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Supporting Information

A near-infrared light-triggered shape-memory polymer with long-time fluorescence imaging in deep tissue

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Supplentary Experimental section

Synthetic Procedures of NIR cross-linker YHD798. The synthetic route of YHD798 is illustrated in Figure S1a. Compound (1) 1-thiophen-2-yl-piperidine-4-carboxylic acid methyl ester and compound (2) 1-thiophen-2-yl-piperidine-4-carboxylic acid are synthesized referred to previous studies. [1,2]

1-thiophen-2-yl-piperidine-4-carboxylic acid 2-methacrylate ethyl ester (3). A mixture of compound (2) (1.05 g, 4.97 mmol), 2-hydroxyethyl methacrylate (0.78 g, 5.97 mmol) and 4-dimethylaminopyridine (0.06 g, 0.50 mmol) were added into a 100 mL three-neck round-bottom flask and dissolved in 20 mL anhydrous dichloromethane. N,N'-diisopropylcarbodiimide (1.25 g, 9.94 mmol) was then added into the solution at 0 °C under nitrogen atmosphere. The mixture was stirred at room temperature for 24 h. The raw product was filtered to remove the solid residue and then purified by column chromatography (petroleum ether : ethyl acetate = 20 : 1) to yield compound (3) as a yellow oil (1.22 g, yield 75.91%). ^{1}H NMR ($CDCl_3$, δ): 6.76 (dd, 1 H), 6.59 (dd, 1 H), 6.10 (m, 2 H), 5.59 (t, 1 H), 4.35 (s, 4 H), 3.52 - 3.47 (m, 2 H), 2.85 – 2.78 (m, 2 H), 2.48 – 2.40 (m, 1 H), 2.03 – 1.83 (m, 7 H).

2,5-bis[(2-methacrylate ethyl-4-carboxylate-piperidylamino) thiophenyl]-croconium (YHD798, 4). A mixture of croconic acid (33 mg, 0.23 mmol) and compound (3) (186 mg, 0.58 mmol) were added into 30 mL solution of toluene/n-butanol (v/v = 1:1) in a 100 mL three-neck round-bottom flask and refluxed under nitrogen atmosphere for 1 h. The reaction solution was cooled to room temperature and filtrated to gain the crude product. The crude product was washed by methanol and

dried under vacuum to yield YHD798 as a black solid (104 mg, yield 60.05%). ^{1}H NMR ($CDCl_3$, δ): 8.71 (d, 1 H), 6.58 (s, 1 H), 6.12 (s, 1 H), 5.62 – 5.61 (m, 1 H), 4.08 – 3.97 (m, 2 H), 3.65 - 3.47 (m, 2 H), 2.75 – 2.69 (m, 1 H), 2.33 – 1.74 (m, 7 H).

In vitro **cytotoxicity experiments.** The human umbilical vein endothelial cells (HUVECs) were supplied by National Key Laboratory of Biotherapy of Sichuan University. The cells were planted in the F12 medium added with 10% (v/v) fetal bovine serum (FBS) and sustained in a humidified atmosphere of 37 °C with 5% CO_2. The sp-1% films were disinfected by soak in 75% (v/v) ethanol for 24 h and irradiation under UV light for 48 h. Each film with size of 5 × 5 × 0.1 mm^3 was placed in the well of a 48-well plate and a total of 2 × 10^4 of HUVECs in 300 μL of the culture medium were seeded in the 48-well plate for 1, 3, 5 days, respectively. The cells were then rinsed with PBS three times and immersed in the M199 medium containing FBS and Alarmarblue (v/v/v = 8 : 1: 1) in dark for 4 h. The optical absorbance at 570 nm (OD570) and 600 nm (OD600) as an indicator of viable cells was recorded on a microplate reader Varioskan Lux (Thermo Scientific, USA). The cell viability was calculated with the following equation:

$$\text{cell viability (ECs\%)} = \frac{117216\times OD_{570} - 80586\times OD_{600}\ (treatment\ group)}{117216\times OD_{570} - 80586\times OD_{600}\ (control\ group)} \times 100\%.$$

