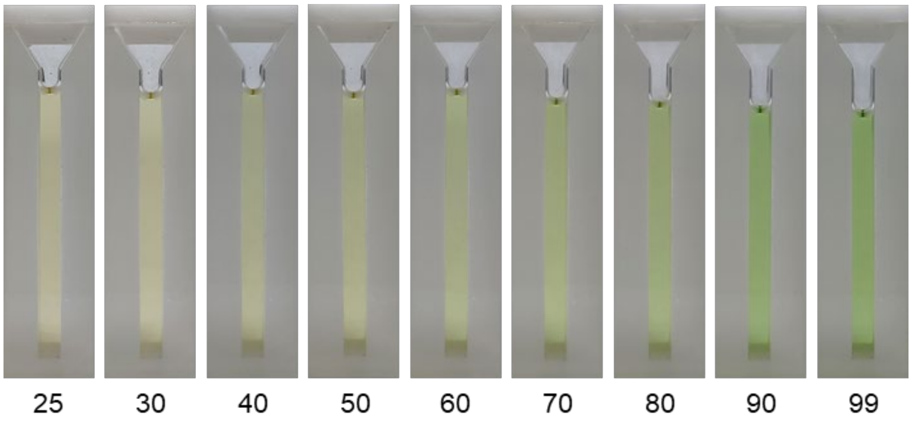


Figure S10. The thermochromism of BPID-TO in DMF solution (5×10^{-4} mM). The sample was equilibrated at each temperature for 5 min.

Figure S11. The mechanochromism of BPID-TO powder under grinding.

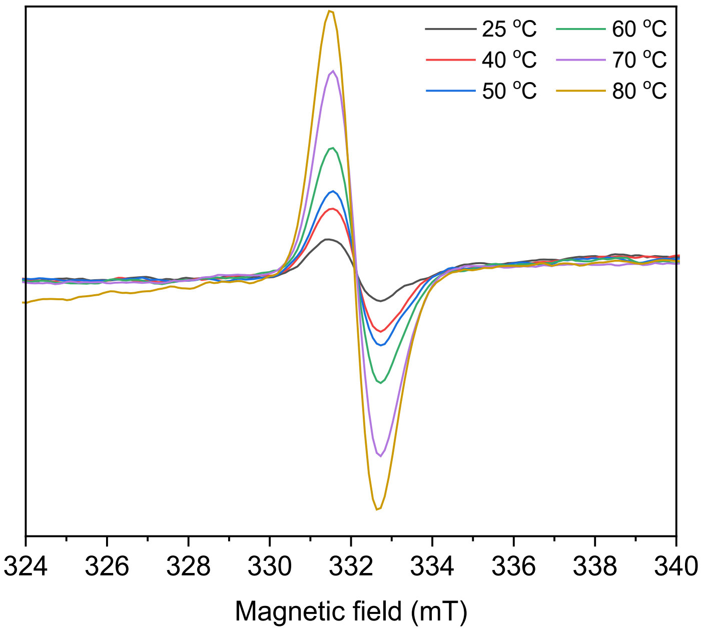


Figure S12. ESR spectra of BPID-TO solution (5×10^{-4} mM in DMF) at various temperatures.

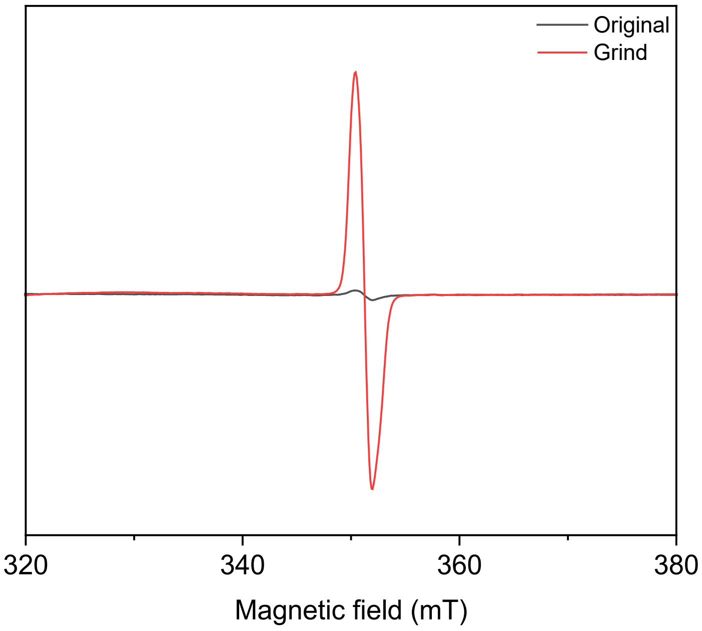
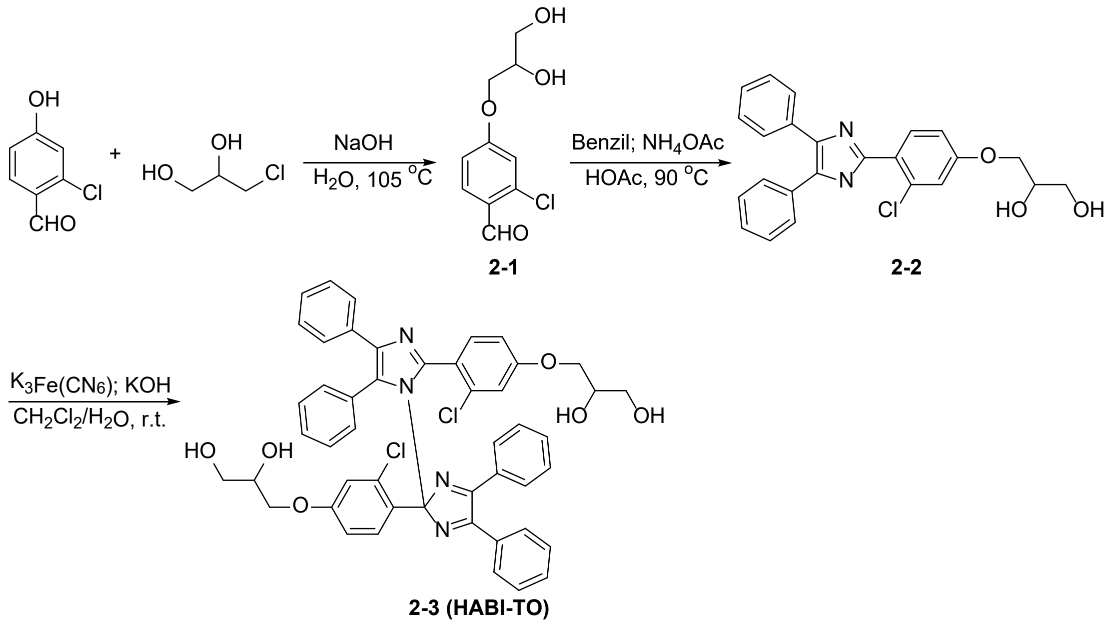


Figure S13. ESR spectra of BPID-TO powder before and after grinding.

