Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information for

Spiropyran-based polymer with stimulus response to water temperature and water content

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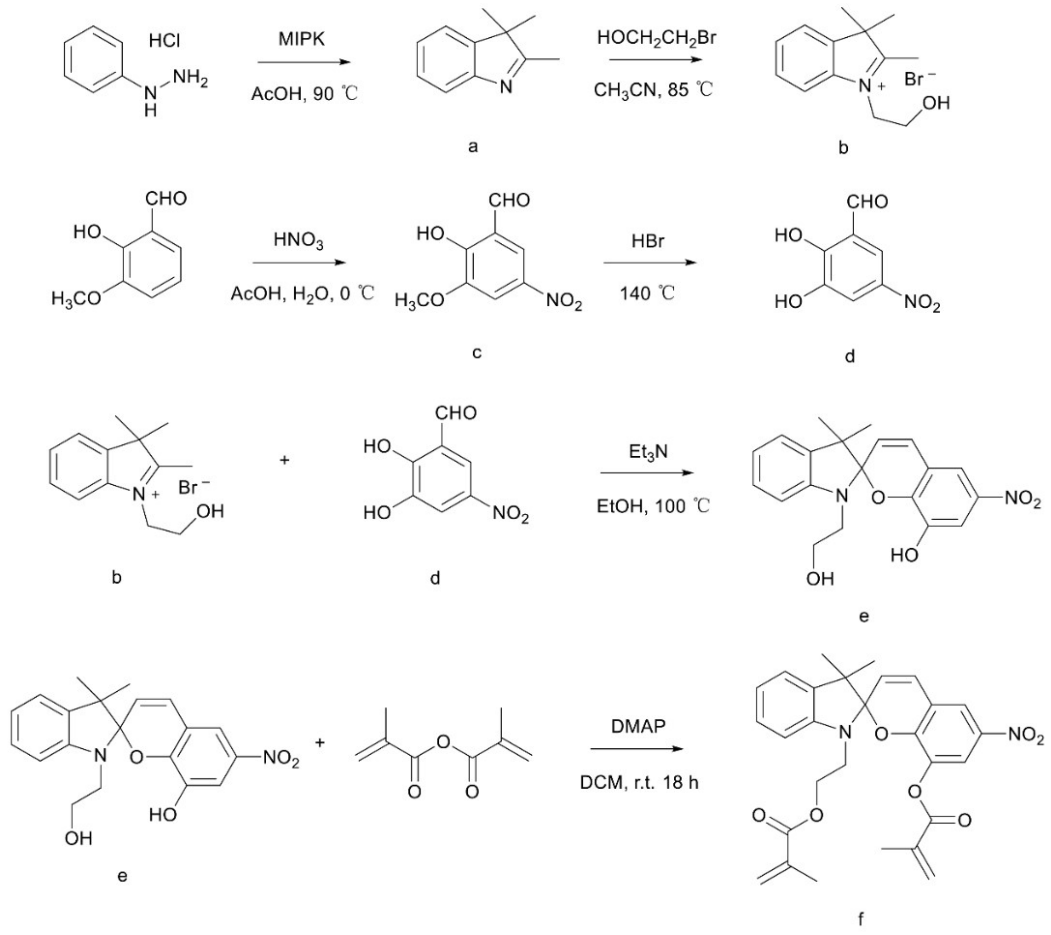
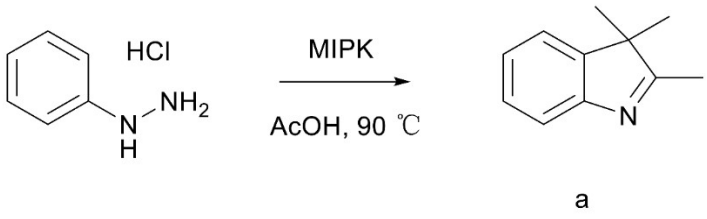
S1. Synthetic procedures

Synthetic scheme of SP



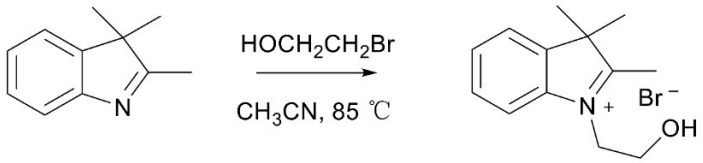
① Synthesis of 2,3,3-trimethyl-3H-indole (**a**)



Phenylhydrazine hydrochloride (7.225 g, 50 mmol, 1.0 equiv.) and 3-methyl-2-butanone (6 mL, 55 mmol, 1.1 equiv.) were dissolved in glacial acetic acid (50 mL) and then heated in 90 ℃ for 12 h under nitrogen. The reaction mixture was cooled to room temperature, and the solvent was removed by reduced pressure rotary evaporation. The residue was diluted with dichloromethane (30 mL), the organic layer was washed with brine (30 mL), saturated aqueous Na_2CO_3 (2 × 30 mL), brine. The organic layer was dried over anhydrous Na_2SO_4, filtered. The solvent was removed by reduced pressure rotary evaporation. The residue was purified by column chromatography eluting with petroleum ether/ ethyl acetate (10:1) to afford pure product as yellow oil (4.42 g, 27.80 mmol, 55.60 % yield). The product will turn red when it is stored for a long time. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.49 (d, J = 7.6 Hz,

1H), 7.24 (dd, J = 1.2, 2.8 Hz 1H), 7.21 (d, J = 2.8 Hz, 1H), 7.14 (t, J = 14.8 Hz, 1H), 2.23 (s, 3H), 1.24 (s, 6H)[1].

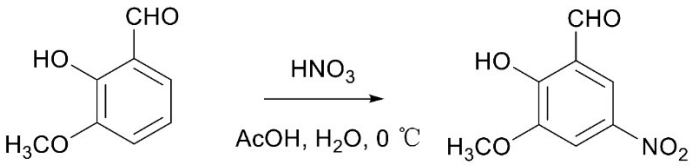
② Synthesis of 1-(-2-hydroxyethyl)-2,3,3-trimethyl-3H-indolium bromide (**b**)



a b

2,3,3-trimethyl-3H-indole (2.83 g, 17.75 mmol, 1 equiv.) and 2-bromoethanol (3.31 g, 26.50 mmol, 1.5 equiv.) were dissolved in acetonitrile (20 mL) and then heated in 85 ℃ for 24 h under nitrogen. The reaction mixture was cooled to room temperature, and the solvent was removed by reduced pressure rotary evaporation. The residue was suspended in hexane (25 mL) and the mixture was sonicated and filtered. The resulting solid was precipitated from chloroform by adding hexane to give a pink solid (3.01 g, 10.60 mmol, 59.71 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.77 (m, J = 8.8 Hz, 1H), 7.61-7.53 (m, 3H), 4.88 (t, J = 9.6 Hz, 2H), 4.19 (t, J = 10 Hz, 2H), 3.14 (s, 3H), 1.65 (s, 6H)[2].

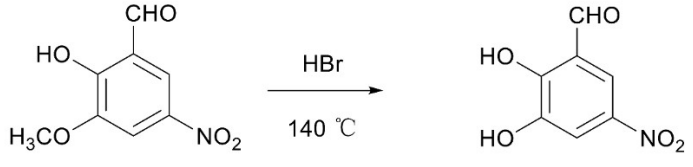
③ Synthesis of 2-hydroxy-3-methoxy-5-nitro-benzaldehyde (**c**)



c

3-methoxysalicylaldehyde (6.0 g, 39.4 mmol, 1 equiv.) was dissolved in the mixed solution of glacial acetic acid (27.6 mL) and distilled water (1.4 mL). The solution was cooled to 0 ℃ in an ice bath and stirred with stirring paddle. Nitric acid (2.87 mL, 43.34 mmol, 1.1 equiv.) was diluted with 7.8 mL glacial acetic acid and added dropwise into the reaction mixture over 50 min. After stirring for 1.5 h, the solution was diluted with 60 mL distilled water. The product was centrifuged and washed with deionized water and repeated three times, and finally dried completely under vacuum to give light yellow powder (3.5 g, 17.77 mmol, 45.09 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 11.72 (s, 1H), 10.00 (s, 1H), 8.22 (d, J = 2.4 Hz, 1H), 7.93 (d, J = 2.4 Hz, 1H), 4.02 (s, 3H)[3].

④ Synthesis of 2,3-dihydroxy-5-nitro-benzaldehyde (**d**)

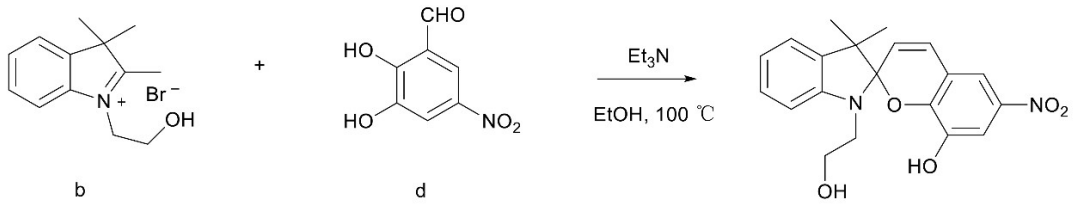


c d

A solution of **c** (3 g, 15 mmol, 1 equiv.) in 48 % aqueous HBr (50 mL, 458 mmol, 30 equiv.) was heated in 140

℃. After 4 h, the solution was diluted with 56 mL of water and cooled to 0 °C. The solution was filtered and the collected solid was washed with water and allowed to dry. The filtrate was extracted with 1:1 ethyl acetate/CH_2Cl_2, dried over Na_2SO_4, filtered, and concentrated in vacuo. The combined crude solids were dissolved in ethyl acetate and activated carbon was added for decolorizing. After filtering, the solvent in filtrate was removed by reduced pressure rotary evaporation. The crude product was recrystallized in boiling ethyl acetate to yield **d** as light yellow needles (0.55 g, 3.0 mmol, 20.04 % yield). ^{1}H NMR (400 MHz, DMSO- d_6, Me_4Si) δ 11.18 (br, 2H), 10.29 (s, 1H), 7.97 (d, J = 2.8 Hz, 1H), 7.77 (d, J = 2.8 Hz, 1H)[3].

