

An effective approach to fabricate high strength polyurethane hydrogels with reversible photochromic performance as a photoswitch

*Guangyao Li^a, Zhicheng Pan^{a,b}, Zhanyu Jia^a, Juan Wang^a, Jianlong Wang^a, Ning
Zhang^a, Mingwang Pan^{*a,b} and Jinfeng Yuan^{*a,b}*

New Journal of Chemistry

a. Institute of Polymer Science and Engineering, School of Chemical Engineering and
Technology, Hebei University of Technology, Tianjin 300130, PR China

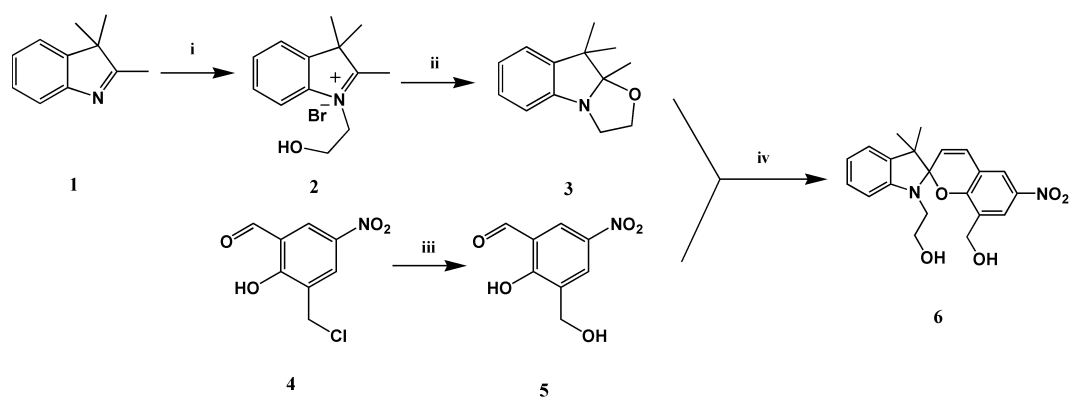
b. Hebei Key Laboratory of Functional Polymers, Hebei University of Technology,
Tianjin 300130, PR China

* Corresponding authors.

E-mail: mwpan@126.com

E-mail: yuanjf@hebut.edu.cn

1.Synthesis of di-hydroxyl SP



Scheme S1. Synthesis of the di-hydroxyl SP.

3-Chloromethyl-5-nitrosalicylaldehyde (5.742 g, 26.63 mmol) was dissolved in 30 mL of acetone and added to a 100 mL round bottom flask containing deionized water (10 mL) and a magnetic stir bar. The solution was heated to reflux with stirring for 20 min. Sodium hydroxide solution (4.45 mL of a 6 M solution) was added dropwise over a period of 10 minutes. The reaction mixture was stirred and refluxed for 3 h then cooled to room temperature. The resulting solution was filtered and chilled to precipitate the product. The material was recrystallized from water to obtain 3.6525 g (69.6% yield) of light green crystals (compound 5). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 11.96 (s, 1 H, Ar-OH), 10.04 (s, 1 H, -C(O)H), 8.60(d, 1 H, Ar-H), 8.54(m, 1 H, Ar-H), 4.89 (s, 2 H, -CH₂OH), 2.16(s,1 H, CH₂OH).