3. Synthesis of HABI-TO



Scheme S2. Synthetic route of HABI-TO.

2.1 Synthesis of compound **2-1**

2-chloro-4-hydroxybenzaldehyde (10 g, 64 mmol), sodium hydroxide (7.66 g, 191.4 mmol) and 160 mL water were added into a 500 mL two-neck round-bottom flask, and a reflux condenser was installed. After purging with nitrogen gas for 10 min, the temperature was raised to 80 ^{o}C and kept for 20 minutes. Then, 3-chloro-1,2-propanediol (22.1 g, 200 mmol) was added and the temperature was raised to 105 ^{o}C. After reacting for 10.5 hours, the reaction system was cooled to room temperature, and 10 wt% hydrochloric acid (4 mL) was added. The reaction was further heated at 80 °C for 1 hour, and the reaction system turned black. After cooling down to room temperature, the aqueous solution was slightly condensed and extracted with ethyl acetate. Organic phase was then collected and dried over anhydrous sodium sulfate. After concentration and further purification by column (petroleum ether: ethyl acetate = 1:2, R_f = 0.2), a yellow oily liquid **2-1** (9.86 g, 67%) was obtained. ^{1} H NMR (400 MHz, CD3OD): δ (ppm) = 10.214 (s, 1H), 7.819-7.797 (d, J = 8.8 Hz, 1H), 7.051-7.045 (d, J = 2.4 Hz, 1H), 7.006-6.980 (dd, J = 1.6 Hz, 8.4 Hz, 1H), 4.855 (s, 2H), 4.180-4.146 (m, 1H), 4.087-4.047 (m, 1H), 4.009-3.985 (m, 1H), 3.686-3.666 (dd, J = 2.4 Hz, 5.2 Hz, 2H); 13C NMR (100 MHz, CD3OD): δ (ppm) = 189.488, 165.369, 140.325, 131.849, 126.936, 116.787, 115.052, 71.142, 70.943, 63.599.

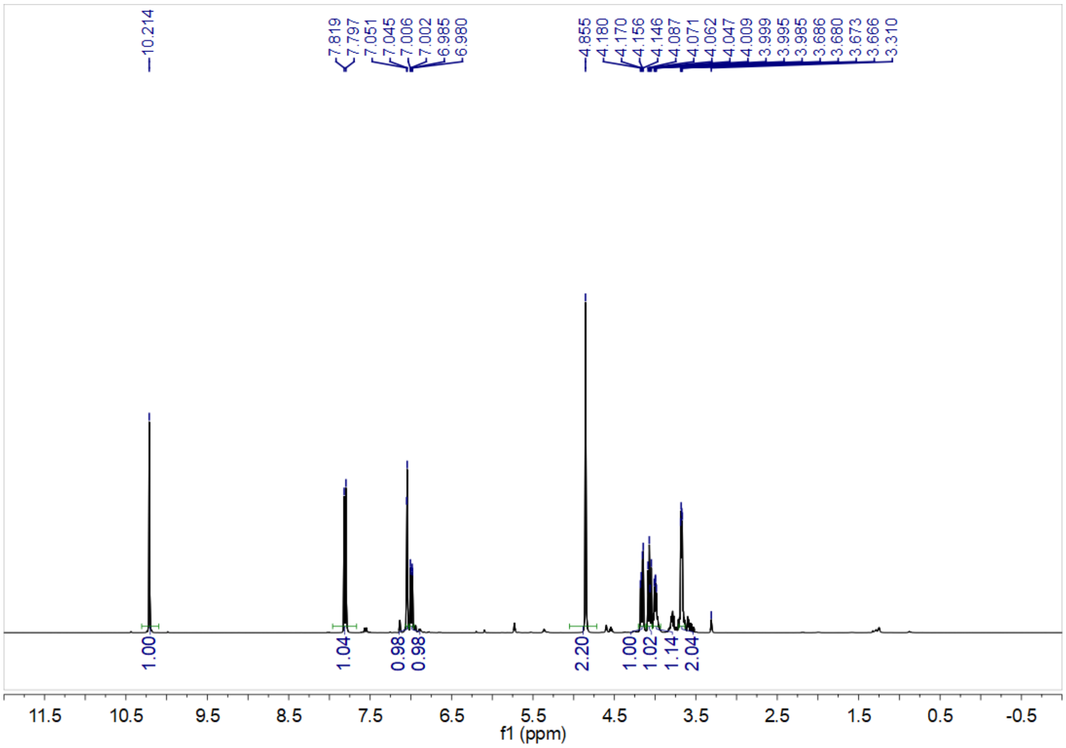


Figure S14. ^{1}H NMR spectrum of compound **2-1** in CD_3OD.

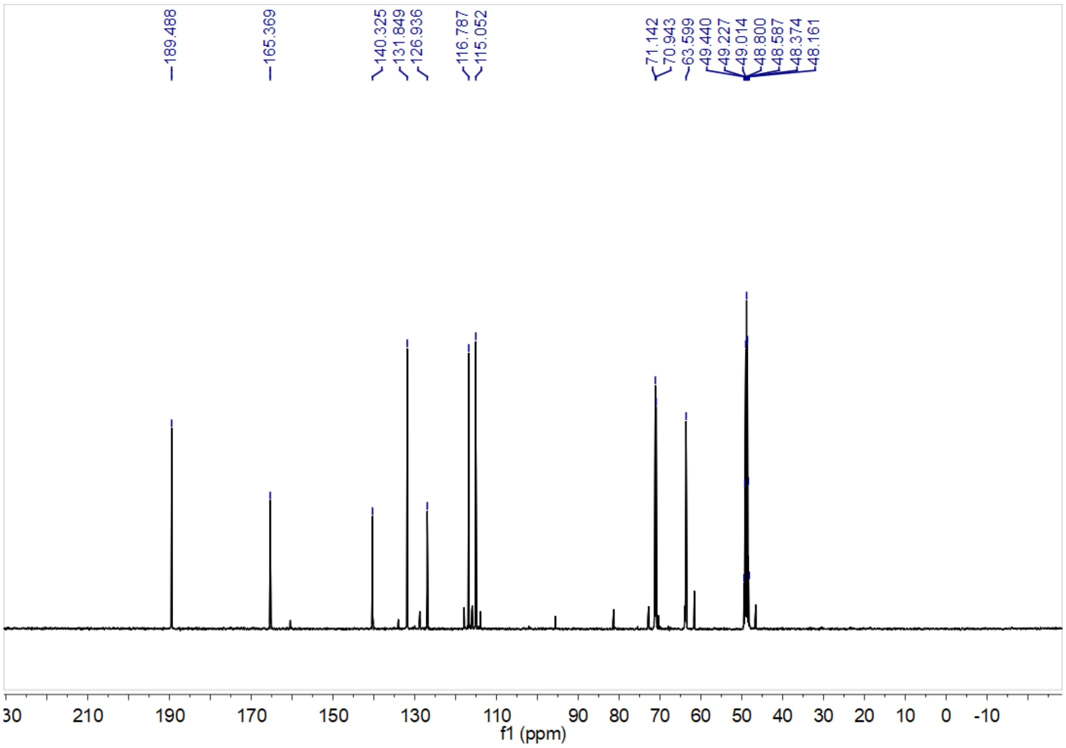


Figure S15. ^{13}C NMR spectrum of compound **2-1** in CD_3OD.