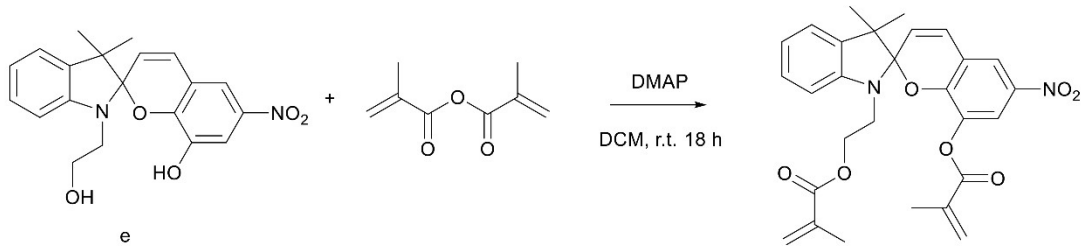
⑤ Synthesis of 1'-(2-hydroxyethyl)-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-8-ol (**e**)



b d e

b (1.48 g, 5.2 mmol, 1 equiv.) and **d** (0.95 g, 5.2 mmol, 1 equiv.) were dissolved in ethanol (50 mL). Triethylamine (1.46 mL, 10.4 mmol, 2 equiv.) was added. Then the mixture was heated in 100 ℃ for 2 h under nitrogen. The solution was concentrated to a third of its original volume by reduced pressure rotary evaporation, cooled, filtered, and the precipitate was washed with cooled ethanol to yield e as a very dark (almost black) green fine powder (1.33 g, 3.61 mmol, 69.42 % yield). ^{1}H NMR (400 MHz, DMSO-d_6, Me_4Si) δ 7.71 (d, J = 2.8 Hz 1H), 7.56 (d, J = 2.8 Hz 1H), 7.11 (d, J = 2 Hz, 1H), 7.10 (d, J = 0.8 Hz, 1H), 7.09 (d, J=1.6 Hz, 1H), 6.77 (t, J = 15.6 Hz, 1H), 6.62 (d, J = 8 Hz, 1H), 5.94 (d, J = 10.4 Hz, 1H), 3.32 (m, 2H), 3.19 (m, 2H), 1.19 (s, 3H), 1.08 (s, 3H)[4].

⑥ Synthesis of 3′,3′-dimethyl-6-nitro-1′-(2-(methacryloyloxy)ethyl)spiro[chromene-2,2′-indoline]-8-yl(2-methylacrylate) (**f**, SP)



e f

Methacrylic anhydride (0.902 g, 0.87 mL, 5.85 mmol, 2.15 equiv.) was dissolved in 10 mL dichloromethane and added very slowly dropwise into the dichloromethane (15 mL) solution of **e** (1.0 g, 2.72 mmol, 1 equiv.) and 4-dimethylaminopyridine (0.033 g, 0.27 mmol, 0.1 equiv.) over 2 h. The solution was stirred in room temperature for 18 h under nitrogen. The mixture was washed with concentrated sodium bicarbonate solution (1 × 25 mL), 1 M hydrochloric acid (1 × 25 mL), water (2 × 25 mL) and brine (1 × 25 mL), then the organic layer was dried over anhydrous Na_2SO_4, filtered. The solvent was removed by reduced pressure rotary evaporation to give **f** (0.5568 g,

1.10 mmol, 40.44 % yield), which is slurry like and in dark purple. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.95 (d, J = 2.4 Hz, 1H), 7.90 (d, J = 2.8 Hz, 1H), 7.12 (m, 1H), 7.00 (d, J = 6.8 Hz, 1H), 6.97 (d, J = 10.4 Hz, 1H), 6.83 (m, 1H), 6.63 (m, 1H), 6.07 (s, 1H), 5.93 (d, J = 10.4 Hz, 1H), 5.87 (s, 1H), 5.56 (s, 1H), 5.38 (s, 1H), 4.26 (m, 2H), 3.36 (m, 2H), 1.92 (s, 3H), 1.62 (s, 3H), 1.24 (s, 3H), 1.18 (s, 3H)[4].

EIS-TOF: m/z calcd for $C_{28}H_{28}N_2O_7$, 504, found, 505(M+H$^+$).

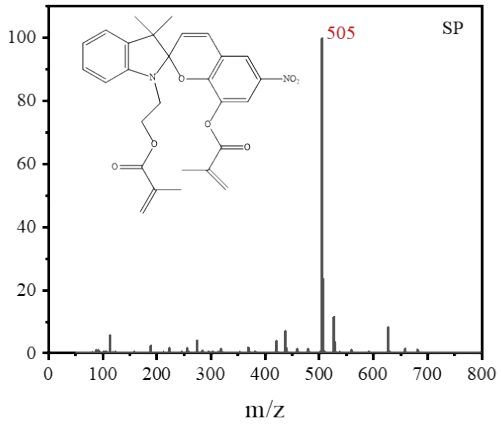
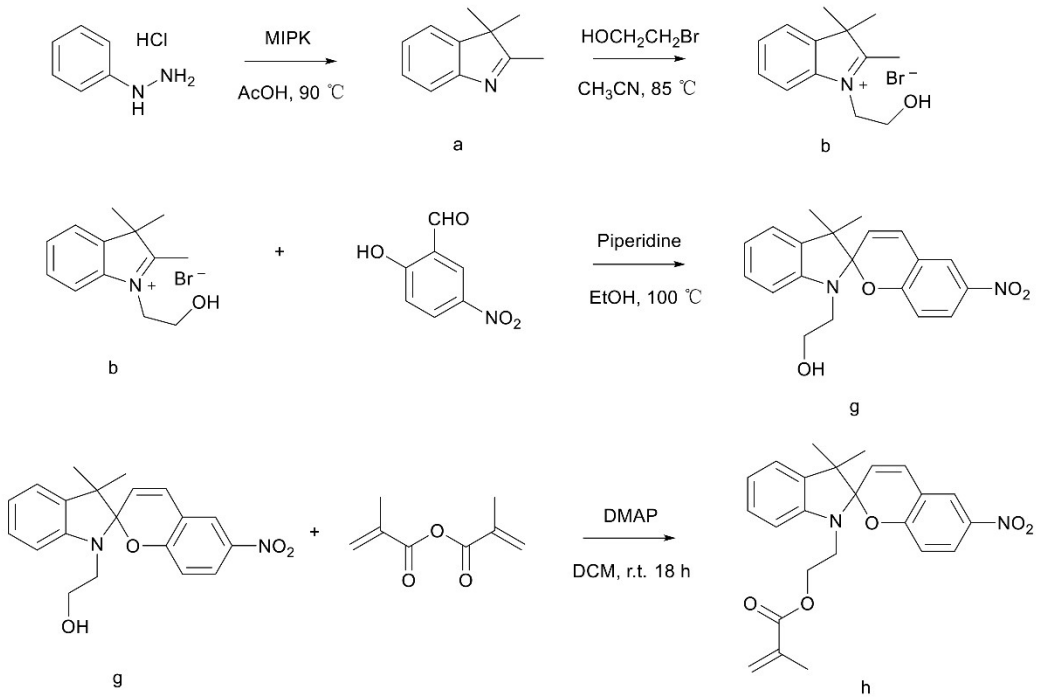


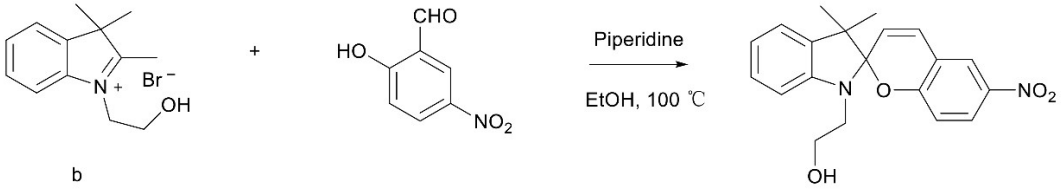
Fig. S1 MS spectrum of SP.

The synthesized SP was dissolved in dichloromethane and prepared into 0.01 mol/L dichloromethane solution, sealed and stored in 2-8 ℃ environment.

Synthetic scheme of SP-control



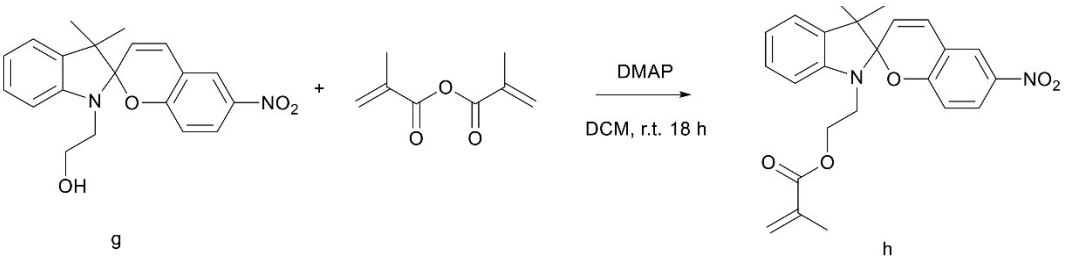
① Synthesis of 3′,3′-Dimethyl-1′-(β-hydroxyethyl)-6-nitrospiro[2H-1-benzopyran-2,2′-indoline] (**g**)



b g

b (1.23 g, 4.32 mmol, 1 equiv.) and 5-Nitrosalicylaldehyde (0.722 g, 4.32 mmol, 1 equiv.) was dissolved in 50 mL ethanol, piperidine (0.43 mL, 4.32 mmol, 1 equiv.) was added. Then the mixture was heated in 100 ℃ for 2 h under nitrogen. The solution was cooled, filtered, and the precipitate was washed with cooled ethanol to yield dark purple powder **g** (0.27 g, 0.767 mmol, 17.76 % yield). ^{1}H NMR (400 MHz, DMSO-d_6, Me_4Si) δ 8.20 (d, J = 2.8 Hz, 1H), 8.00 (dd, J = 2.8, 2.8 Hz, 1H), 7.18 (d, J = 10.4 Hz, 1H), 7.11 (d, J = 6.4 Hz, 1H), 7.10 (s, 1H), 6.88 (d, J = 8.8 Hz, 1H), 6.78 (t, J = 14.4 Hz, 1H), 6.65 (d, J = 8 Hz, 1H), 6.03 (d, J = 10.4 Hz, 1H), 3.57-3.42 (m, 2H), 3.27-3.12 (m, 2H), 1.20 (s, 3H), 1.10 (s, 3H).