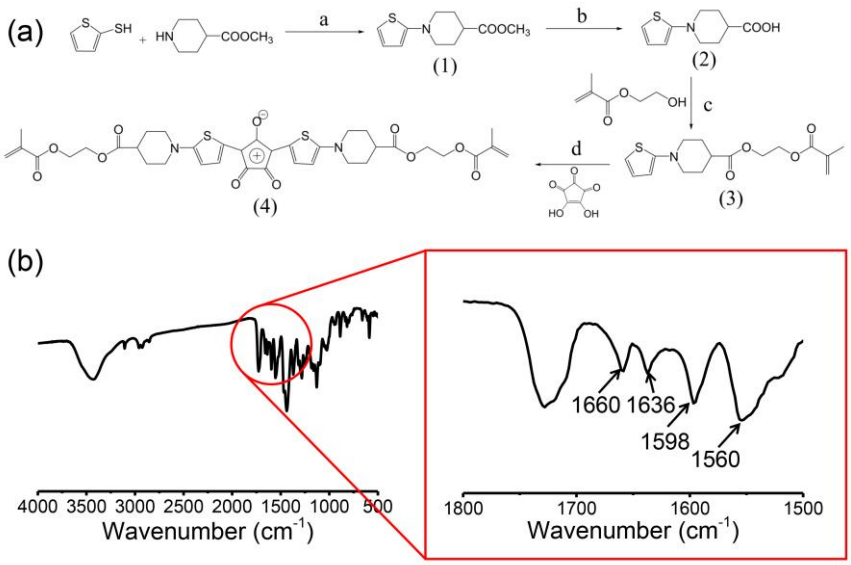

Figure S1. (a) Synthetic route of croconaine dye YHD798. a: 20 mL toluene, N_2, 120 °C. b: 0.5 mol/L NaOH solution, 105 °C. c: DMAP, DIC, dried DCM, N_2, 25 °C. d: toluene/ n-butanol (v/v = 1:1), N_2, 120 °C. (b) FTIR spectra of YHD798.

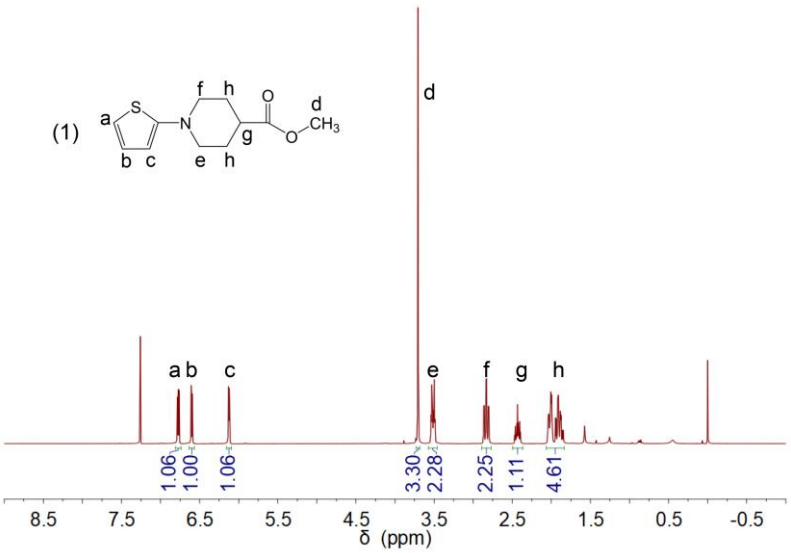

Figure S2. ^{1}H NMR spectra of compound (1).