2.2 Synthesis of compound **2-2**

To a 100 mL three-neck flask, added benzil (0.92 g, 4.34 mmol) and ammonium acetate (2.68 g, 34.72 mmol). Three cycles of pump-fill was perform to fill the flask with nitrogen. Compound **2-1** (1 g, 4.34 mmol) in glacial acetic acid was then added to the flask, and an additional 16 mL glacial acetic acid was added. After heated at 90 ^{o}C for 100 min, the solution was immediately poured into a sodium hydroxide aqueous solution (a mixture of 13 g sodium hydroxide and 400 mL ice water) and stirred for 10 minutes. Upon standing, a pale-yellow precipitate formed and was removed by filtration. The precipitate was washed with water once, and all the aqueous phase was collected and extracted once with ethyl acetate. The organic phase was separated and dried over anhydrous magnesium sulfate. After filtration and concentration, and dry in a vacuum oven at 45 °C for 2 hours, the the crude product was purified by column (DCM : methanol = 40:1, R_f = 0.3). Compound **2-2** was obtained as a light chartreuse powder (700 mg, 38.4%). ^{1}H NMR (400 MHz, CD3OD): δ (ppm) = 7.675-7.654 (d, J = 8.4 Hz,1H), 7.490-7.472 (d, J = 7.2 Hz, 4H), 7.352-7.266 (m, 6H), 7.182-7.176 (d, J = 2.4 Hz, 1H), 7.071-7.043 (dd, J = 2.4 Hz, J = 8.4 Hz,1H), 4.165-3.969 (m, 3H), 3.723-3.643 (m, 2H); ^{13}C NMR (100 MHz, CD3OD): δ (ppm) = 161.545, 145.380, 134.719, 133.455, 129.346, 129.036, 128.252, 123.545, 116.940, 114.452, 71.408, 70.703, 63.771.

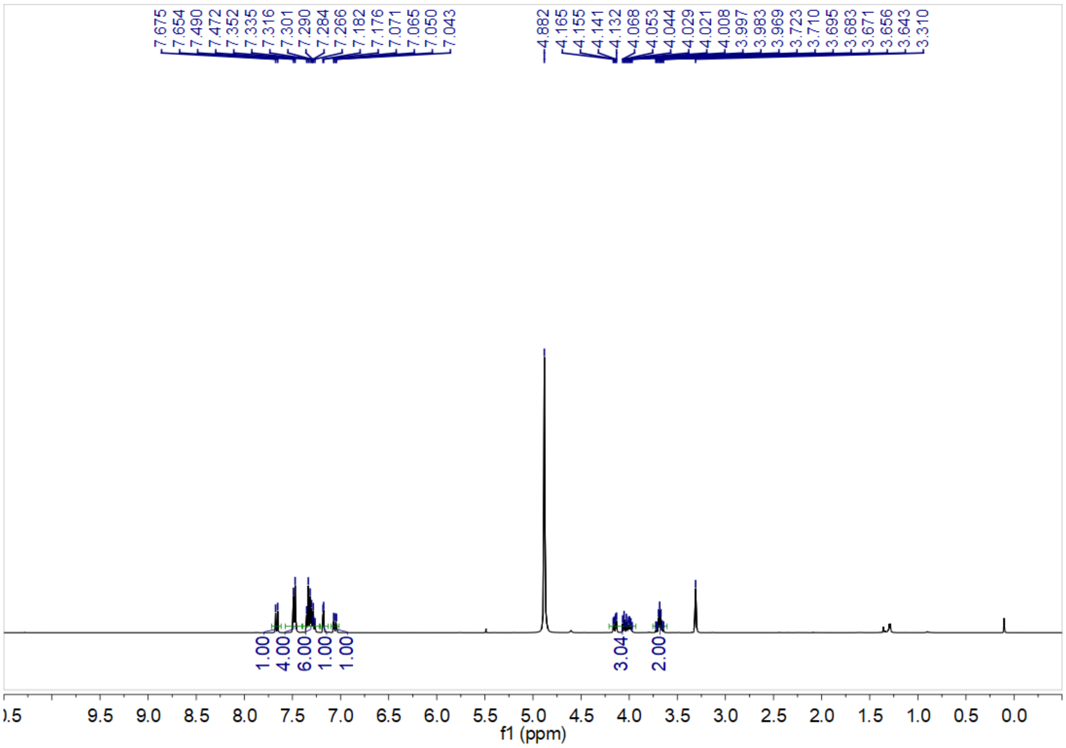


Figure S16. ^{1}H NMR spectrum of compound **2-2** in CD_3OD.

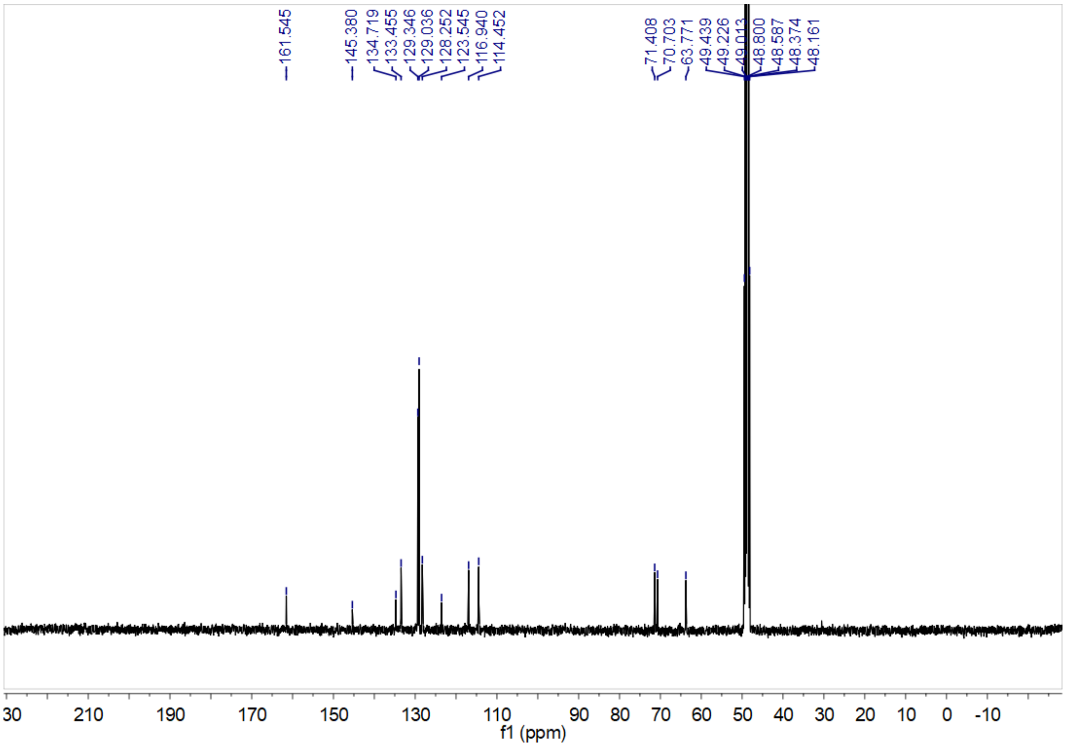


Figure S17. ^{13}C NMR spectrum of compound **2-2** in CD_3OD.

