Electronic Supplementary Information

Thiol-ene Chemistry Incorporates a New Spiropyran-Contained-Polyurethane Ionogel with Photochromic, Photomechanical and Photoconductive Properties

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1. Materials and Methods

1.1 Materials

5-hydroxy-1,2,3,3-tetramethyl-3H-indole-1-ium iodide, 2,3-dihydroxy-5-nitrobenzaldehyde were purchased from Shanghai Bider Pharmaceutical Technology Co., Ltd. Poly (ethylene glycol) (PEG, M_n = 1000), dibutyltin dilaurate (DBTDL), hydroxypropyl acrylate (HPA), trimethylolpropane tris(3-mercaptopropionate) (TMPMP), 1-Ethyl-3-methylimidazolium tetrafluoroborate([EMIM][BF_4], 98%), 1-ethyl-3-methylimidazolium bis(tri-uoromethylsulfonyl) imide ([EMIM][TFSI], 98%) and 2-hydroxy-2-methylpropiophenone (PI 1173) were purchased from Energy Chemicals Co., Ltd. Lithium bis (trifluoromethanesulphonyl) imide (LiTFSI) and hexamethylene diisocyanate (HDI) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

1.2 Synthesis of a dihydroxyspiropyran monomer (1',3',3'-trimethyl-6-nitrospiro[chromen-2,2'-indoline]-5',8-diol)

2,3-Dihydroxy-5-nitrobenzaldehyde (91.5 mg, 0.5 mmol), 5-hydroxy-1,2,3,3-tetramethyl-3H-indol-1-ium iodide (158 mg, 0.5 mmol) and piperidine (42.6 mg, 0.5 mmol) were dissolved in ethanol, heated to 100 °C under argon atmosphere, and stirred for 3 h. After then, the mixture was cooled to room temperature and filtered. The precipitate was washed with ethanol and dried overnight at 40 °C under vacuum to get the spiropyran monomer (1',3',3'-trimethyl-6-nitrospiro [chromen-2,2'-indoline]-5',8-diol).

1.3 Synthesis of Polyurethane (PUA) ionogel

1.3.1 Synthesis of Polyurethane Acrylate Prepolymer

HDI (3.00 g, 18 mmol), and DBTBL (0.05 g) were added into a 150 mL three-necked flask and stirred. Then, a mixture of PEG (10.00 g, 10.00 mmol) and LITFSI (0.50 g) dissolved in THF was dropwise added under nitrogen atmosphere, and heated at 45 ℃ for 40 min. Afterwards, a capping reagent of HPA (3.5 g, 27 mmol) was further dropwise added slowly. The reaction was kept for 2 h, and the solution of polyurethane

acrylate prepolymer was then obtained. Finally, the prepolymer was put under vacuum at 30 ℃ to remove the solvent, which was denoted as prePUA.

1.3.2 Preparation of Polyurethane (PUA) ionogel

The prePUA (1 g) and TMPMP (0.2 g, 0.5 mmol) were mixed evenly, and was refrigerated for 1 d to eliminate bubbles. Then the mixture was thawed, and a certain amount of [EMIM][TFSI] was further incorporated as well as PI 1173 (0.05 g) and stirred slowly until homogeneous. The default mass ratio of IL in preSP-PUA was set to 50 ωt%. Lastly, the mixture was cast on a Teflon mold and cured under a UV curing machine, and successively dried for 48 h at room temperature, and the ionogel was prepared, which was denoted as PUA / [EMIM][TFSI]. The SP-PUA had no incorporated IL.