② Synthesis of 3,3-Dimethyl-1-(β-methacryloyloxyethyl)-6′-nitrospiro[indoline-2,2′-(2H,1)benzopyran] (**h**, SP-control)



g h

Methacrylic anhydride (0.241 g, 0.233 mL, 1.57 mmol, 1.15 equiv.) was dissolved in 10 mL dichloromethane and added very slowly dropwise into the dichloromethane (10 mL) solution of **g** (0.48 g, 1.36 mmol, 1 equiv.) and 4-dimethylaminopyridine (0.0166 g, 0.136 mmol, 0.1 equiv.) over 2 h. The solution was stirred in room temperature for 18 h under nitrogen. The mixture was washed with concentrated sodium bicarbonate solution (1 × 25 mL), 1 M hydrochloric acid (1 × 25 mL), water (2 × 25 mL) and brine (1 × 25 mL), then the organic layer was dried over anhydrous Na_2SO_4, filtered. The solvent was removed by reduced pressure rotary evaporation to give **h** (0.3459 g, 0.823 mmol, 60.49 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 8.00 (m, 2H), 7.20 (m, 1H), 7.08 (d, J = 7.2 Hz, 1H), 6.90 (q, J = 10.4 Hz, 2H), 6.74 (q, J = 27.2 Hz, 2H), 6.07 (s, 1H), 5.86 (d, J = 10 Hz, 1H), 5.56 (s, 1H), 4.3 (t, J = 12.8 Hz, 2H), 3.59-3.39 (m, 2H), 1.91 (s, 3H), 1.28 (s, 3H), 1.16 (s, 3H).

EIS-TOF: m/z calcd for $C_{24}H_{24}N_2O_5$, 420, found, 421($M+H^+$).

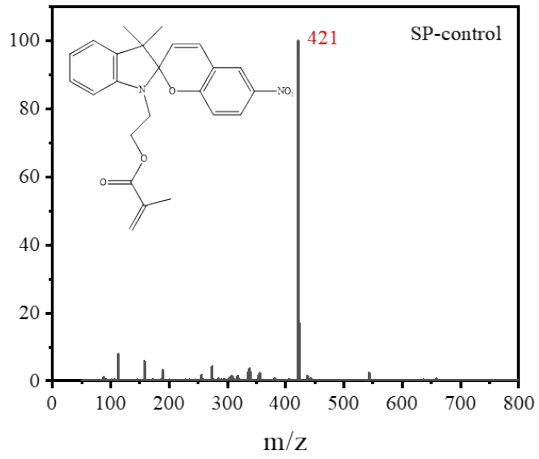


Fig. S2 MS spectrum of SP-control.

The synthesized SP-control was dissolved in dichloromethane and prepared into 0.01 mol/L dichloromethane solution, sealed and stored in 2-8 ℃ environment.

Preparation of PHEA-SP and PHEA-SP-control

Hydroxyethyl acrylate is used to remove the polymerization inhibitor using an alkaline alumina chromatography column before use. A certain amount of SP, polyethylene glycol diacrylate (PEGDA), 0.0168 g photoinitiator phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (4×10^{-5} mol) and 4.2 mL of hydroxyethyl acrylate (0.04 mol) were ultrasonically mixed and dissolved to form a mixed solution. 1 mL of the above mixture was added to the PTFE mold (20 mm × 20 mm × 3 mm) and polymerized under light at a wavelength of 405 nm (light intensity: 2 mW/cm^2) for 15 minutes to obtain PHEA-SP polymer sheets. A similar method was used to prepare a copolymer sheet of hydroxyethyl acrylate and SP-control (PHEA-SP-control), but the SP is replaced by SP-control, and the rest remains unchanged.

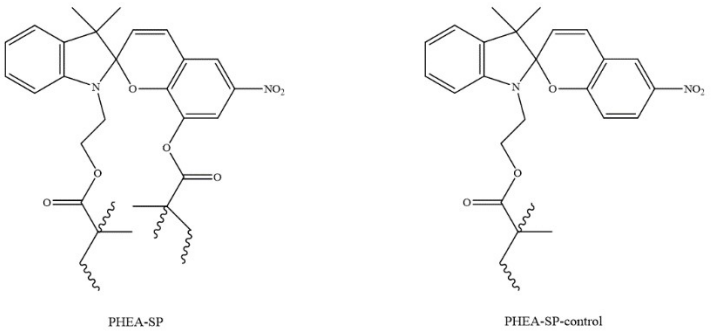


Fig. S3 Structure scheme of PHEA-SP and PHEA-SP-control.

S2. Single factor regulation

2.1 Regulation of the SP content in PHEA-SP

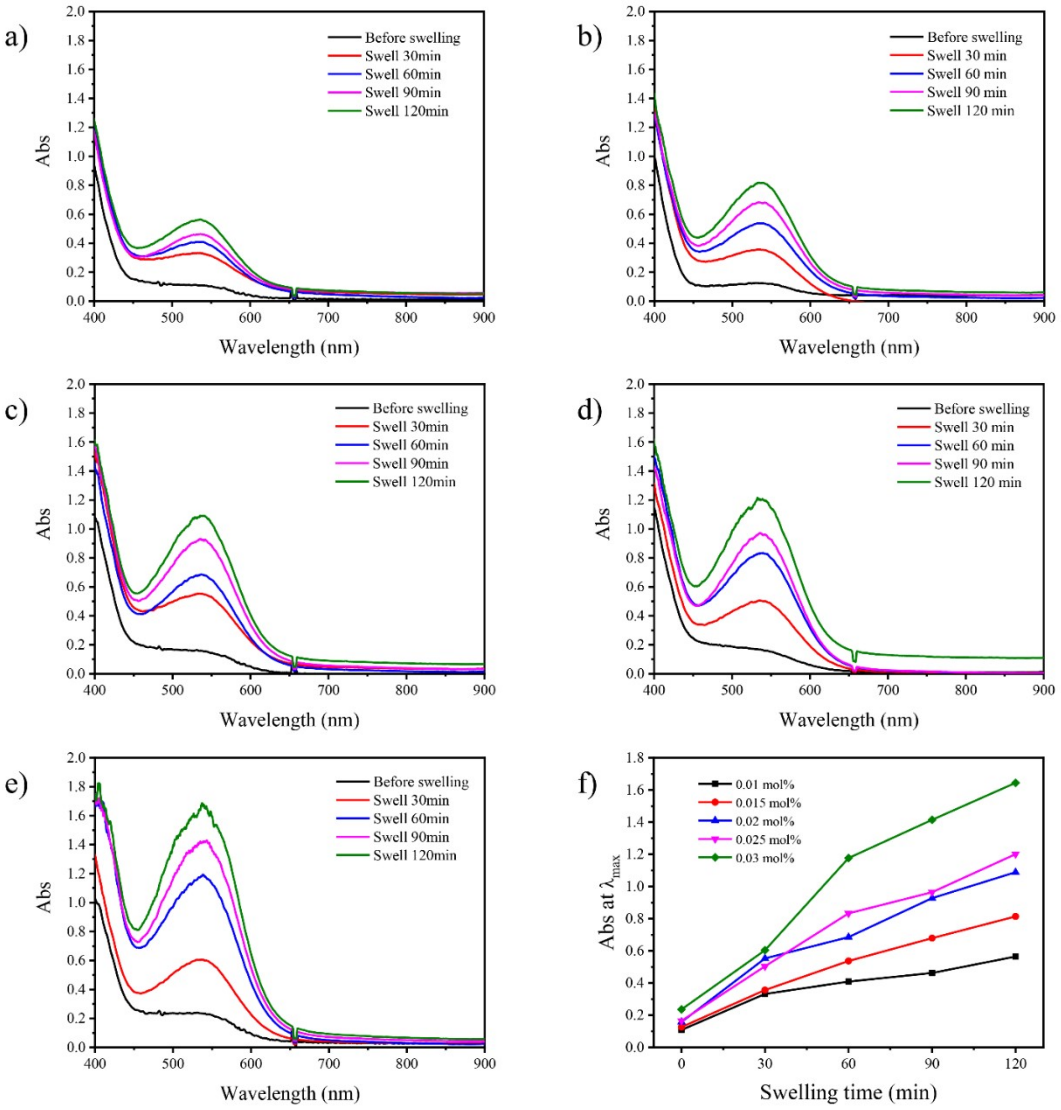


Fig. S4 Time-dependent change in absorption spectrum of PHEA-SP containing (a) 0.01 mol% SP, (b) 0.015 mol% SP, (c) 0.02 mol% SP, (d) 0.025 mol% SP, (e) 0.03 mol% SP swelling in 25 ℃ water in the dark. (f) Absorbance at λ_{max} as a function of the swelling time for PHEA-SP with different SP content in 25 ℃ water in the dark.

Under the condition of keeping the crosslinker content at 1 mol%, swelling the same time, the absorbance at λ_{max} of PHEA-SP increases with the increase of SP content (from 0.01 mol% to 0.03 mol%). This is because under the same swelling degree, the more spiropyran cross-linking points, the greater the number of spiropyran isomerization from SP form to MC form, and the greater the range of absorbance changes.

Considerations are as follows when choosing the SP content in PHEA-SP: (1) Absorbance value of 1 indicates that 90% of the light has been absorbed. Larger absorbance will show a larger error. (2) The increase of SP content will make the monomer solution darker, which is not conducive to the photopolymerization. Actually, when the

content of SP reached 0.02 mol%, the polymerization speed was obviously slow. When the content of SP reached 0.03 mol%, some unpolymerized monomer remained at the bottom of the mold after polymerization. (3) When the SP content is 0.015 mol%, there is a good linear relationship between the absorbance and swelling time of PHEA-SP. All in all, the content of SP was chosen to be 0.015 mol%.