2.3 Synthesis of compound **2-3**

To a 250 mL two-neck bottle, added compound **2-2** (1.0 g, 2.4 mmol). The flask was filled with argon by three cycles of pump-fill. Dry dichloromethane (40 mL) was added to dissolve the compound. The flask was then wrapped with aluminum foil. Potassium hydroxide (2.7 g, 48 mmol) and potassium ferricyanide (8 g, 24 mmol) were dissolved with 40 mL of water and sparged with argon for 10 minutes. The aqueous solution was then added to the flask through a syringe. After vigorous stirring at room temperature for 12 hours, the reaction mixture was diluted with dichloromethane and washed with water three times. The organic phase was dried with $MgSO_4$. After filtration, dichloromethane was concentrated, and product was purified by column (PE was used for impurities; EA was used for product, $R_f = 0.2$). Compound **2-3** was obtained as a chartreuse solid (830 mg, 83%). Compound **2-3** has is photosensitive, and the preparation of NMR sample could not avoid the exposure to ambient light. As a result, the NMR peaks showed a combination of HABI and radical species. Nevertheless, the integration of hydrogen signals in the NMR is consistent with the proton number. ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) = 7.666-6.127 (m, 26H), 4.181-3.310 (m, 10H); ^{13}C NMR (100 MHz, CD3OD): δ (ppm) = 169.826, 160.781, 160.351, 160.241, 145.385, 139.089, 139.022, 136.089, 135.935, 134.887, 134.224, 132.886, 132.802, 132.453, 132.153, 131.507, 131.381, 130.514, 130.389, 130.252, 129.995, 129.911, 129.283, 129.034, 128.839, 128.717, 128.669, 128.096, 127.613, 127.329, 127.128, 119.503, 118.078, 116.858, 114.997, 114.077, 113.942, 112.922, 111.869, 111.799, 80.666, 80.509, 71.255, 71.144, 70.458, 63.855, 63.712, 61.434, 61.336. FT-MS: m/z = 838.2398 [M + H $^+$] (Calculated 838.2408 for $[C_{48}H_{41}Cl_2N_4O_6]^+$).

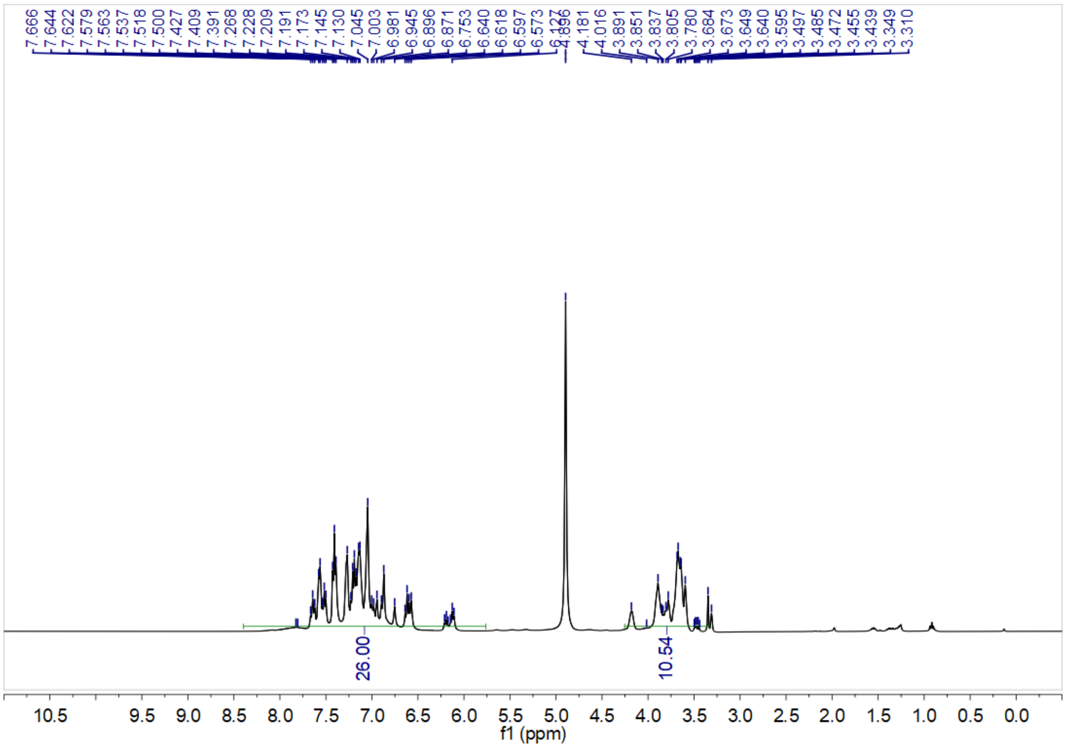


Figure S18. ^{1}H NMR spectrum of compound **2-3** (HABI-TO) in CD_3OD.