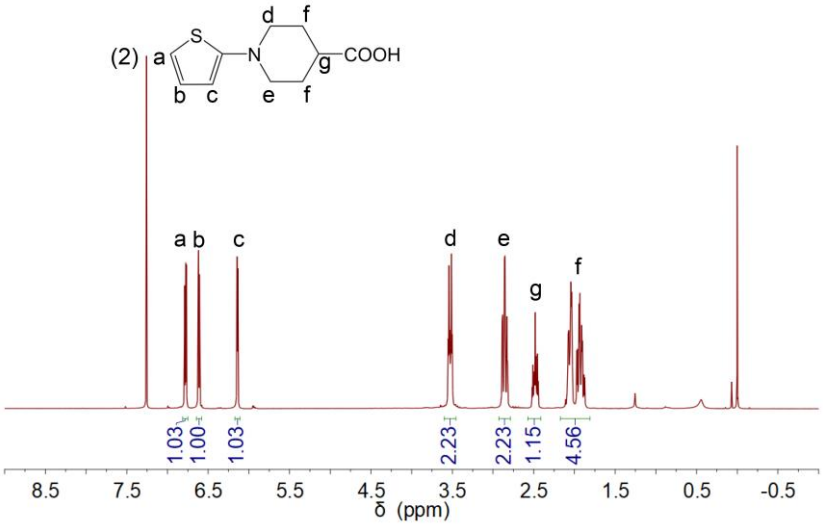

Figure S3. ^{1}H NMR spectra of compound (2).

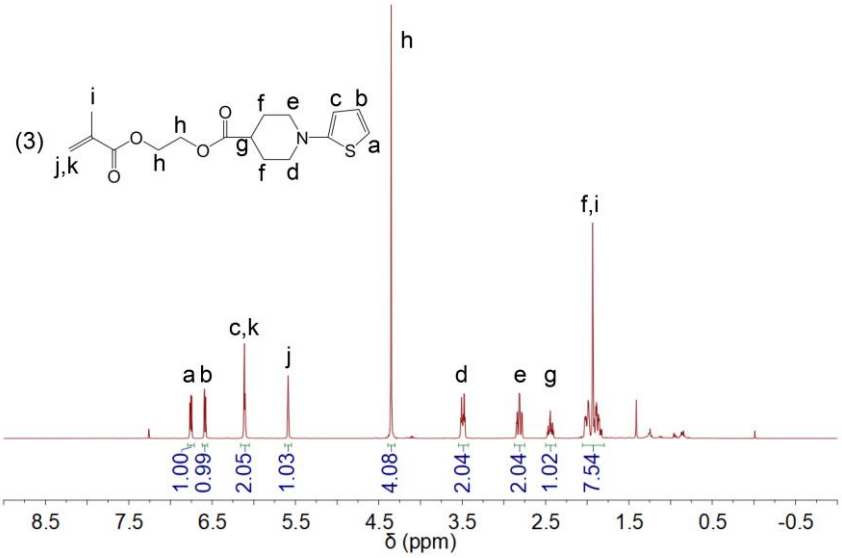

Figure S4. ^{1}H NMR spectra of compound (3).

From the ^{1}H-NMR spectrum of compound 3 (**Figure S4**), the peaks at 3.50, 2.80, 2.42 and 1.88 ppm are attributed to the piperidine atom. The peaks at 6.75, 6.59 and 6.10 ppm are related to the thiophen atom, and the peaks at 6.10 and 5.59 ppm are related to the carbon-carbon double bond hydrogen atoms (-CH=CH-). The characteristic peaks of the thiophen atom shift from 6.75, 6.59 and 6.10 ppm to 8.71, 6.58 ppm, which confirms the successful condensation reaction between compound 3 and croconic acid.