2.2 Regulation of the crosslinker content in PHEA-SP

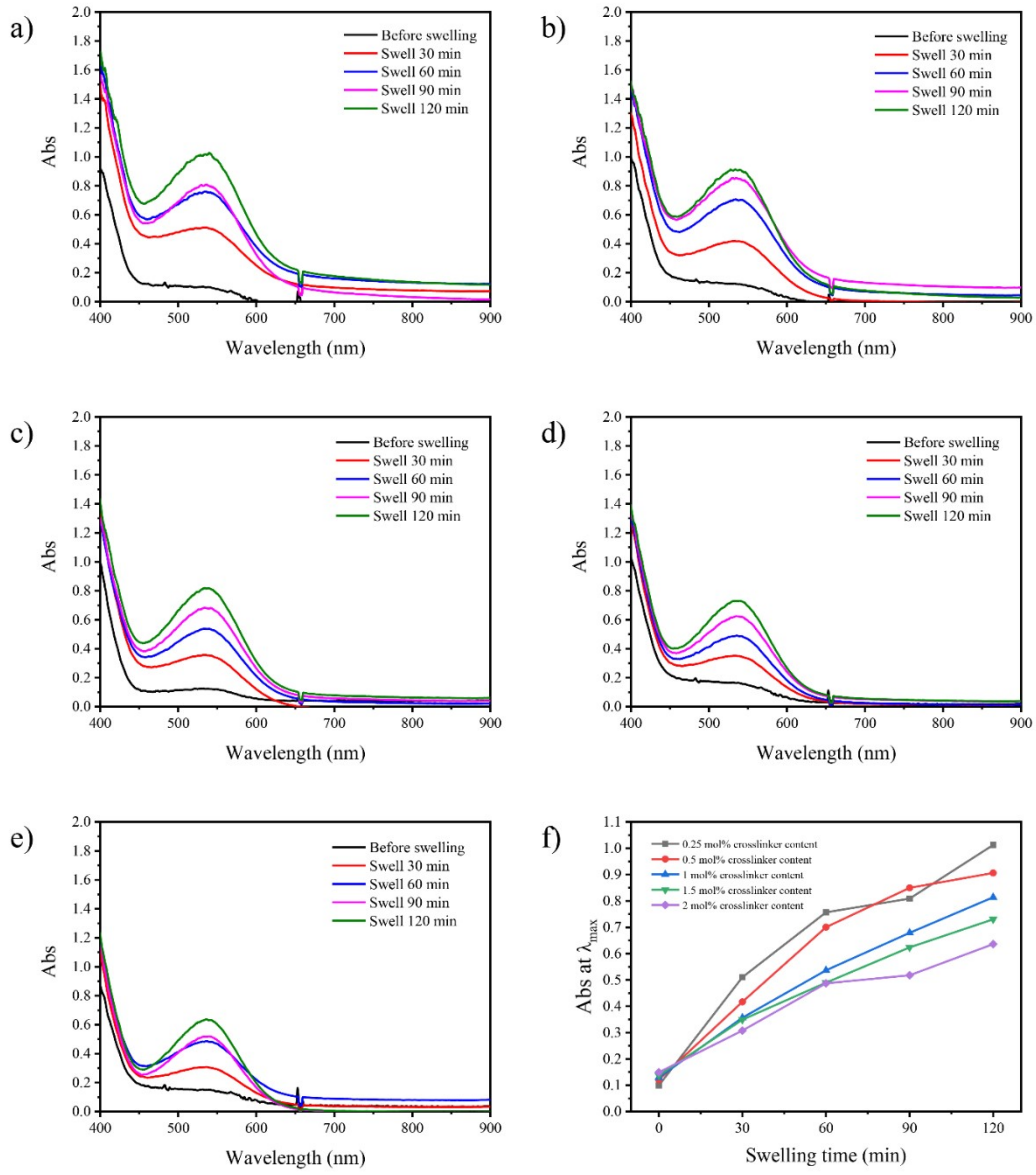


Fig. S5 Time-dependent change in absorption spectrum of PHEA-SP containing (a) 0.25 mol% crosslinkers, (b) 0.5 mol% crosslinkers, (c) 1 mol% crosslinkers, (d) 1.5 mol% crosslinkers, (e) 2 mol% crosslinkers SP swelling in 25 ℃ water in the dark. (f) Absorbance at λ_{max} as a function of swelling time for PHEA-SP with different crosslinker content in 25 ℃ water in the dark.

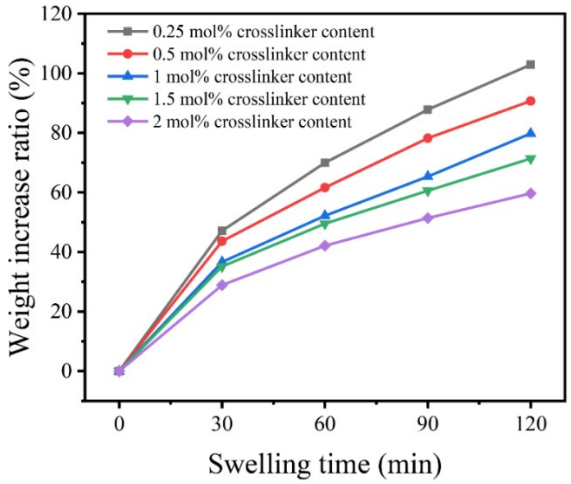


Fig. S6 Weight increase ratio as a function of swelling time for PHEA-SP with different crosslinker content in 25 ℃ water in the dark.

Under the condition of keeping the SP content at 0.015 mol%, swelling the same time, the absorbance at λ_{max} of PHEA-SP increased with the decrease of crosslinker content (from 2 mol% to 0.25 mol%) and the swelling ratio also increased. This is because that the larger the crosslinking degree of polymer, the more the swelling is restricted, the smaller the number of spiropyran isomerization from SP form to MC form, the slower rate and the smaller amplitude of absorbance changes.

There are several considerations in choosing suitable crosslinker content: (1) When the content of crosslinker is too large, the swelling of PHEA is limited, and the change of absorbance is limited. (2) When the content of crosslinker is too small, the swelling rate is too fast, and the stability of the system is bad. The linear relationship between absorbance and swelling time is not good. (3) When the content of crosslinker is 1 mol% and 1.5 mol%, the absorbance changes smoothly. In conclusion, the content of crosslinker was selected as 1 mol%.

S3. Other data

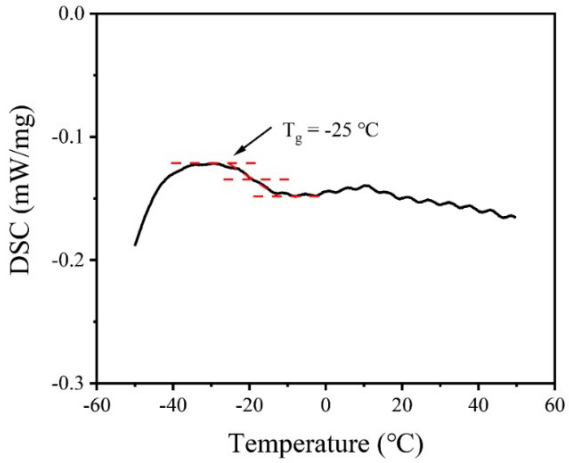


Fig. S7 DSC curves of PHEA-SP.

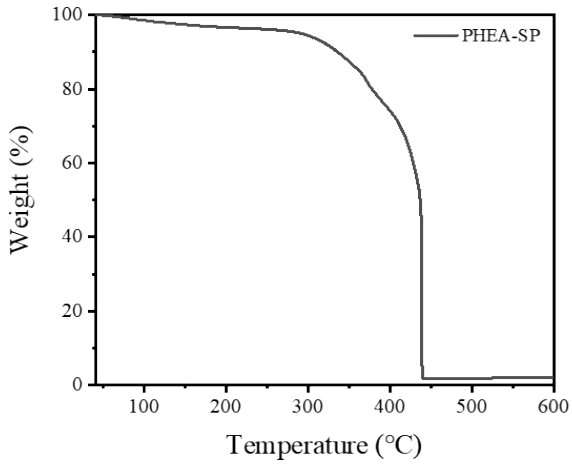


Fig. S8 TGA curves of PHEA-SP.

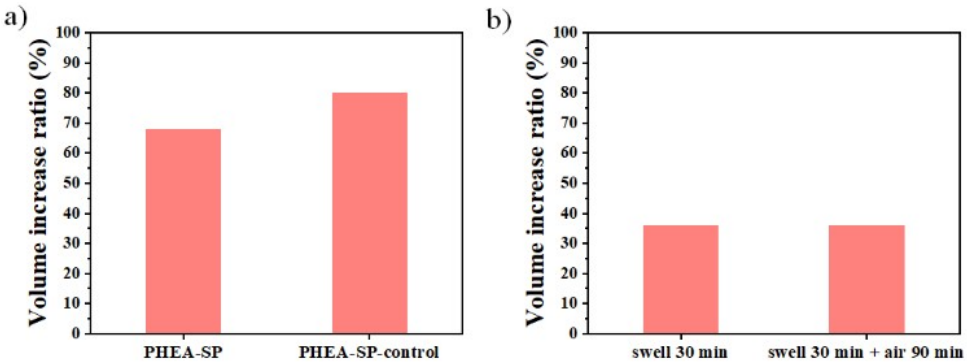


Fig. S9 (a)Volume increase ratio of PHEA-SP and PHEA-SP-control in 25 ℃ water in the dark for 120 min; (b) Volume increase ratio of PHEA-SP in 25 ℃ water in the dark for 30 min then in 25 ℃ dark environment for 90 min.