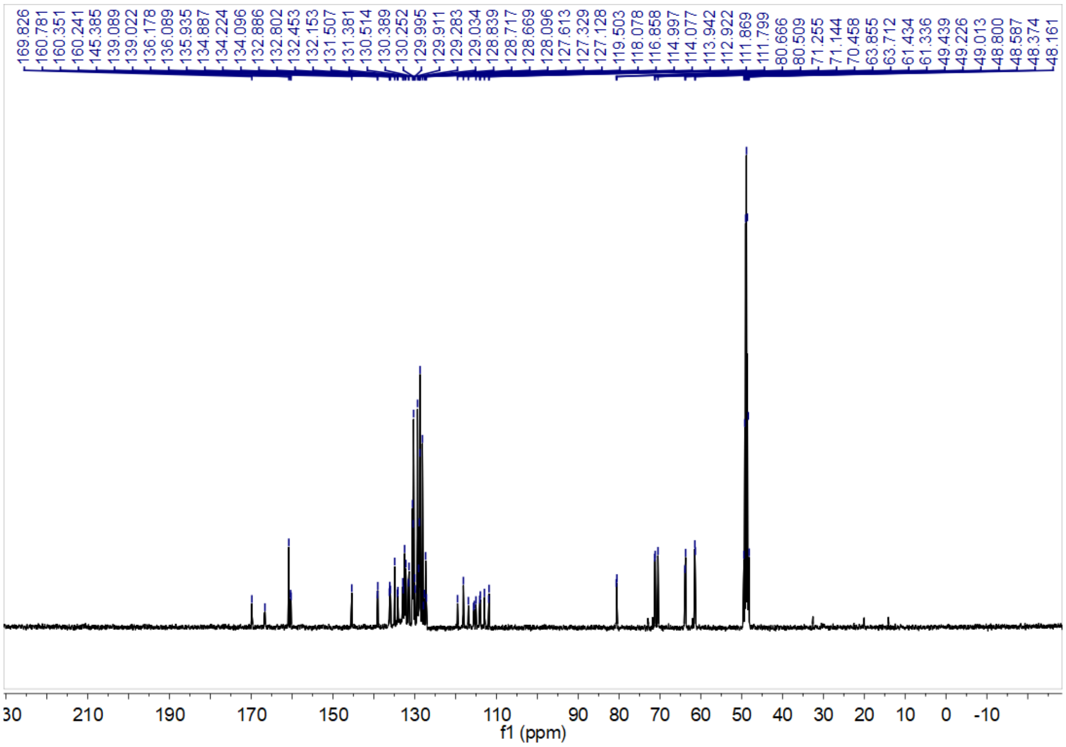


Figure S19. ^{13}C NMR spectrum of compound **2-3** (HABI-TO) in CD_3OD.

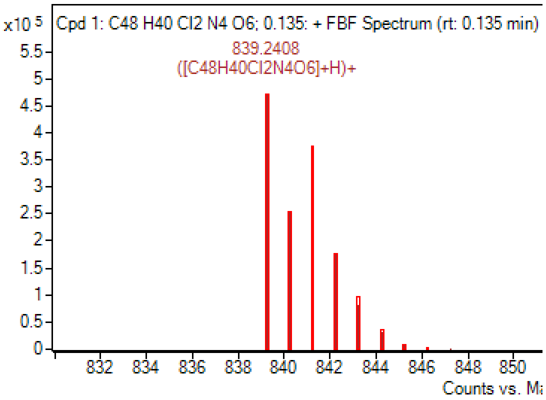


Figure S20. FT-MS spectrum of compound **2-3** (HABI-TO).

IV. Fabrication and properties of polymers

1. Preparation of polyurethane polymers

The synthetic procedures of four polymers are similar**.** We describe the synthetic procedure for **PUB2** polymer, and the crosslinker content was changed accordingly for synthesis of other polymers. Detailed composition of each polymer can be found in Table S1.

To a 50 mL dry Schlenk flask, was added polytetrahydrofuran (PTMEG, M_n = 1000 g/mol, 1 g, 1 mmol). The flask was pumped with vacuum for 10 min and refilled with argon. Dry THF (5 mL), 1,6-hexamethylene diisocyanate (HDI, 230 μL, 1.3 mmol) and dibutyltin dilaurate (DBTDL, 10 μL) were then added and the reaction was proceeded under argon for 1 hour. Next, TEOA (19.8 mg, 0.133 mmol, in 0.7 mL dry THF) and compound **1-3** (32 mg, 0.05 mmol, in 1.3 mL dry THF) were added, and the reaction was stirred for additional 1.5 h. The viscous was then poured into a customized Teflon mold. To remove bubbles, the mold was subjected to centrifuge. Uniform **PUB2** polymer films were obtained after drying at room temperature.

Table S1. Composition table of the fabrication of polyurethane polymers

Sample	PTMEG (mmol)	HDI (mmol)	BPID-TO (mmol)	HABI-TO (mmol)	TEOA (mmol)	DBTDL (μL)	Total THF (mL)
PUB1	1	1.3	0.01	-	0.187	10	7
PUB2	1	1.3	0.05	-	0.133	10	7
PUc	1	1.3	-	-	0.2	10	7
PUH	1	1.3	-	0.05	0.133	10	7

2. Fabrication of laminated film

A **PUH** film was hung in a plastic tank, which contains 75 mL THF, and the polymer was not in contact with THF. The tank was sealed and set in the dark. After 6 hours, the **PUH** absorbed THF vapor and turned into a swollen state. This film was then transferred into a Teflon mold and viscous **PUB2** solution was poured onto the **PUH** film. The mold was then sealed and set at room temperature for 16 hours. A two-layer film formed and was further dried at room temperature for 5 h. The film was then sandwiched between two PTFE plates and dried at 40 °C for 4 h and then under vacuum at 40 °C for 4 hours. A film laminated with **PUH** and **PUB2** was obtained.

3. Thermo-responsive properties of polymer films

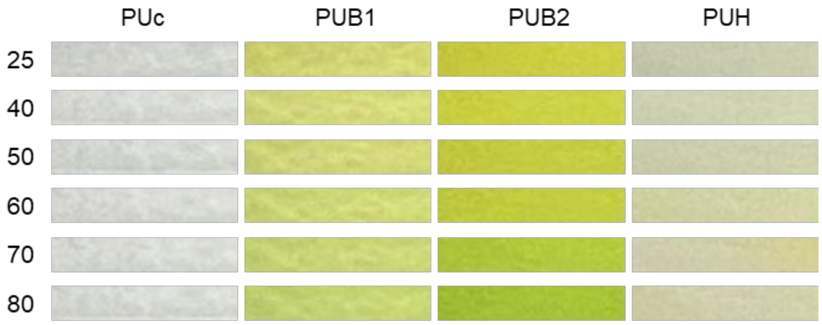


Figure S21. Thermochromism study of polyurethane films: images were taken after polymer films were equilibrated at each temperature for 5 min.

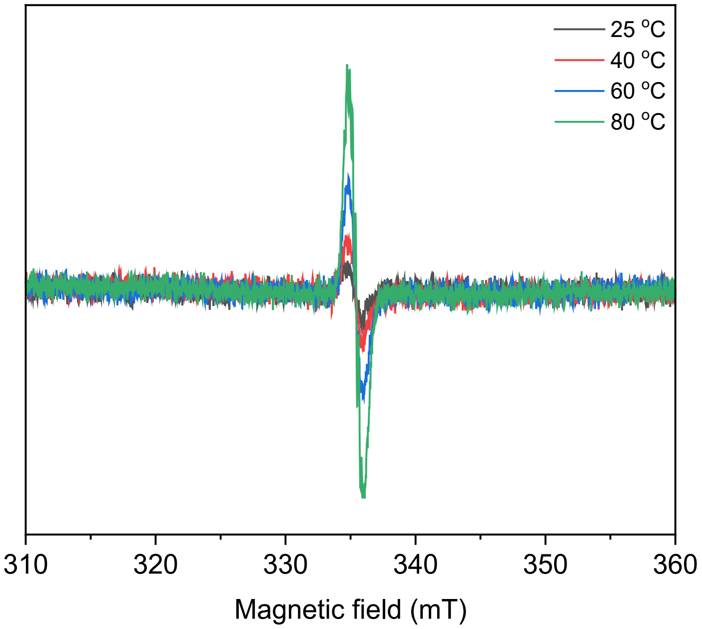


Figure S22. ESR spectra of **PUB2** polymer film at different temperatures.