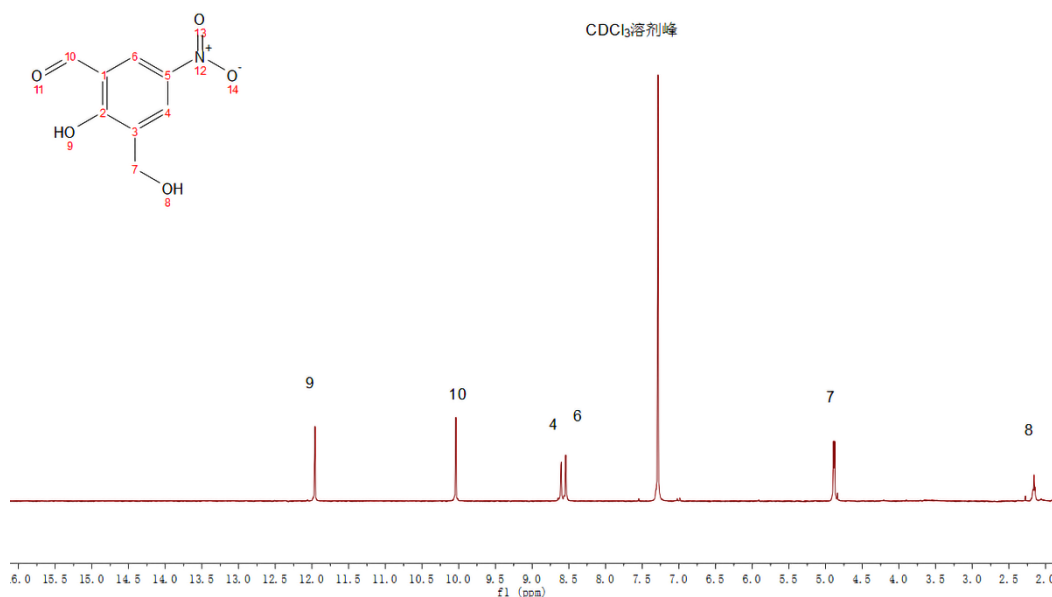


Figure S1. ^1H NMR of compound 5.

A mixture of 2,3,3-trimethylindolenine (compound 1, 2.61 g, 16 mmol) and 2-bromoethanol (2.46 g, 20 mmol) was heated at 100°C for 3.5h to get a solid (compound 2). Anhydrous potassium hydroxide (315 mg, 5.62 mmol) was ground in a mortar and pestle to a fine powder. 1-(2-hydroxyethyl)-2,3,3-trimethyl-3Hindolium bromide (1.00 g, 3.51 mmol) was added and the mixture ground until a fine paste was achieved and the color changed from purple to yellow. The paste was extracted with petroleum ether, and the extracts dried over anhydrous sodium sulfate, filtered, concentrated, then dried in vacuo to obtain 712 mg (>99% yield) of a yellow oil (compound 3). ^1H NMR (400 MHz, CDCl_3) δ : 7.17 (m, 1 H, Ar-H), 7.04-6.69 (m, 1 H, Ar-H), 6.84 (m, 1H, Ar-H), 6.67 (m, 1 H, Ar-H) 3.74-3.62 (m, 2 H, $-\text{NCH}_2\text{CH}_2\text{O}-$), 3.44 (m, 2 H, $-\text{NCH}_2\text{CH}_2\text{O}-$), 1.35 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 1.10(s, 3 H, $\text{C}(\text{N})(\text{O})\text{CH}_3$).

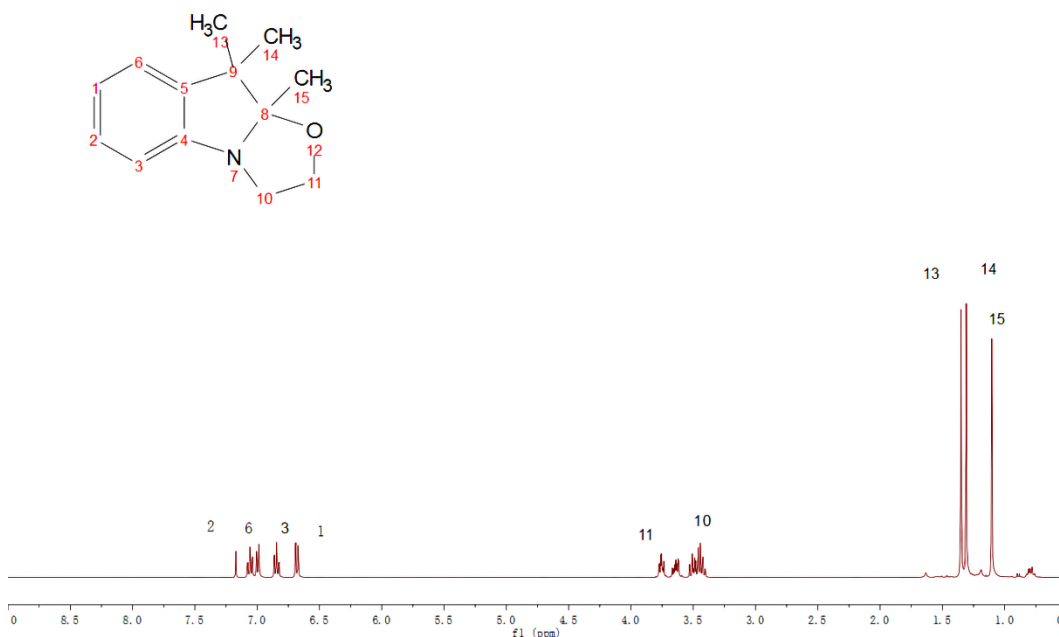


Figure S2. ^1H NMR of compound 3.