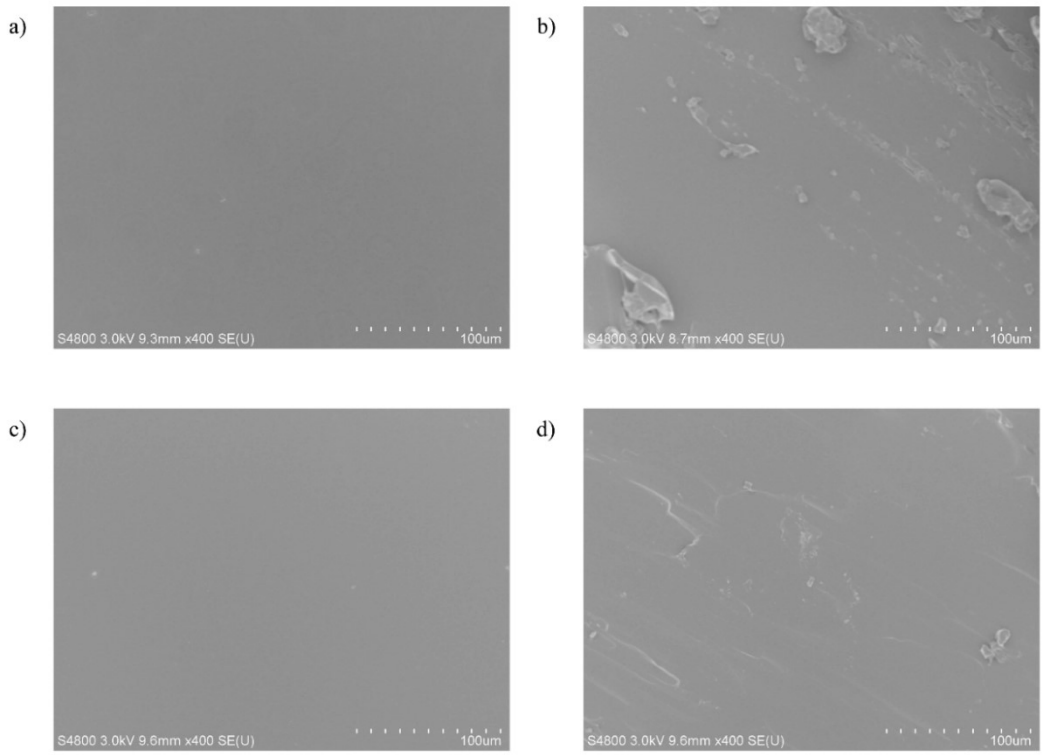


Fig. S10 (a) Surface and (b) cross section SEM image of PHEA-SP before swelling. (c) Surface and (d) cross section SEM image of PHEA-SP after the process of swelling 2 h in 25 ℃ water in the dark and vacuum drying at room temperature.

PHEA-SP is prepared by bulk polymerization, which has a dense structure in both surface and cross section (Fig. S5 a, b). Swelling did not significantly damage the macrostructure of the polymer (Fig. S5 c, d). The rough surface in Fig. S5 b, d is caused by scalpel cutting during sample preparation.

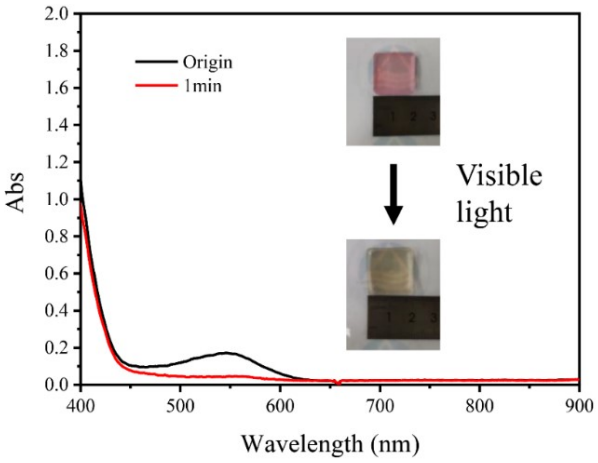


Fig. S11 Absorption spectrum of PHEA-SP-control before pretreatment and after 1 min visible light pretreatment (50 mW/cm^2). Illustrations are actual photos of PHEA-SP-control before and after visible light illumination.

The reason why the initial color of PHEA-SP-Control is quite different from PHEA-SP is that the SP and MC forms of spiropyrans with different structures have different energy level distributions, thus affecting their balance between SP and MC isomerization in the same environment[5].

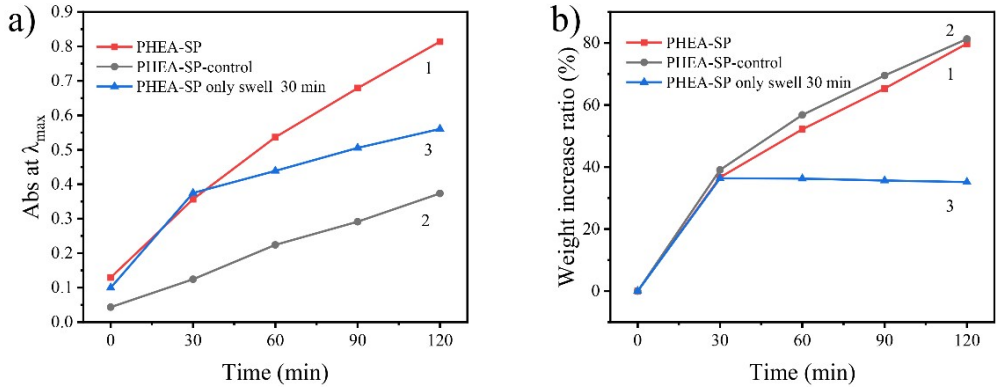


Fig. S12 (a) Absorbance at λ_{max} as a function of time for PHEA-SP in 25 ℃ water in the dark for 120 min (line 1), PHEA-SP-control in 25 ℃ water in the dark for 120 min (line 2) and PHEA-SP in 25 ℃ water in the dark for 30 min then in 25 ℃ dark environment for 90 min (line 3). (b) Weight increase ratio as a function of time for PHEA-SP in 25 ℃ water in the dark for 120 min (line 1), PHEA-SP-control in 25 ℃ water in the dark for 120 min (line 2) and PHEA-SP in 25 ℃ water in the dark for 30 min then in 25 ℃ dark environment for 90 min (line 3).

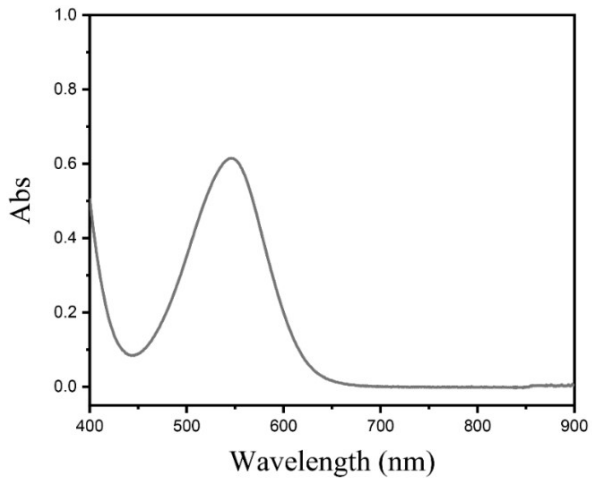


Fig. S13 Absorption spectrum of 10^{-3} mol/L SP ethanol solution.

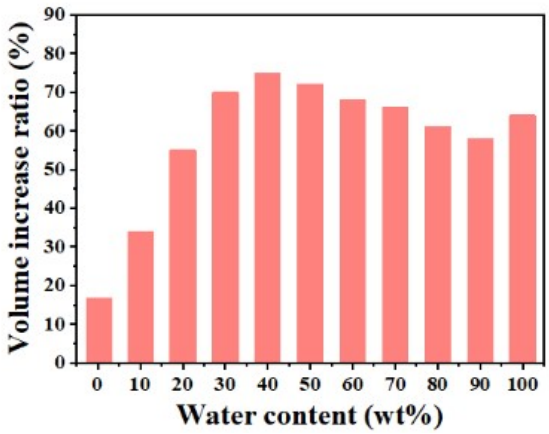


Fig. S14 The histogram of volume increase ratio of PHEA-SP after swelling in 25 ℃ mixed solvent of water and ethanol with different water con-tent for 2 h in the dark.

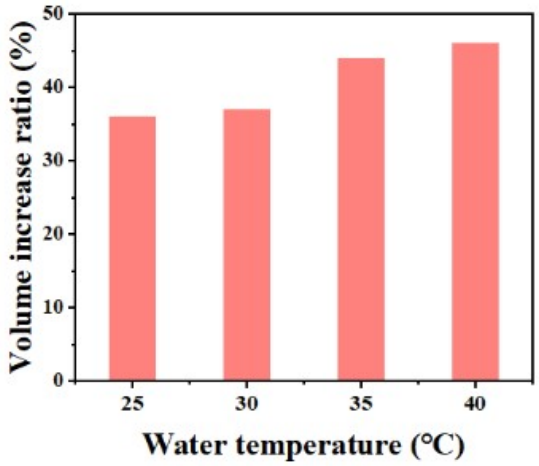
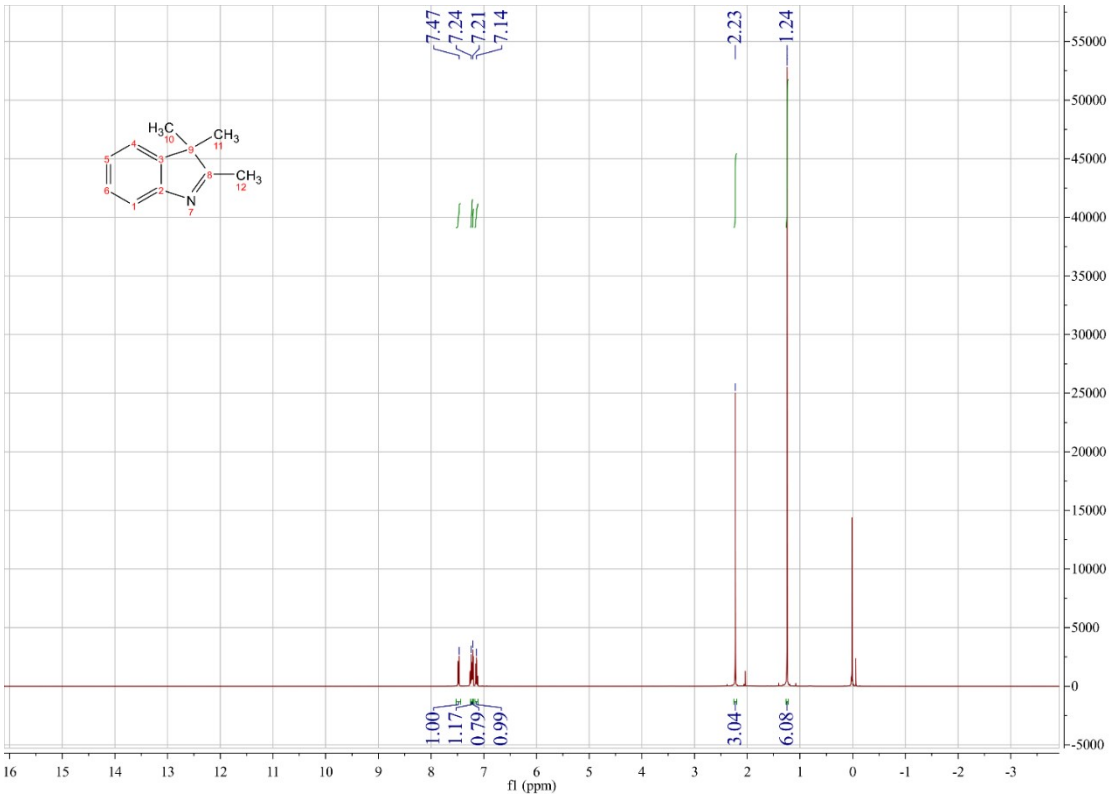
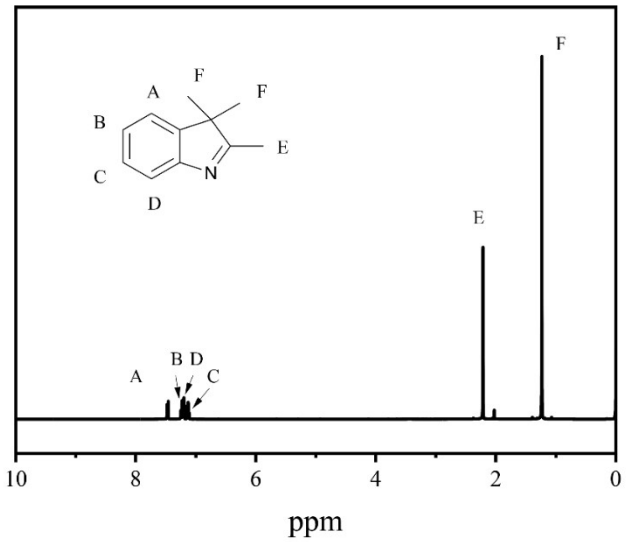