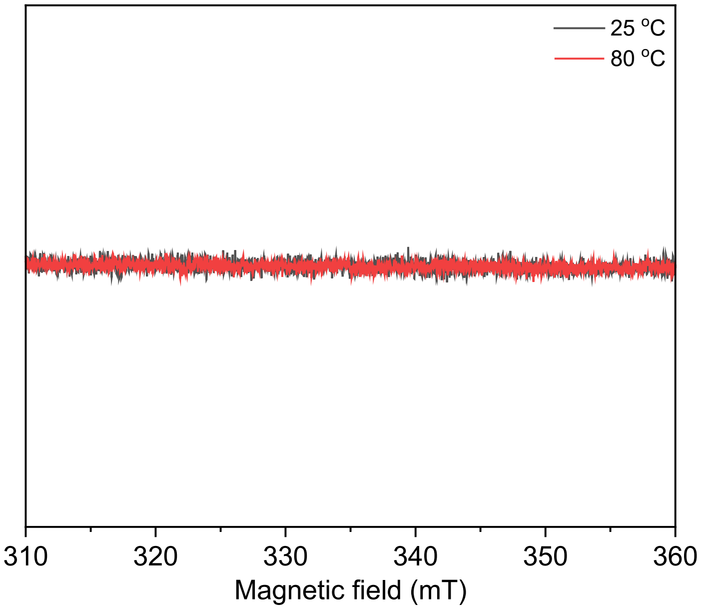


Figure S23. ESR spectra **PUH** polymer film at different temperatures.

4. Mechanoresponsive properties of polymer films

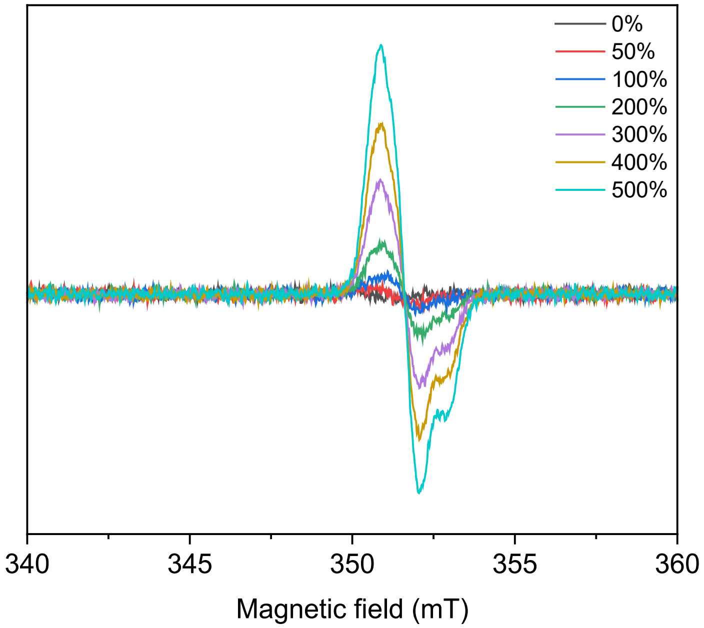


Figure S24. ESR spectra of **PUB2** polymer film at different strains.

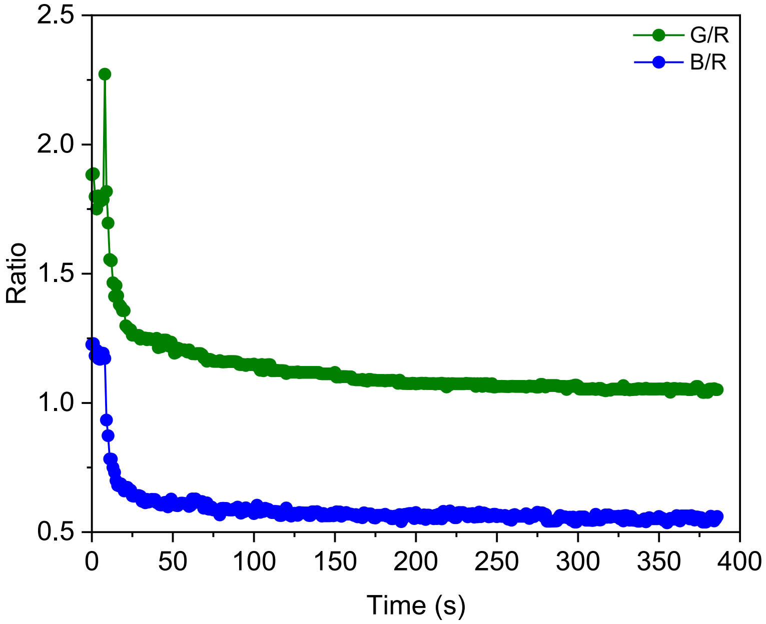


Figure S25. The evolution of chromism in **PUB2** polymer film after stretched to 500% stain and subsequent relaxed.

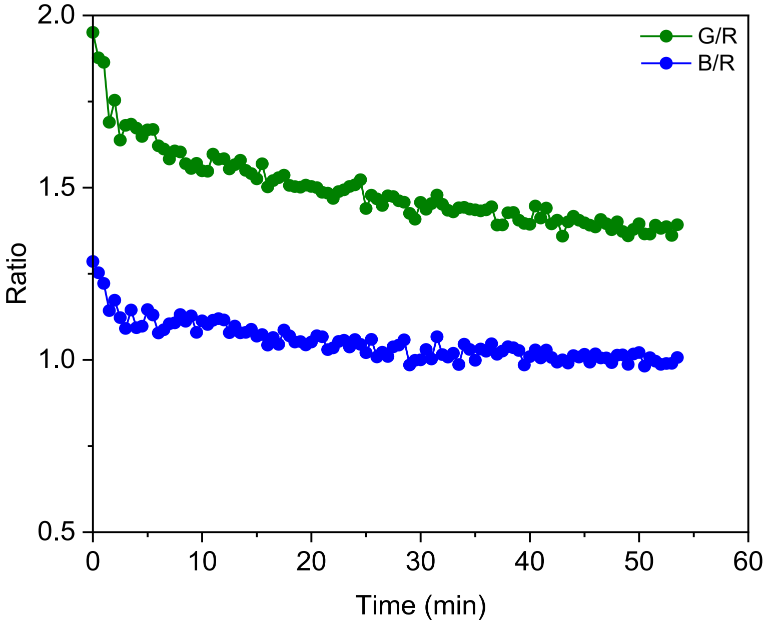


Figure S26. The evolution of chromism in a **PUB2** polymer film maintained at 500% stain. According to the original G/R value of ~0.98, the color fading completes in several hours.