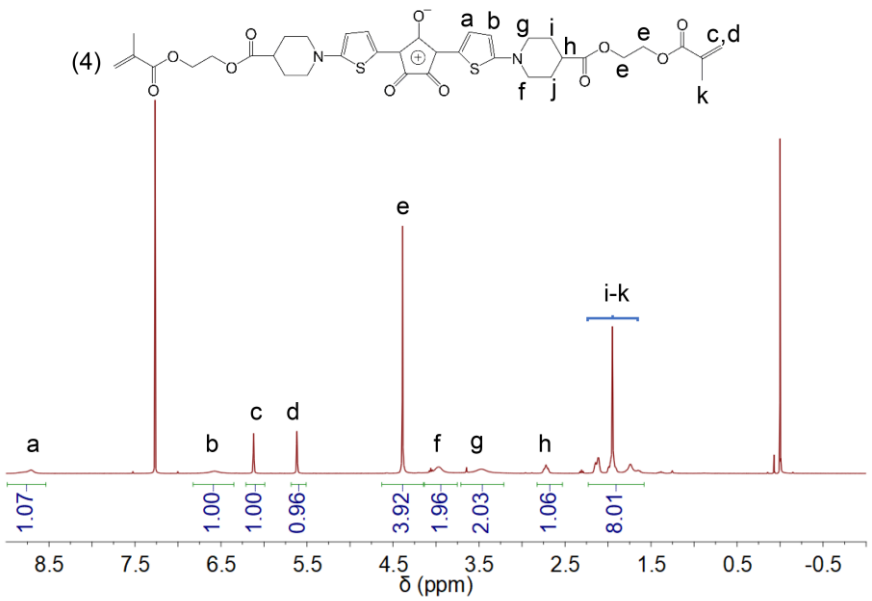

Figure S5. ^{1}H NMR spectra of compound (4).

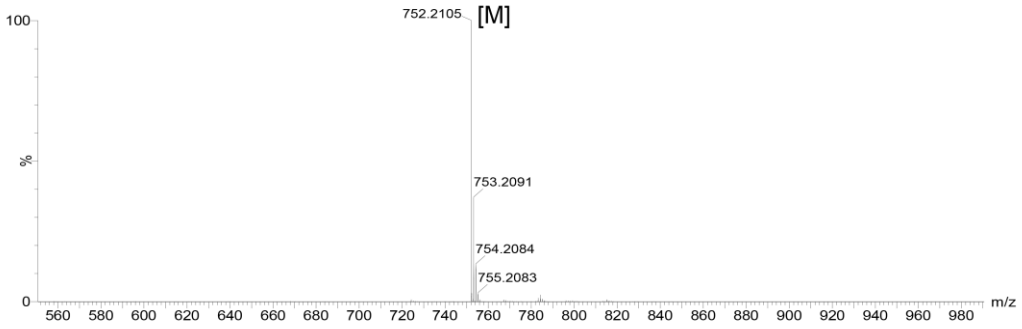

Figure S6. HR-EI-MS spectra of compound (4).

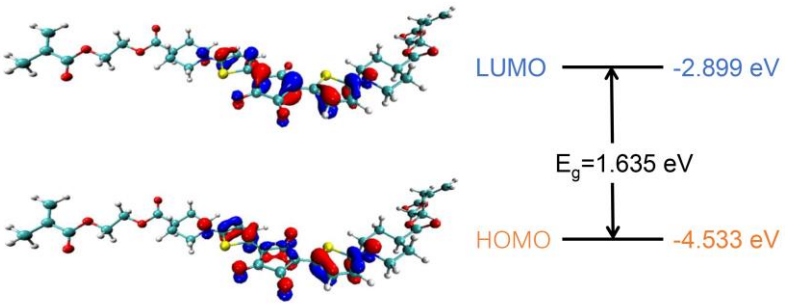

Figure S7. Molecular orbitals of the ground states of YHD798 calculated by B3LYP/TZVP.

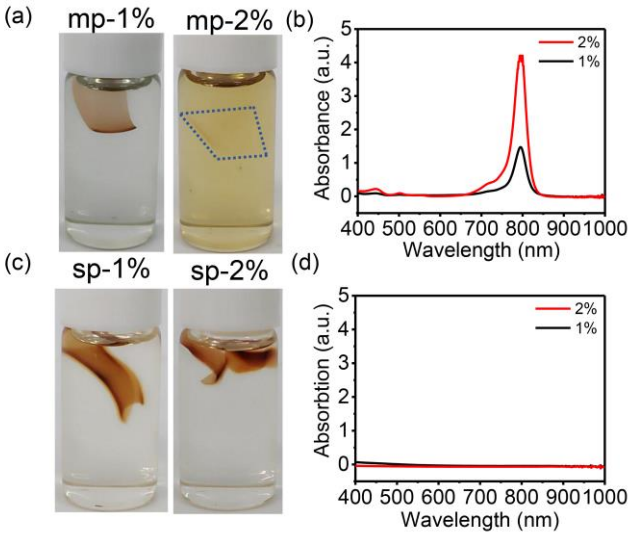

Figure S8. Photographs of gel content experiment of (a) mp-1%, 2% and (c) sp-1%, 2%. UV-vis absorption spectrum of the solution after soaking (b) mp-1%, 2% and (d) sp-1%, 2% films.