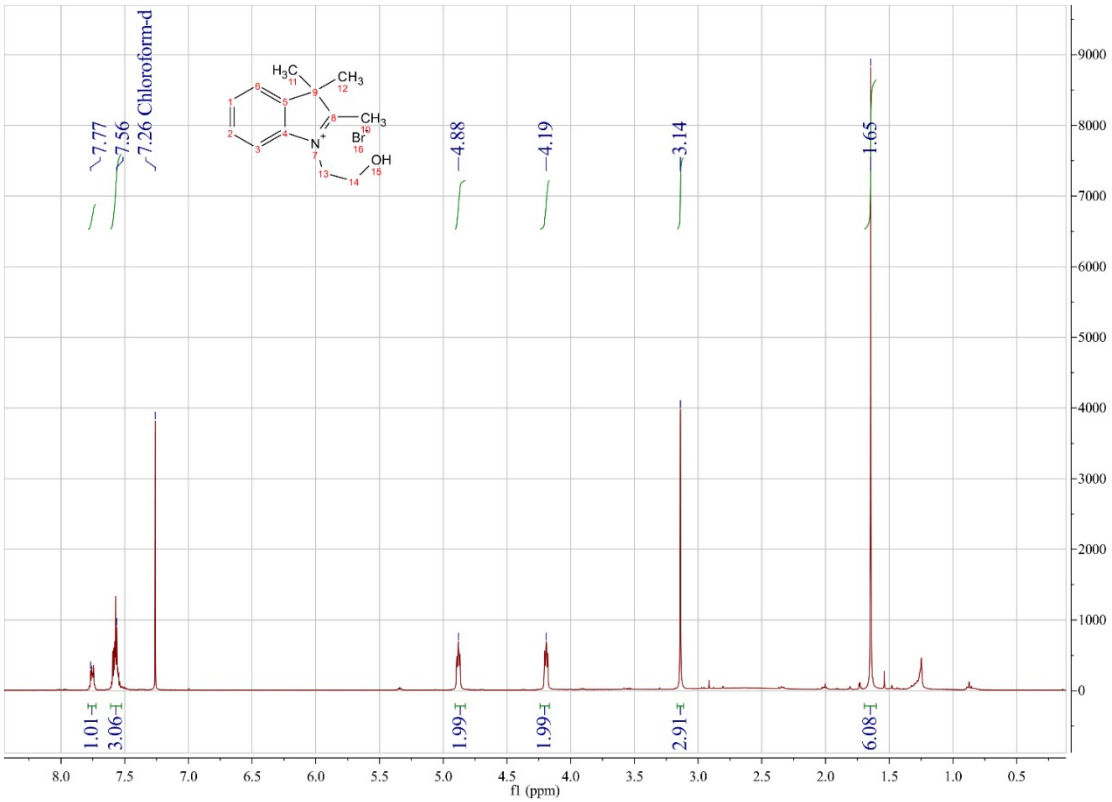
Fig. S15 The histogram of volume increase ratio of PHEA-SP swelled in different temperature water for 30 min in the dark.

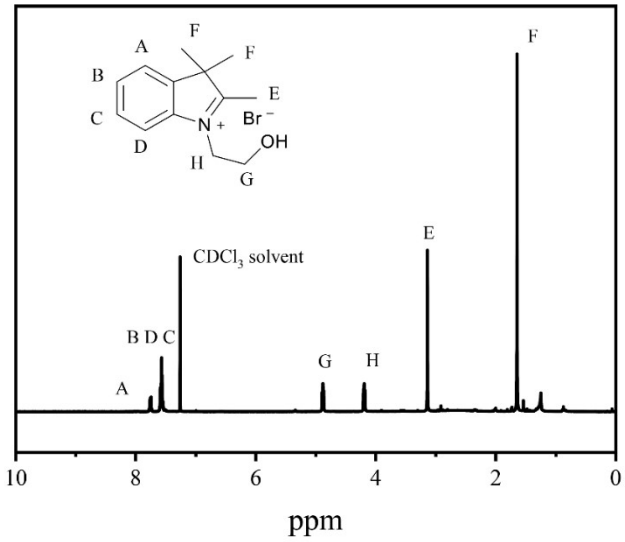
S4. ^{1}H NMR spectrum



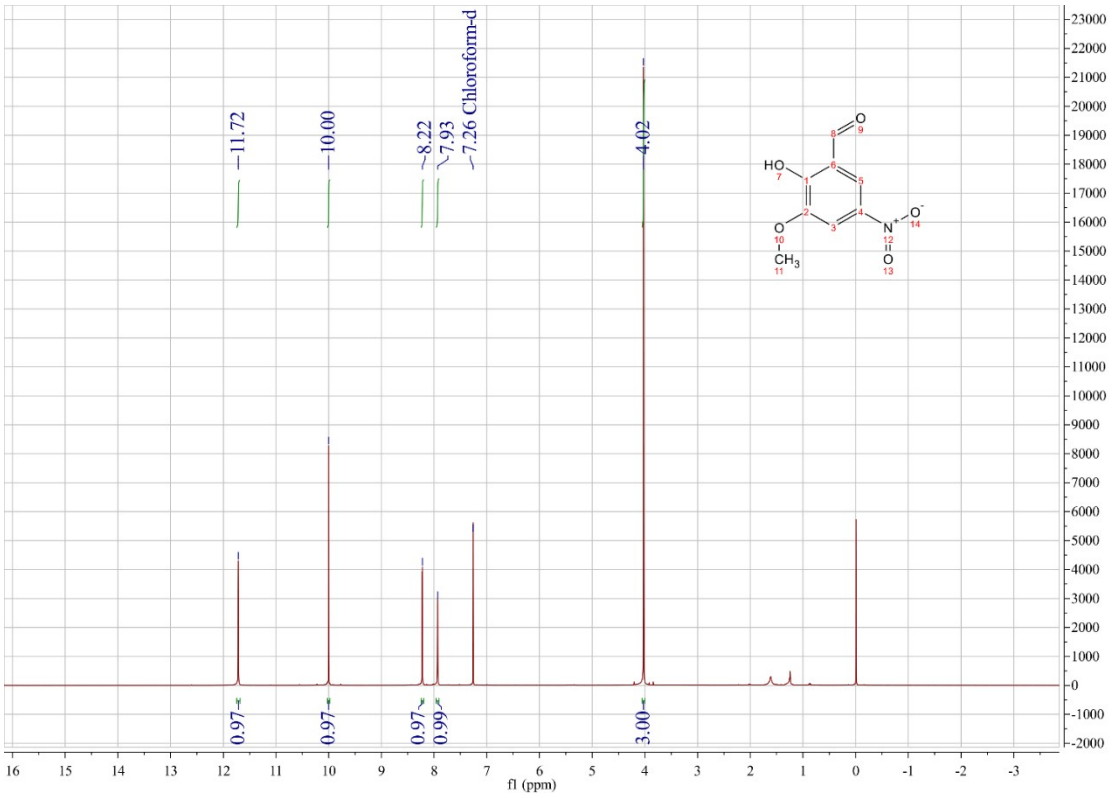


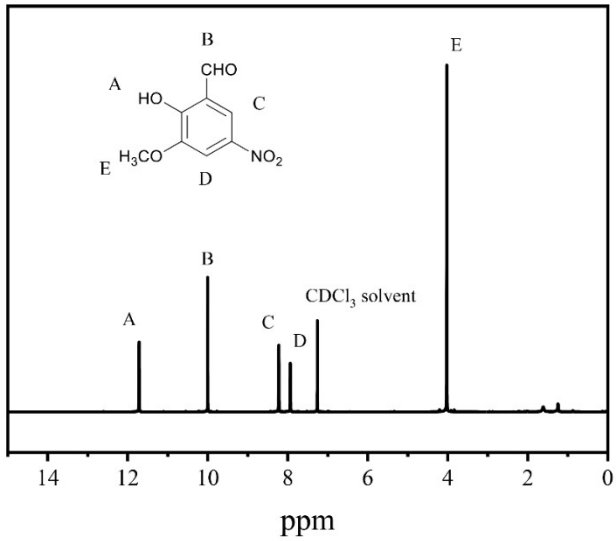
^{1}H NMR for 2,3,3-trimethyl-3H-indole (a)