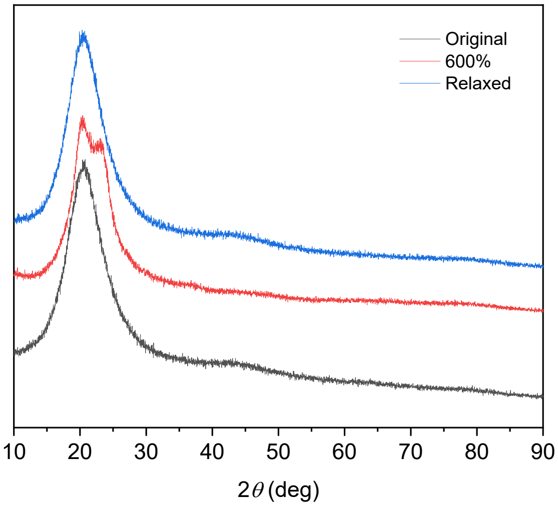


Figure S27. Wide angle X-ray diffraction analysis of **PUB2** film at different states. Gray line: original sample; red line: fixing the film at 600% strain; blue line: after removing load and the sample relaxed to a constant length.

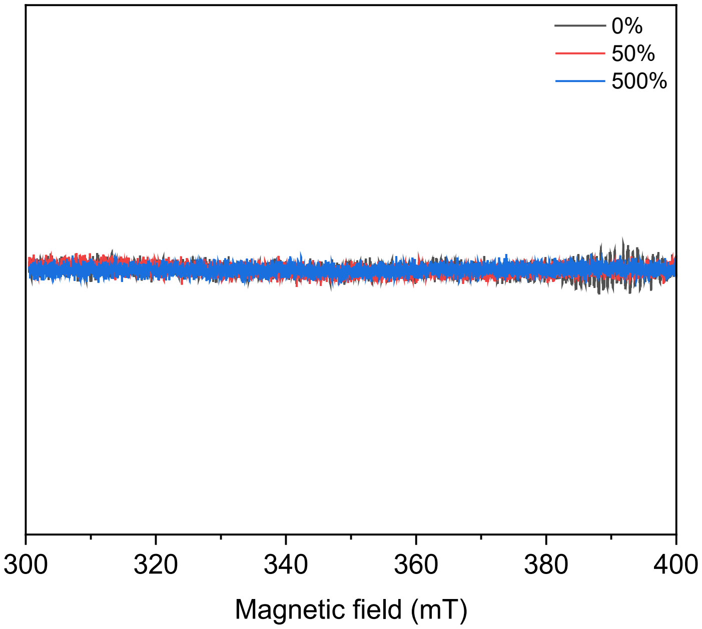


Figure S28. ESR spectra of **PUH** polymer film at different strains.

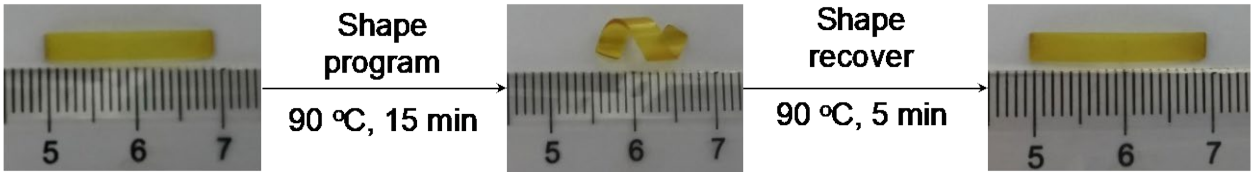


Figure S29. PUB2 film was subjected to the thermal morphing at 90 oC for 15min and then cooled for 5min while fixed. Subsequent heating at 90 °C for 5 min achieved shape recovery.

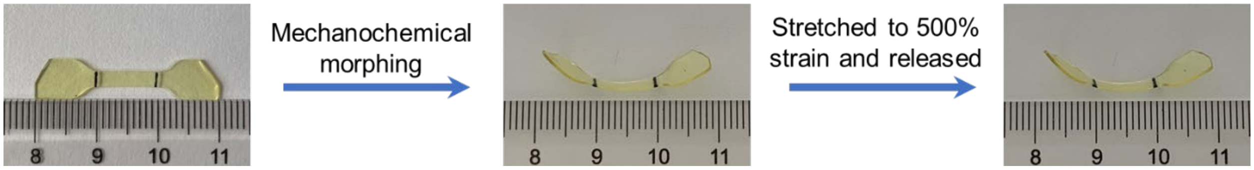


Figure S30. PUB1 film was first subjected to the mechanochemical morphing procedure and then mechanical activation to study the mechanochemical shape recovery behavior.

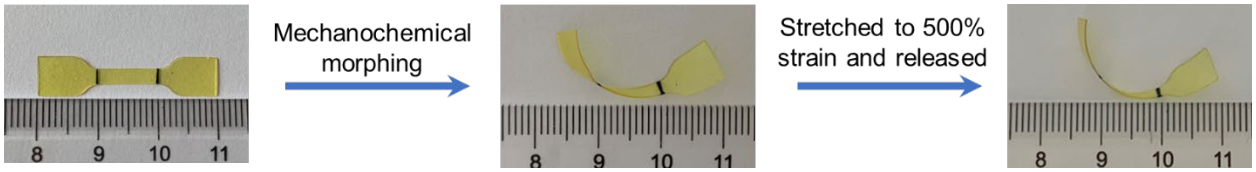


Figure S31. PUB2 film was first subjected to the mechanochemical morphing procedure and then mechanical activation to study the mechanochemical shape recovery behavior.

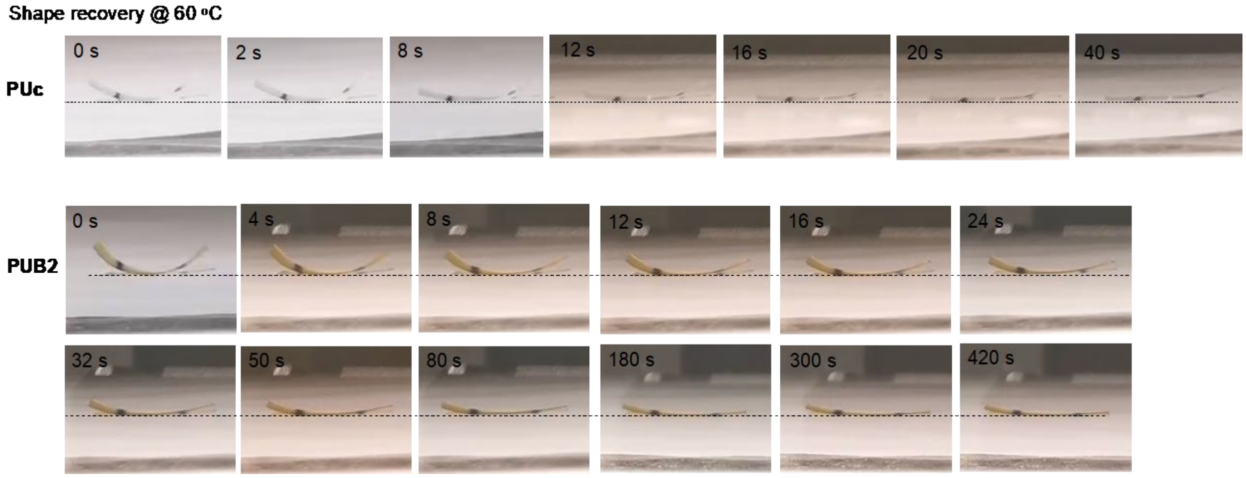


Figure S32. Shape recovery of programmed **PUc** (top) and **PUB2** (bottom) polymer films at 60 °C. Photos were taken at various times, and the dotted lines was drawn to guide the distinguish of shape evolution. The shape recovery of **PUc** reached near steady state after ~16 s, and it took >180s for **PUB2** to reach steady state.