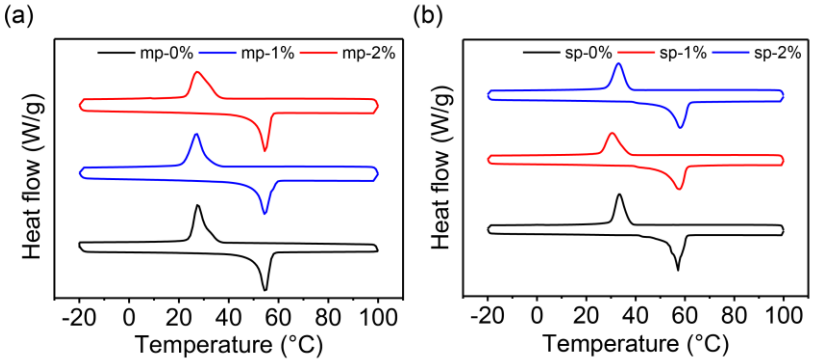

Figure S9. Complete DSC curves of (a) mp-0%, 1%, 2% and (b) sp-0%, 1%, 2%.

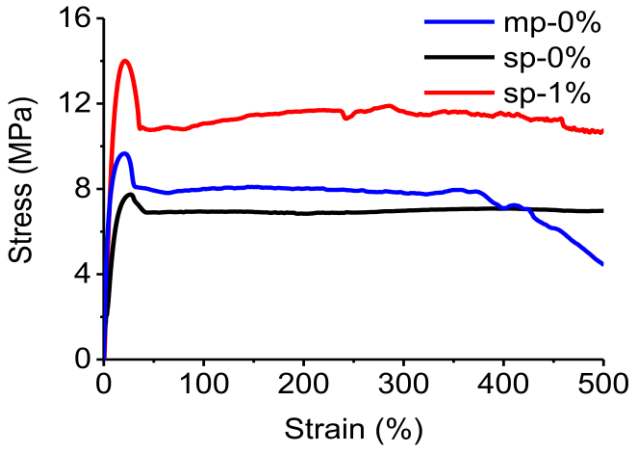

Figure S10. Strain-stress curves of mp-0%, sp-0% and sp-1%.

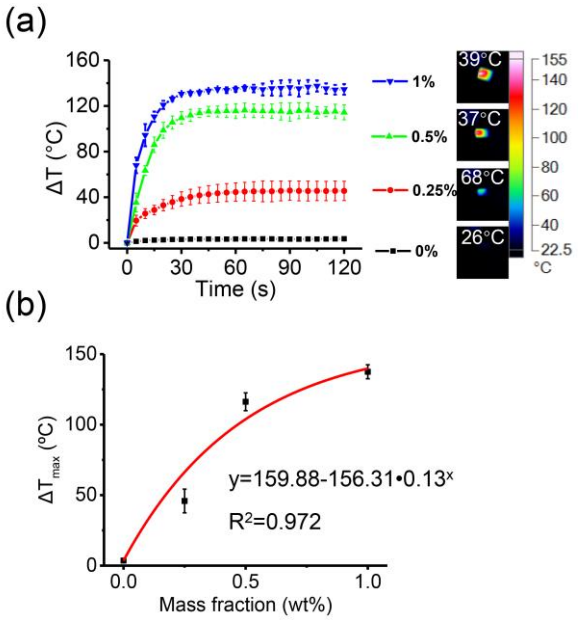

Figure S11. (a) Photothermal curves of mp-x% (x=0, 0.25, 0.5, 1) films irradiated by 0.5 W/cm^2 by using an 808 nm laser. (b) Fitting curve of the maximum temperature change and mass fraction of YHD798.