3-Hydroxymethyl-5-nitrosalicylaldehyde (compound 5, 576 mg, 2.92 mmol) was dissolved in 10 mL of ethanol in a 50 mL round bottom flask. Water (10 mL) was added followed by the addition of compound 3 (712 mg, 3.50 mmol). The reaction mixture was heated to reflux while stirring and monitored by TLC. The reaction was determined to be complete after a period of 5 h. During the reaction, an iridescent precipitate formed on the sides of the flask. The mixture was allowed to cool to room temperature and then concentrated on a rotary evaporator to remove ethanol. Water (10 mL) was added and the mixture was brought to a boil. The solution was filtered and this procedure was then repeated. The product was washed with benzene to remove unreacted starting materials. The resulting brown powder was directly recrystallized from roughly 70% acetonitrile (aq) solution to give 477 mg (39% yield) of dark red iridescent crystals (compound 6). ^1H NMR (400 MHz, DMSO- d_6) δ : [8.13 & 8.10] (d, 2 H, Ar-H), 7.17 (d, 1 H, ArCH=CH-), 7.12 (m, 2 H, Ar-H), 6.81 (t, 1 H, Ar-H), 6.69 (d, 1 H, Ar-H), 6.07 (d, 1 H, -CH=CHAr), 4.43 (m, 2 H, ArCH₂OH), [3.80, 3.73, & 3.65] (m, 2 H, NCH₂CH₂OH), [3.40 & 3.31] (m, 2 H, NCH₂CH₂OH), [1.27 & 1.18] (s, 3 H, C(CH₃)₂). HRMS (ESI): [M+H]⁺ calculated for C₂₁H₂₂N₂O₅, 383.1607; found, 383.1606.

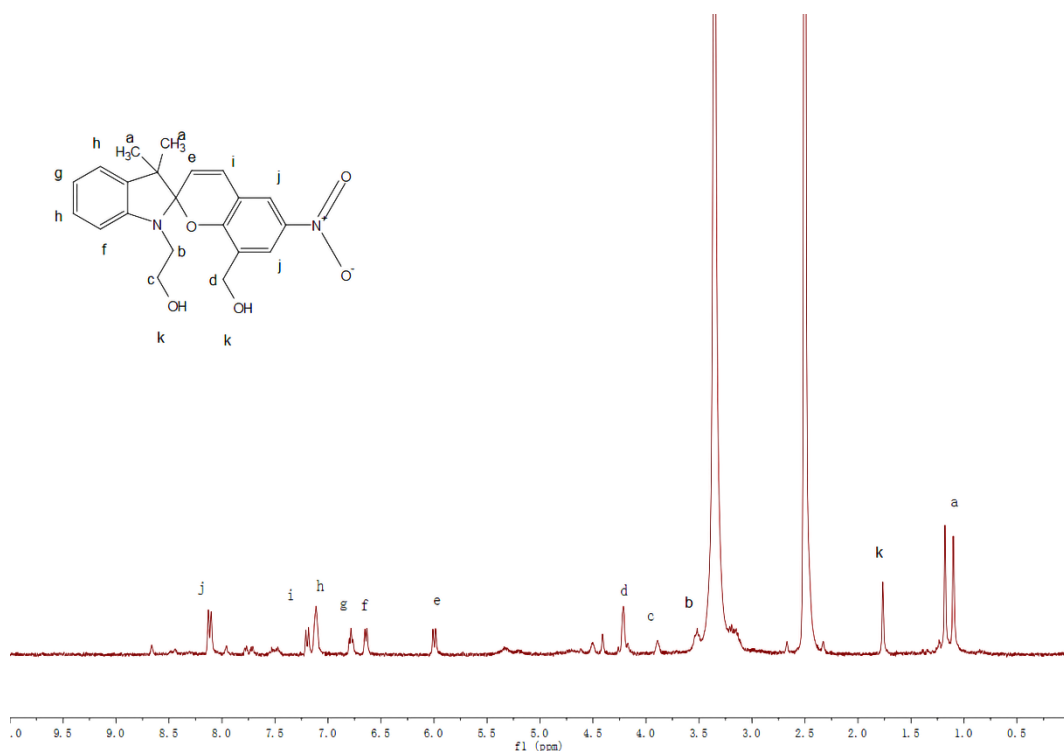


Figure S3. ^1H NMR of compound 6.