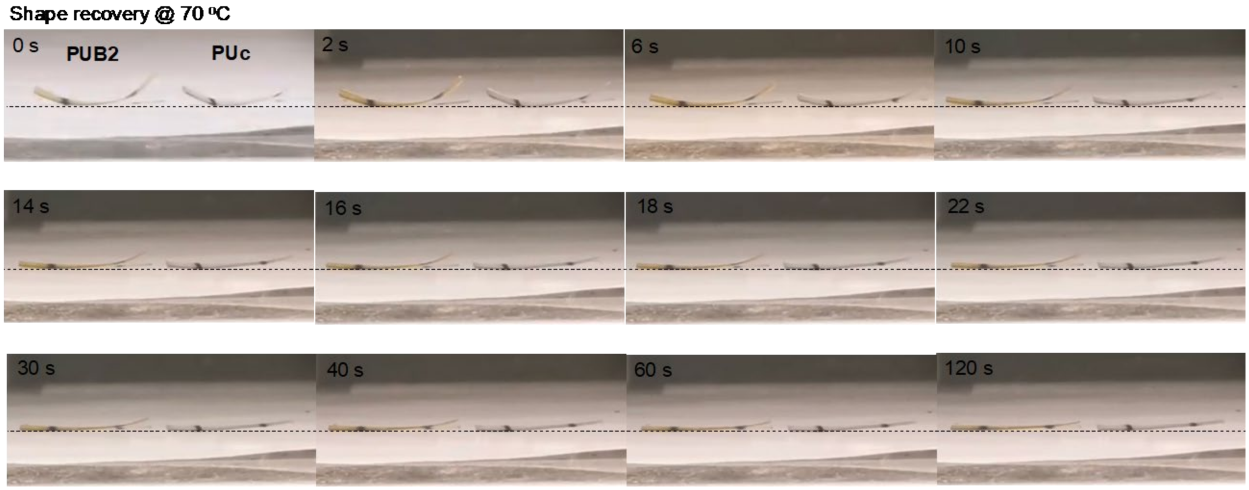


Figure S33. Shape recovery of programmed **PUB2** (left sample) and **PUc** (right sample) polymer films at 70 °C. Photos were taken at various times, and the dotted lines was drawn to guide the distinguish of shape evolution. The shape recovery of **PUBc** reached near steady state after ~16 s, and it took ~40s for **PUB2** to reach steady state.

5. Photo-responsive properties of polymer films

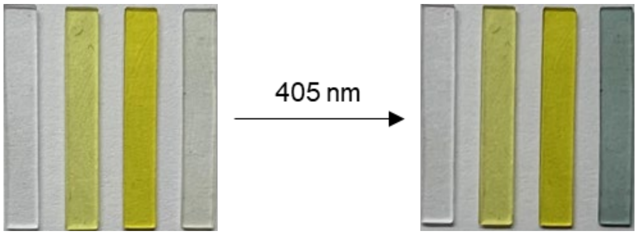


Figure S34. Images of polymer films after 405 nm light irradiation. From left to right: **PUc, PUB1, PUB2, and PUH.**

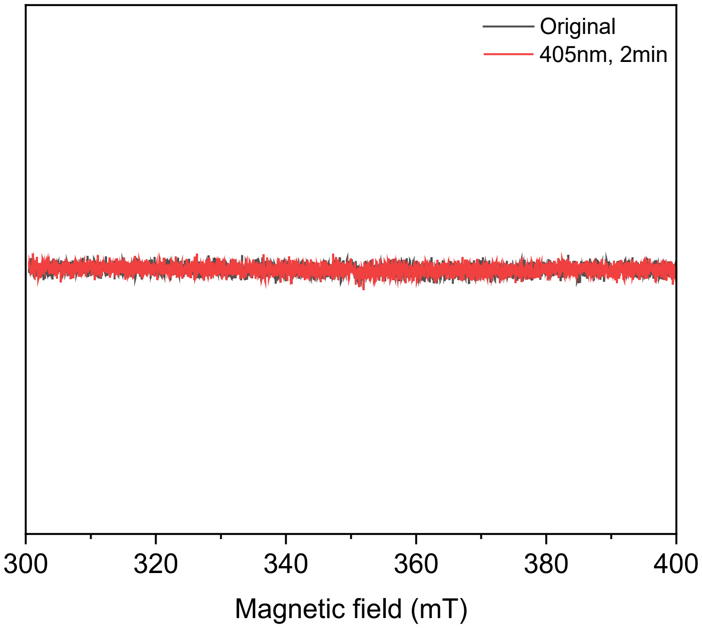


Figure S35. ESR spectrum of **PUB2** polymer film after 2 min of 405 nm light irradiation.

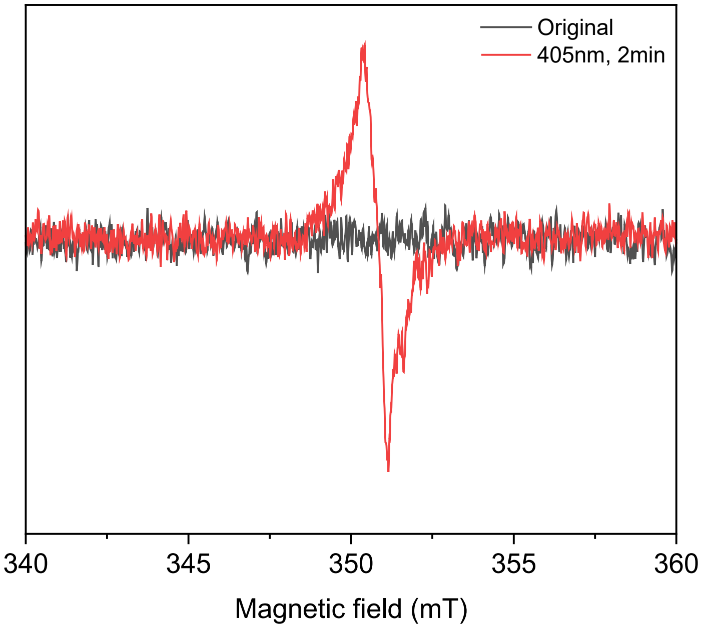


Figure S36. ESR spectrum of **PUH** polymer film after 2 min of 405 nm light irradiation.