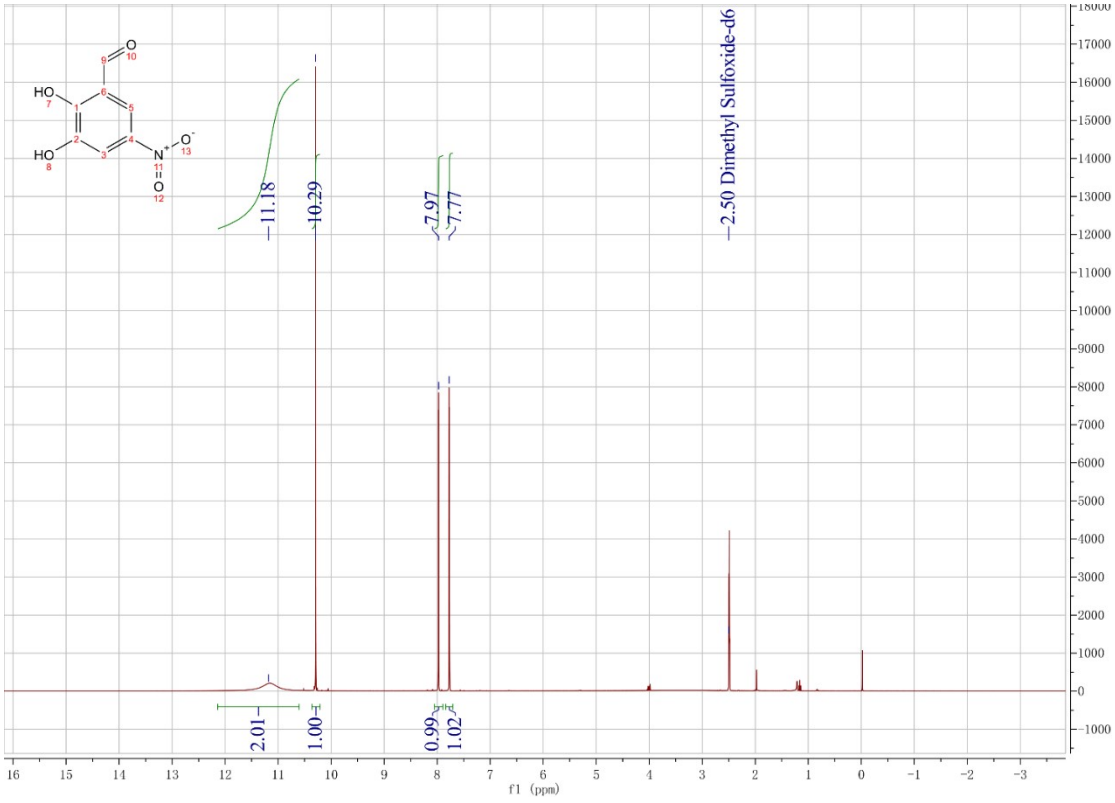


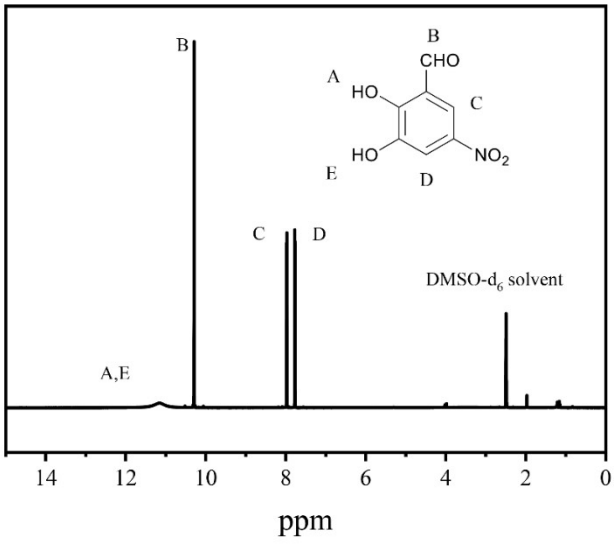
^{1}H NMR for 1-(-2-hydroxyethyl)-2,3,3-trimethyl-3H-indolium bromide (b)



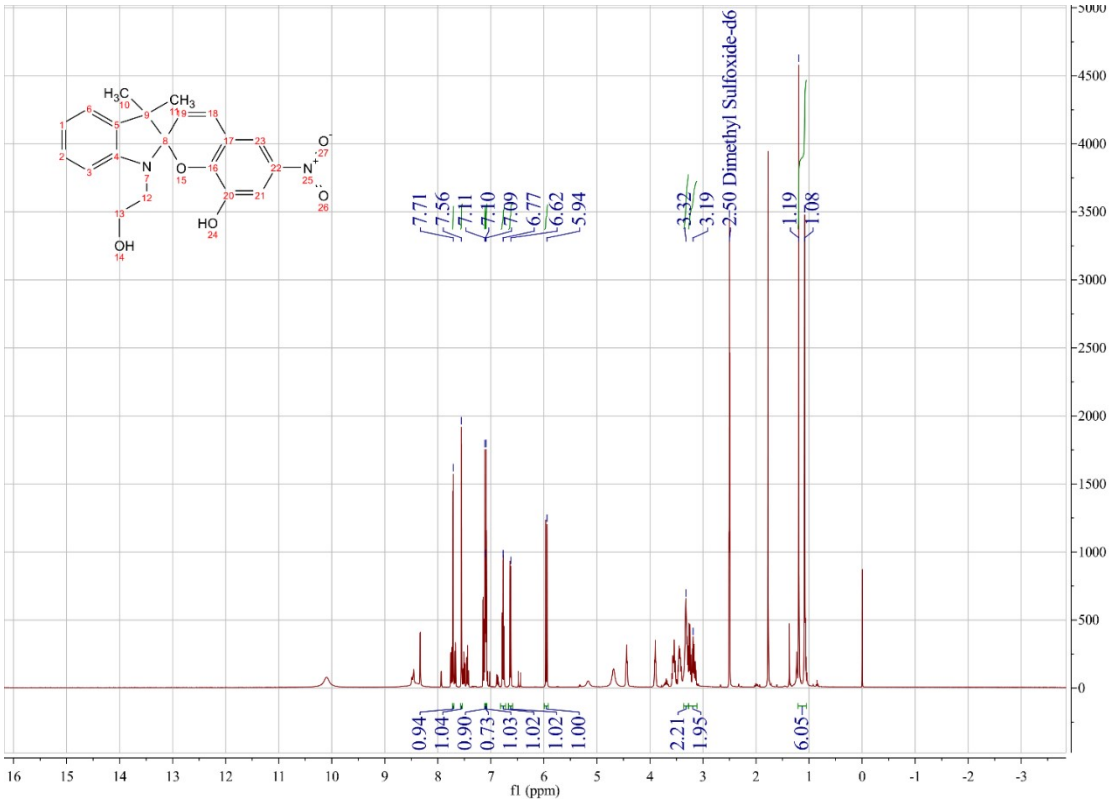


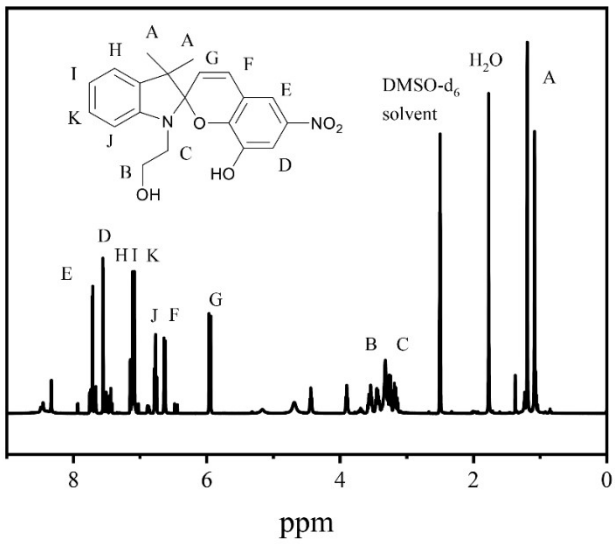
^{1}H NMR for 2-hydroxy-3-methoxy-5-nitro-benzaldehyde (c)