2. Supplementary Figures

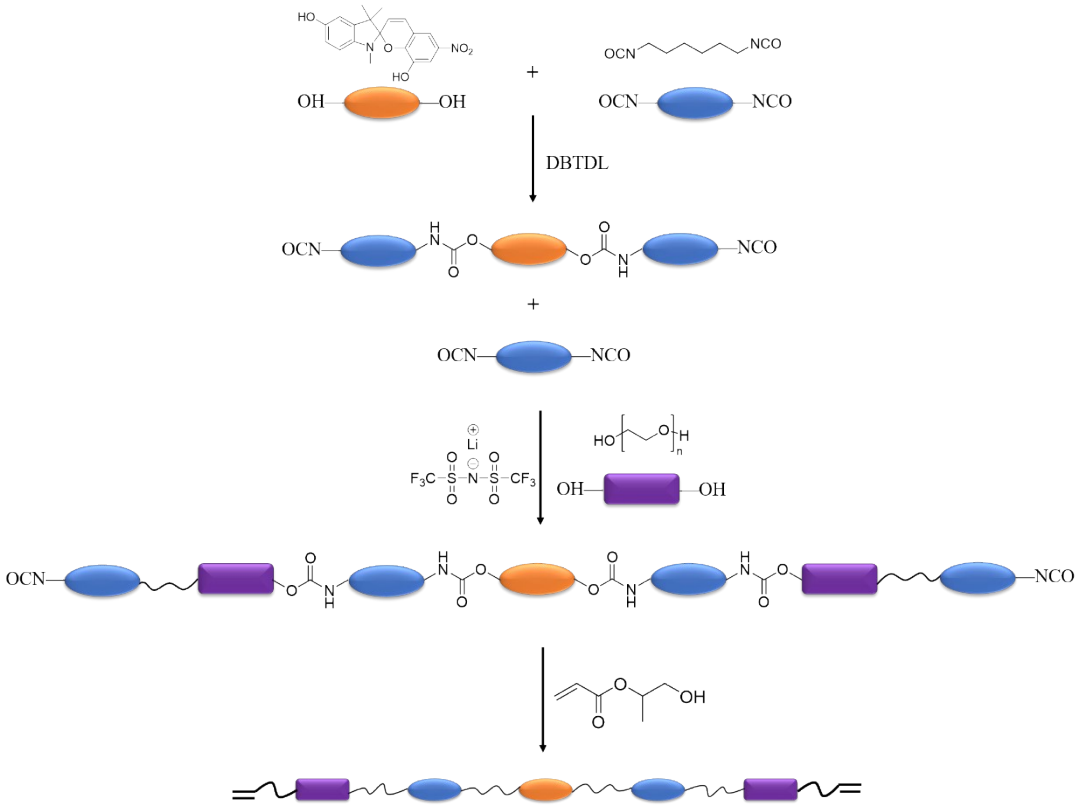

Figure S1 The synthesis route of spiropyran-contained-polyurethane acrylate prepolymer (preSP-PUA) where the spiropyran is represented as the ring-closed form

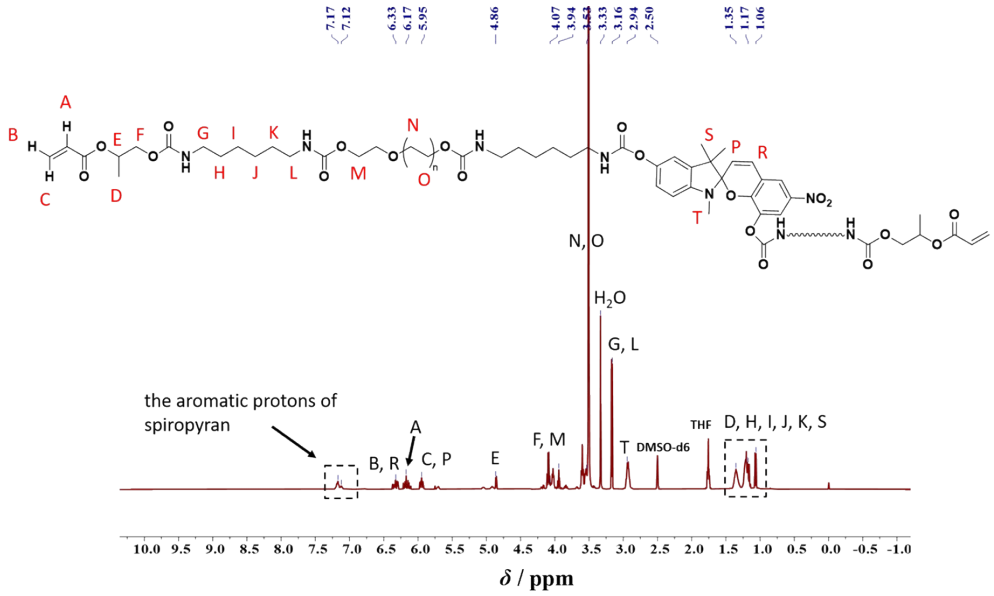

Figure S2 The ^{1}H-NMR spectrum of preSP-PUA.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.17 (m, 5H), 6.33 (m, 2H), 6.17 (m, 1H), 5.95 (dd, 2H), 4.86 (m, 1H), 4.07-3.94 (m, 4H), 3.53 (m, 88H), 3.16 (t, 4H), 2.94 (s, 3H), 1.35 ~ 1.06 (m, 17H).