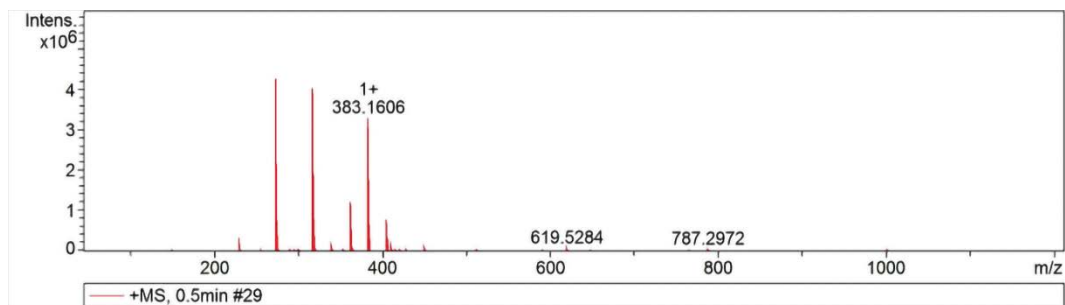


Figure S4. HRMS(ESI) spectrum of compound 6.

2. Extraction text

Table S1 Mass of PU-SP-4 hydrogel

Mass before extration(g)	Mass after extration(g)	Mass reduction ratio (%)
0.2105	0.2045	2.8
0.2108	0.2045	3.0
0.2107	0.2046	2.9

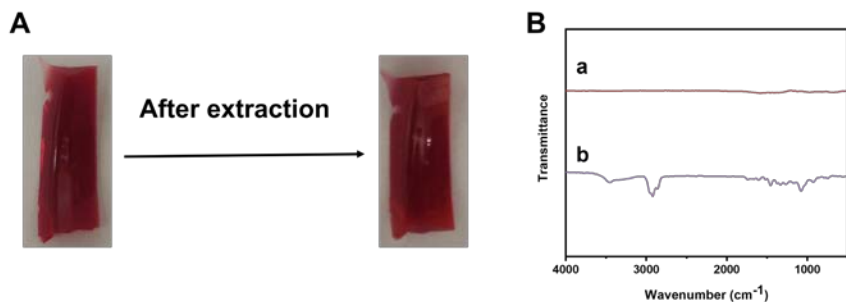


Figure S5. (A) Photo of PU-SP-4 hydrogel and (B) FT-IR spectra of (a) leaching liquor, (b) SP solution.

3. Fluorescence spectroscopy of PU-SP-x hydrogels

In order to further confirm that the spiropyran took part in the chemical reaction, the fluorescence spectrum of the PU-SP hydrogel was recorded. All samples were activated by 365 nm ultraviolet light for 2 h in order to make ring-closed non-fluorescent SP activated into a ring-opening fluorescent MC. It can observe from the photo in Figure S6A that with the increase of SP content in PU-SP hydrogel, the color deepens obviously under ultraviolet light irradiation at 365 nm, but PU-SP-2 has the highest brightness, which is the same as The fluorescence spectra (Figure S6B). The reason is the SP concentration is too high, which leads to fluorescence quenching. Compared with the fluorescence emission peak of PU-SP-0, PU-SP hydrogel has an obvious fluorescence emission peak at 670 nm, and a certain degree of redshift may be due to the reaction between hydroxyl of SP and the isocyanate of PU prepolymer. The results showed that the spiropyran participated in the chemical reaction to prepare the PU-SP hydrogel.

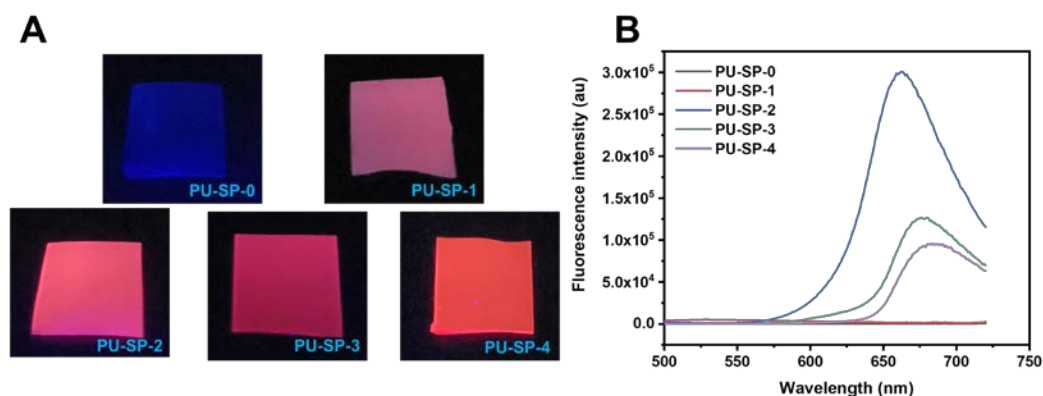


Figure S6. (A) Photos of luminous PU-SP hydrogels and (B) Fluorescence emission spectra.