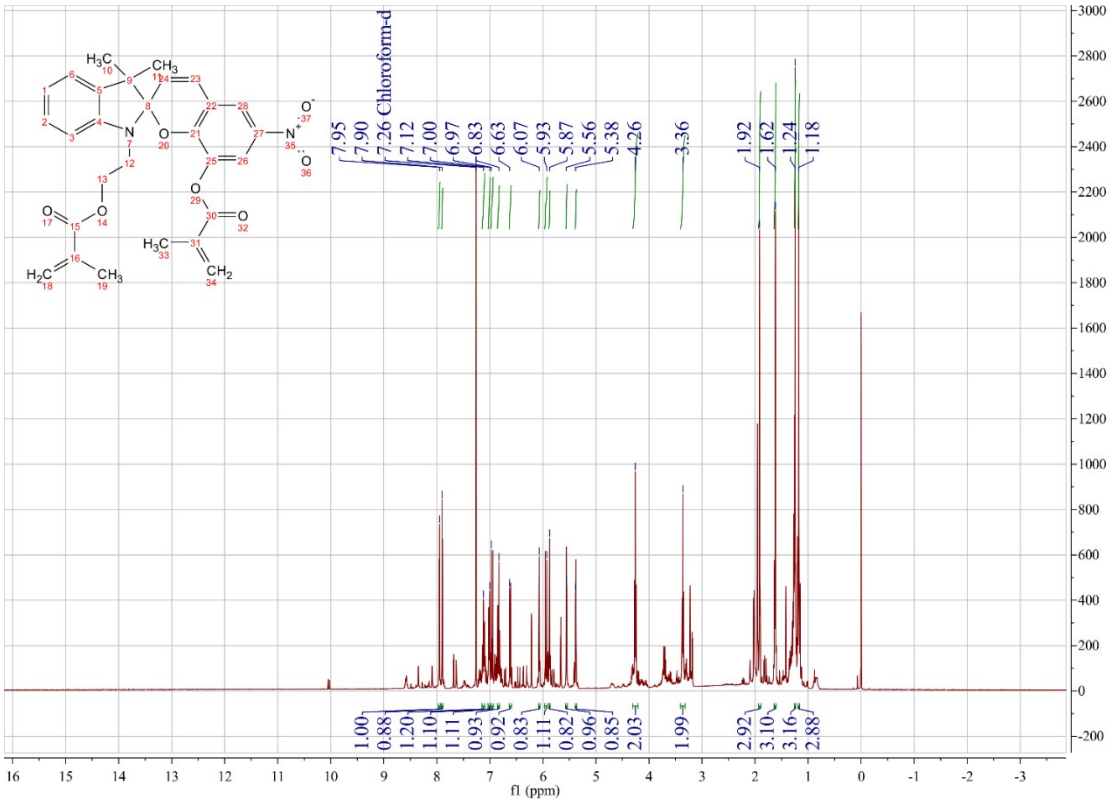


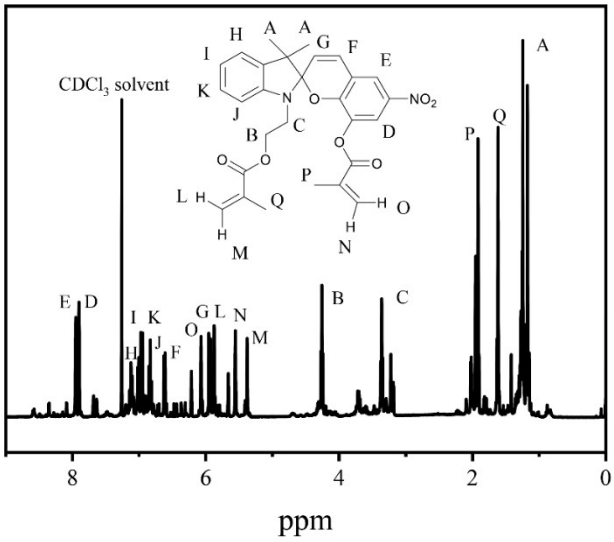
^{1}H NMR for 2,3-dihydroxy-5-nitro-benzaldehyde (d)



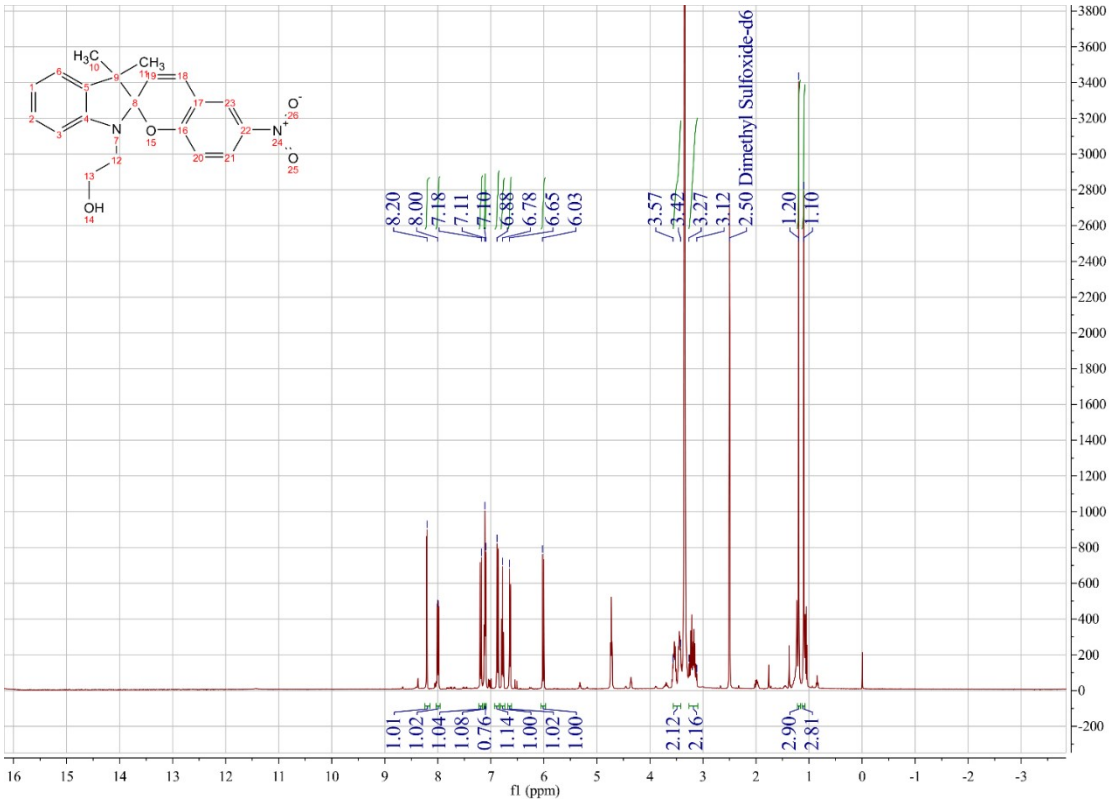


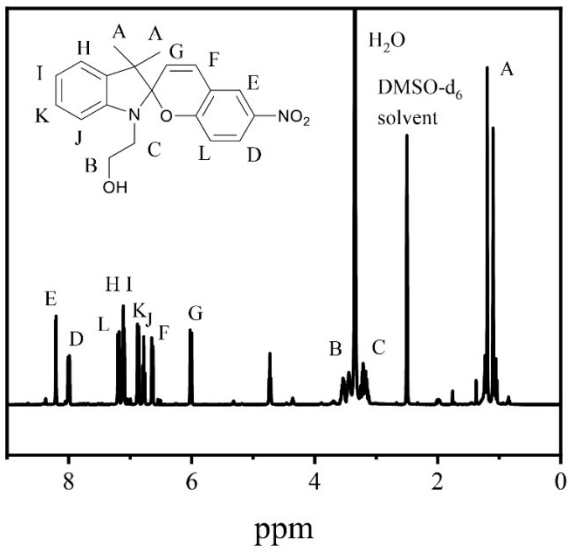
[1]H NMR for1'-(2-hydroxyethyl)-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-8-ol (e)



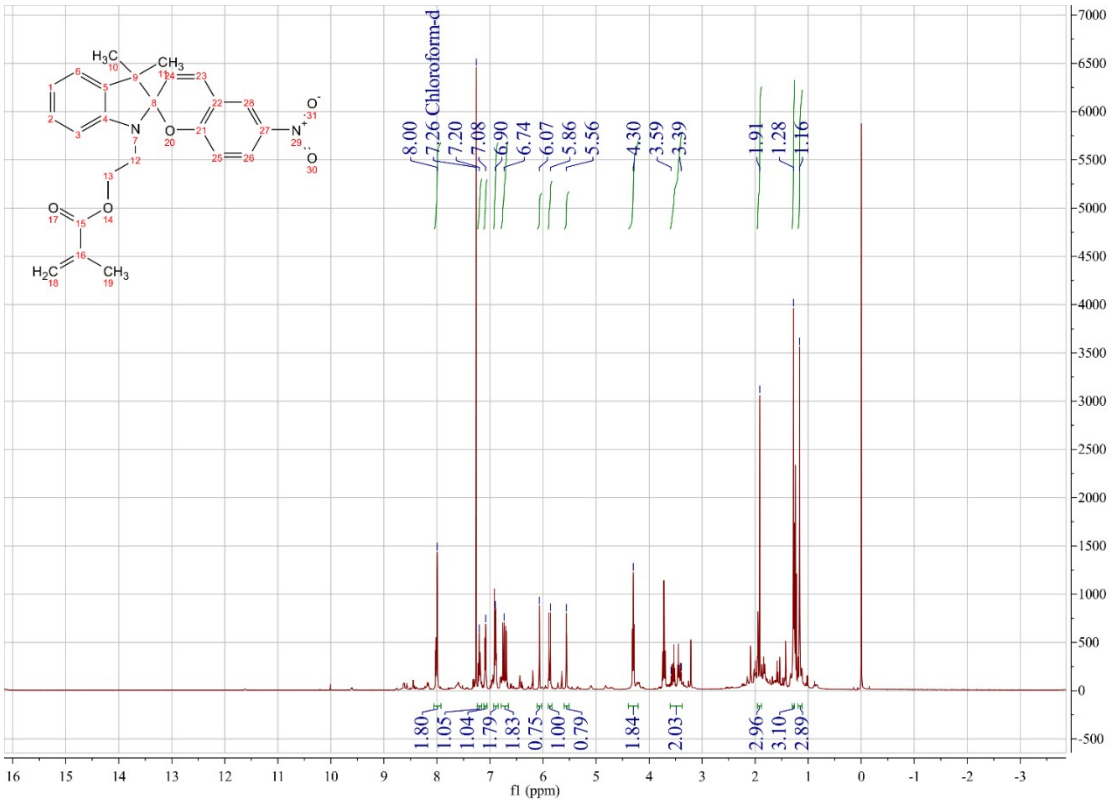


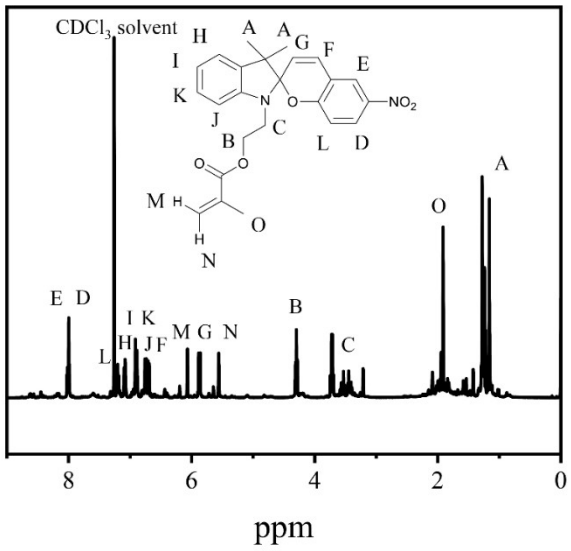
^{1}H NMR for 3′,3′-dimethyl-6-nitro-1′-(2-(methacryloyloxy)ethyl)spiro[chromene-2,2′-indoline]-8-yl(2-methylacrylate) (f, SP)





[1]H NMR for 1'-(2-hydroxyethyl)-3',3'-dimethyl-6-nitrospiro(2H-1-benzopyran-2,2'-indoline) (g)





[1]H NMR for 1'-(2-methacryloxyethyl)-3',3'-dimethyl-6-nitrospiro(2H-1-benzopyran-2,2'-indoline) (h, SP-control)

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