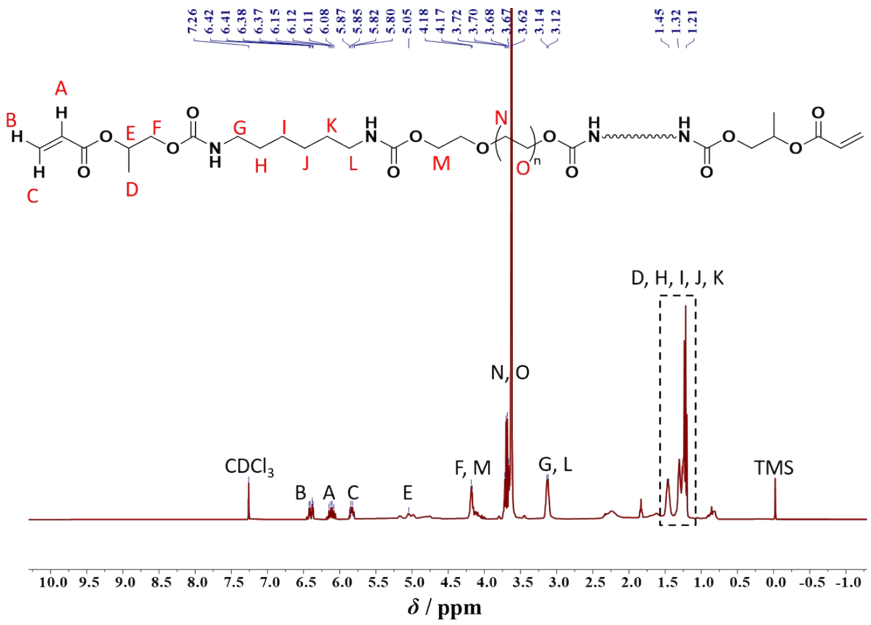

Figure S3 The ^{1}H-NMR spectrum of prePUA.

^{1}H NMR (400 MHz, Chloroform-d), δ 6.40 (dd, 1H), 6.11 (dd, 1H), 5.80 (dd,1H), 5.05 (m, 1H), 4.18 (m, 4H), 3.70 (m, 88H), 3.12 (t, 4H), 1.46~1.21 (m, 11H).