4. Recipes for synthesis of PU-TMP-x hydrogels

Table S2 Recipes for synthesis of PU-TMP hydrogels

Sample code	Mole ratio of OH to NCO	PEG2000 (g)	IPDI (g)	TMP (g)	SP (g)	wt% of TMP
PU-TMP-8	1:1.15	5.00	2.56	0.67	0.0041	8
PU-TMP-7	1:1.15	5.00	2.18	0.54	0.0041	7
PU-TMP-6	1:1.15	5.00	1.92	0.44	0.0041	6
PU-TMP-5	1:1.15	5.00	1.64	0.35	0.0041	5
PU-TMP-4	1:1.15	5.00	1.40	0.27	0.0041	4

5. Swelling behaviors of PU-TMP-x hydrogels

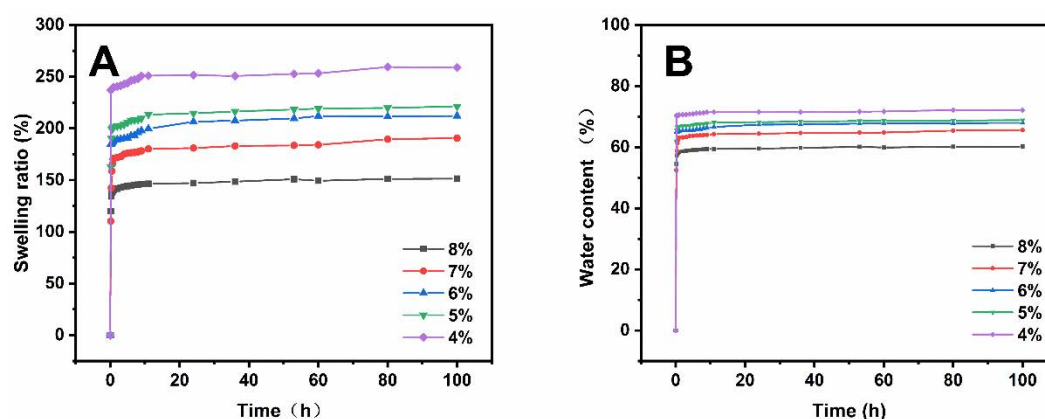


Figure S7. (A) Swelling ratio with time of PU-TMP-x; (B) Water content with time of PU-TMP-x.

The effect of TMP content on the swelling property was studied. As we can be seen from Figure S7A, the swelling rate of PU-SP hydrogel decreases from 259% to 151% as the TMP mass fraction decreases from 8% to 4%, and the water content of PU-SP hydrogel also decreases from 72% to 60% (Figure S7B). The monotonic decrease in water content and swelling rate can be attributed to the increase in the degree of cross-linking with the content of spiropyran increased, resulting in a compact network structure, which makes it more and more difficult for water to enter PU- SP hydrogel network.