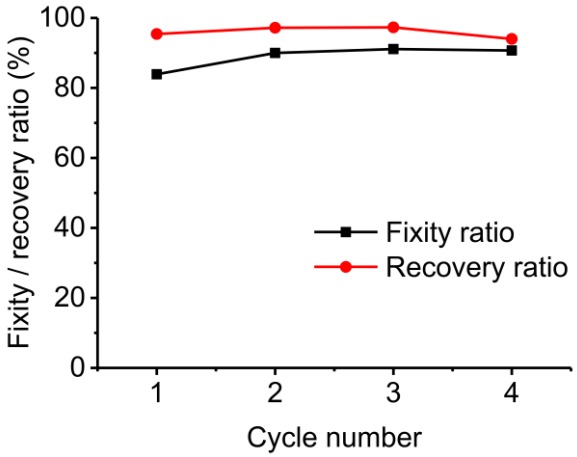

Figure S12. Cycling shape memory performance of sp-1% film under NIR light irradiation (808 nm, 0.5 W/cm^2).

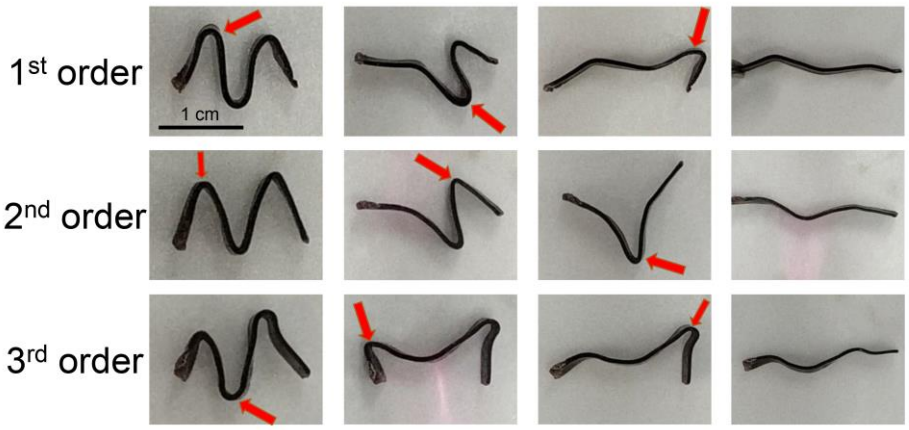

Figure S13. Photographs of demonstrative experiments of NIR-induced shape memory performance: A "M"-shape sample was irradiated with a 808 nm laser at 0.5 W/cm^2 in different orders. 1st order is left, middle, right. 2nd order is left, right, middle. 3rd order is middle, left, right.

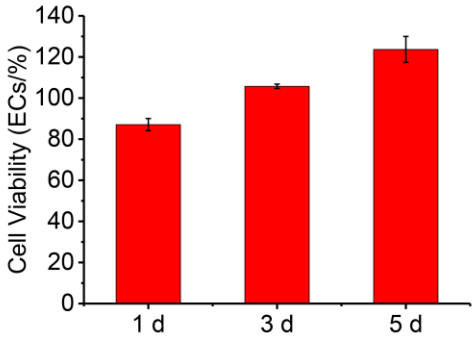

Figure S14. Cytotoxicity of sp-1% film co-cultured with HUVECs for 1, 3, 5 days.

REFERENCES

1. Song, X.; Foley, J. W. A new water-soluble near-infrared croconium dye. *Dyes Pigments* **2008**, *78* (1), 60-64.

2. Liu, L.; Liu, M.-H.; Deng, L.-L.; Lin, B.-P.; Yang, H. Near-infrared chromophore functionalized soft actuator with ultrafast photoresponsive speed and superior mechanical property. *J. Am. Chem. Soc.* **2017**, *139* (33), 11333-11336.