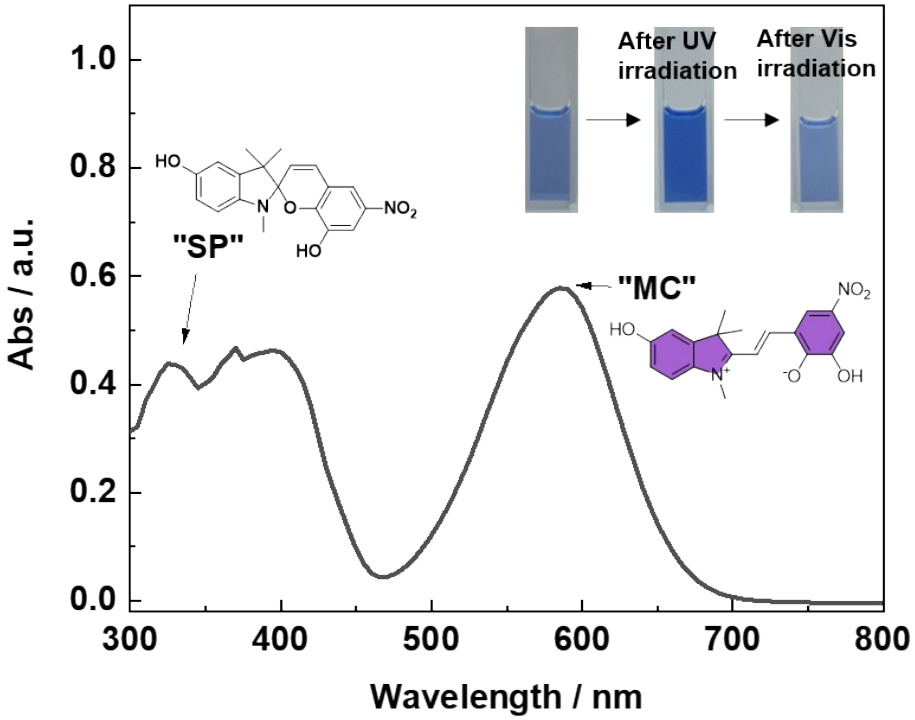

Figure S4 The UV-visible absorbance spectrum of DHSP in THF

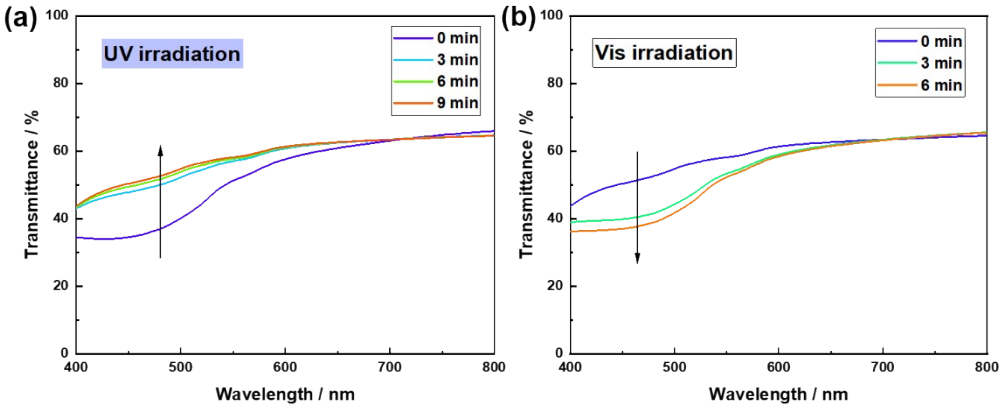

Figure S5 The transmittance of the ionogels in the visible light range (400~800 nm) that studies on the isomerization reaction in the SP-PUA / [EMIM][TFSI] between "MCS form" and "MC-form": (a) under UV light irradiation and (b) under vis light irradiation

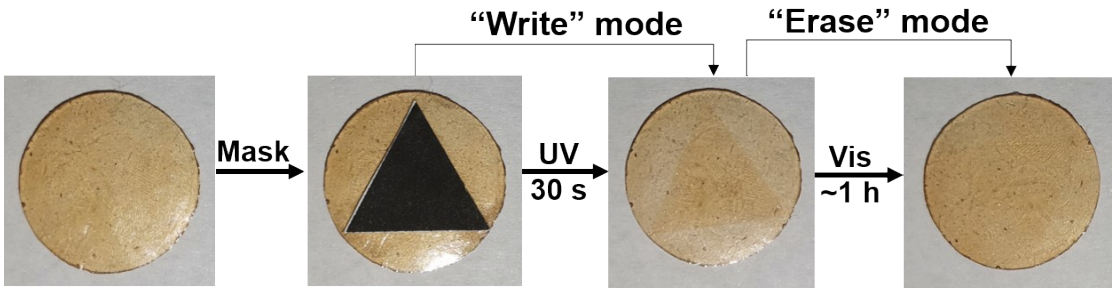

Figure S6 Photo-switchable patterns on the circular SP-PUA / [EMIM][TFSI] with a 2-fold increased content of [EMIM][TFSI] under the UV light with a photomask (30s, in "Write" mode) and subsequently under the visible light (~1h, in "Erase" mode)

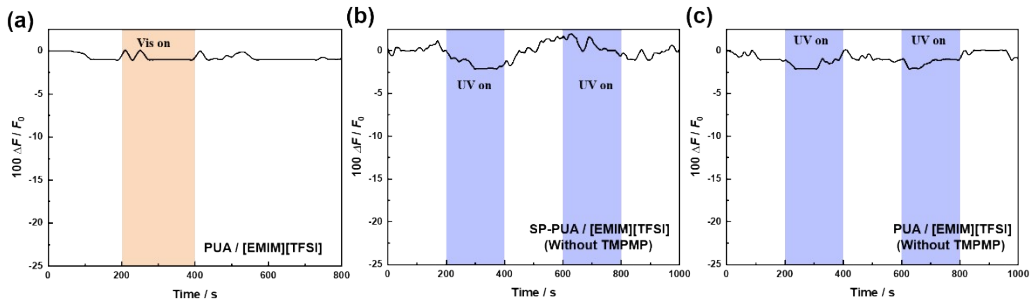

Figure S7 The photomechanical properties. (a) Under visible light irradiation: PUA / [EMIM][TFSI]; (b, c) under UV light irradiation: (b) SP-PUA / [EMIM][TFSI] without TMPMP and (c) PUA / [EMIM][TFSI] without TMPMP.

Table S1 The average molecular weight and polydispersity index of the preSP-PUA

Sample	M_n / (g mol^{-1})	M_w / (g mol^{-1})	PDI
preSP-PUA	5785	11289	1.89