6. Tensile test of PU-TMP-x hydrogels

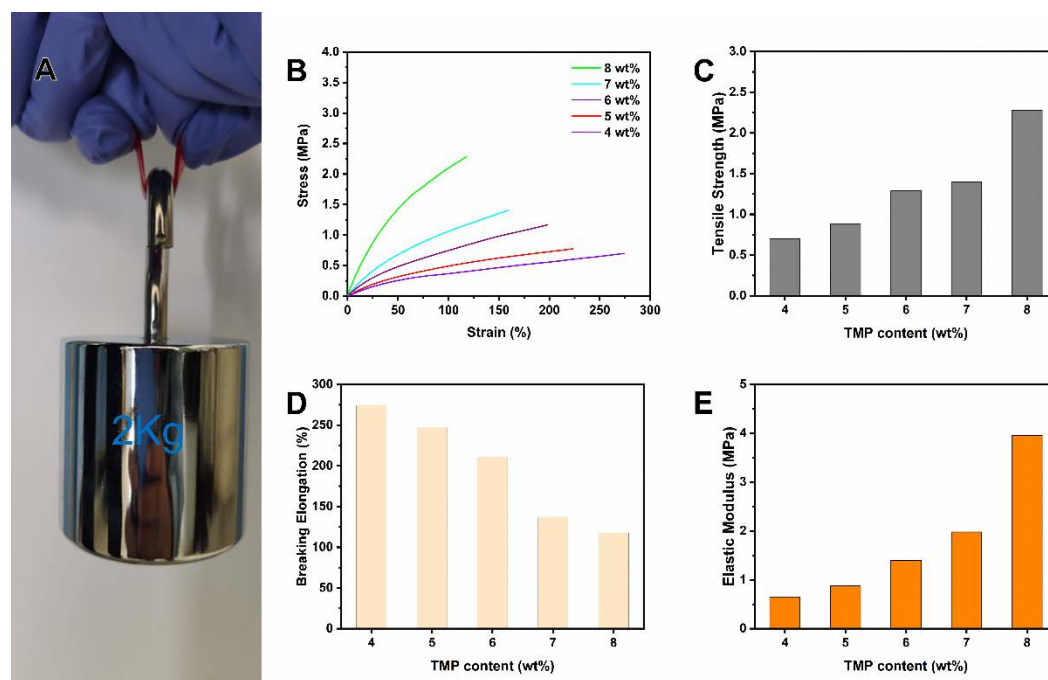


Figure S8. (A) Photo of weight capacity (B) Tensile strain-stress curves of PU-SP hydrogels; Mechanical properties of PU-SP hydrogels: (C) Tensile strength; (D) Breaking strain; (E) Elastic modulus.

After that, the influence of the crosslinking degree which also is the key factor of hydrogels' mechanical properties was further investigated through tensile experiments. As shown in Figure S8, when the TMP content increases from 4 wt% to 8 wt%, the tensile strength increases from 0.7 to 2.28 MPa, which is more than 3 times to PU hydrogel (0.7 MPa). The elastic modulus increased from about 0.65 to 3.96 MPa, which was more than 6 times to PU hydrogel (0.65 MPa). However, the increase in TMP content reduced the elongation at break to 117%, which may be due to the increase of cross-linking degree, causing the increase in chain rigidity.

7. Fluorescence spectroscopy of PU-TMP-x hydrogels

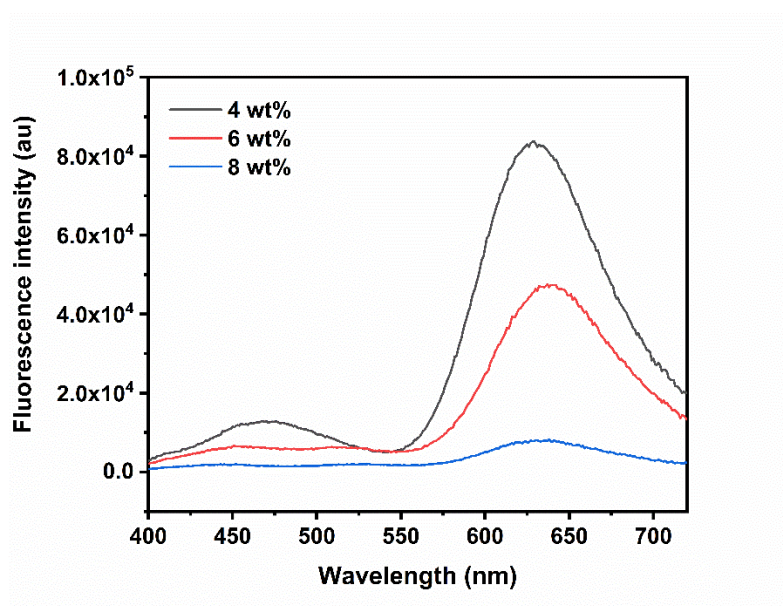


Figure S9. Fluorescence spectra of PU-TMP hydrogels.

Non-fluorescent SP is activated to fluorescent MC by isomerization reaction. Therefore, the photochromic behavior of hydrogels can be characterized by fluorescence spectrum. It can be observed that PU-TMP hydrogels have an obvious fluorescence emission peak at about 625 nm after irradiation of same time, which is the characteristic emission peak of MC. It is obvious that the fluorescence intensity decreases with the increase of TMP content, which can attribute to the movement of molecular chain segment. With the decrease of crosslinking density, the molecular chain segments are more flexible, which is conducive to the isomerization reaction, and SP is easier to isomerize into MC, resulting in the increase of fluorescence intensity. It indicates that the irradiation speed can be promoted by adjusting the cross-linking network density.