

Supporting Information for

**Photobase-catalysed anionic thiol-epoxy click
photopolymerization under NIR irradiation: from
deep curing to shape memory**

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1. Experimental Section

Materials

Lanthanide-doped UCNP β -NaYF₄:18%Yb, 0.5%Tm nanoparticles were purchased from Shanghai Keyan Phosphor Technology Co., Ltd. Pentaerythritol-tetrakis-3-mercaptopropionate (PE-1) was purchased from Japan Showa Denko, Chembridge International Corp (Taiwan), and used without any purification. Bisphenol A diglycidyl ether (BADGE) was obtained from Jiangsu Sanmu Group Co. Ltd. Phenylacetic acid, sulfuric acid, and phenoxyacetic acid were purchased from Aladdin Industrial Co. 1,5,7-Triazabicyclo [4.4.0]dec-5-ene (TBD), triethylamine (TEA) were bought from J&K Scientific Ltd. All chemical reagents were used as received without further purification. The thioxanthone photobase generators were synthesized according to the literature¹.

Characterization:

UV-Vis absorption spectra of PBGs were taken in acetonitrile by a spectrophotometer UV-3600 Plus (SHIMADZU), while the emission spectrum of UCNP was measured in hexane by CARY Eclipse series fluorescence spectrophotometer. For steady state photolysis tests, the acetonitrile solution containing PBG (10^{-4} mol L⁻¹) and UCNP (0.3 wt%) was irradiated with a NIR light (8.9 W cm⁻²) intermittently and the temperature was kept below 60 °C. The conversions of thiol and epoxy groups after NIR induced photopolymerization were measured using an ATR Fourier-transform infrared (ATR-FTIR) spectroscopy (Thermal Fisher Nicolet iS10 series). Differential scanning calorimeter (DSC) NETZSCH DSC204 was used to determine the kinetics of the curing process. All of the irradiated thiol-epoxy samples were analyzed under isothermal and nonisothermal conditions in a constant N₂ atmosphere with a gas flow of 10 mL/min and a heating rate of 5°C/min.

Preparation and photocuring of the photopolymerizable samples

The photocurable formulations were prepared by mixing UCNP (0.4 wt%) with 3 wt% photobase generators dissolved in the mixture of thiol monomer PE-1 and epoxy monomer BADGE (molar ratio 1:2). For the polymerization kinetics study: about 20 mg of the materials was transferred to an aluminum DSC pan, irradiated under a 980 nm NIR laser (8.9 W cm⁻²) intermittently and the temperature of the samples was controlled below 40°C (monitored by a thermal imager) to prevent premature gelation. For deep photopolymerization: the photocurable samples were injected into a glass tube (17.78 cm long with an outer radius of 5 mm and an inner radius of 4 mm). Then the glass tube was vertically exposed to a fiber coupled laser system intermittently (980 nm, Changchun New Industries Optoelectronics Technology) with an intensity of 29.7 W cm⁻² and the temperature of the samples was controlled below 80°C. After 10 min accumulated irradiation, the tube was placed in an oven at 80°C for 1h. The cured samples were transferred out of the tube and the uncured parts were washed away by acetone. The conversions of functional groups after photopolymerization were measured using an ATR Fourier-transform infrared spectroscopy, monitoring the absorbance intensities of thiol (peak at 2500 cm⁻¹) and epoxy (peak at 860 cm⁻¹)

Shape recovery process of the cured samples

The cured straight stick was firstly heated to 75°C on a hot plate, then deformed to a temporary “S” shape, fixed by cooling to 23°C. The curly stick was then reheated to 75°C on the hot plate or selectively irradiated by a 980 nm NIR laser to actuate the shape recovery process.

2. Figures



Fig S1. Blue fluorescence emitted from UCNPs under 980 nm NIR light irradiation.

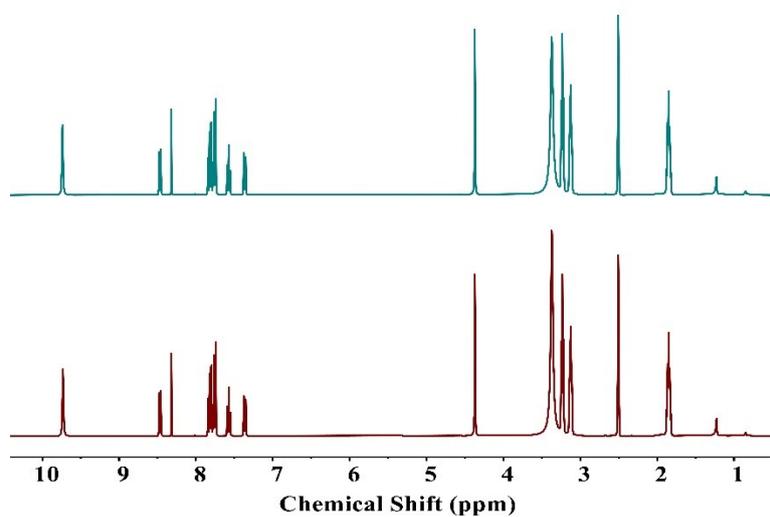


Fig S2. ¹H-NMR spectra of TX-TBD without heating (up) and heated at 60°C for 1h (down).

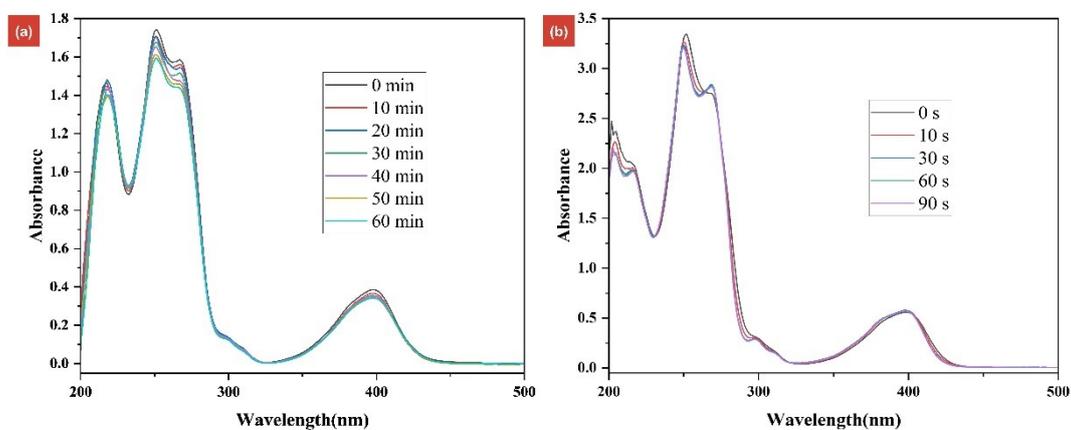


Fig S3. Photolysis of the PBG under (a) upconversion fluorescence and (b) 365 nm LED irradiation.

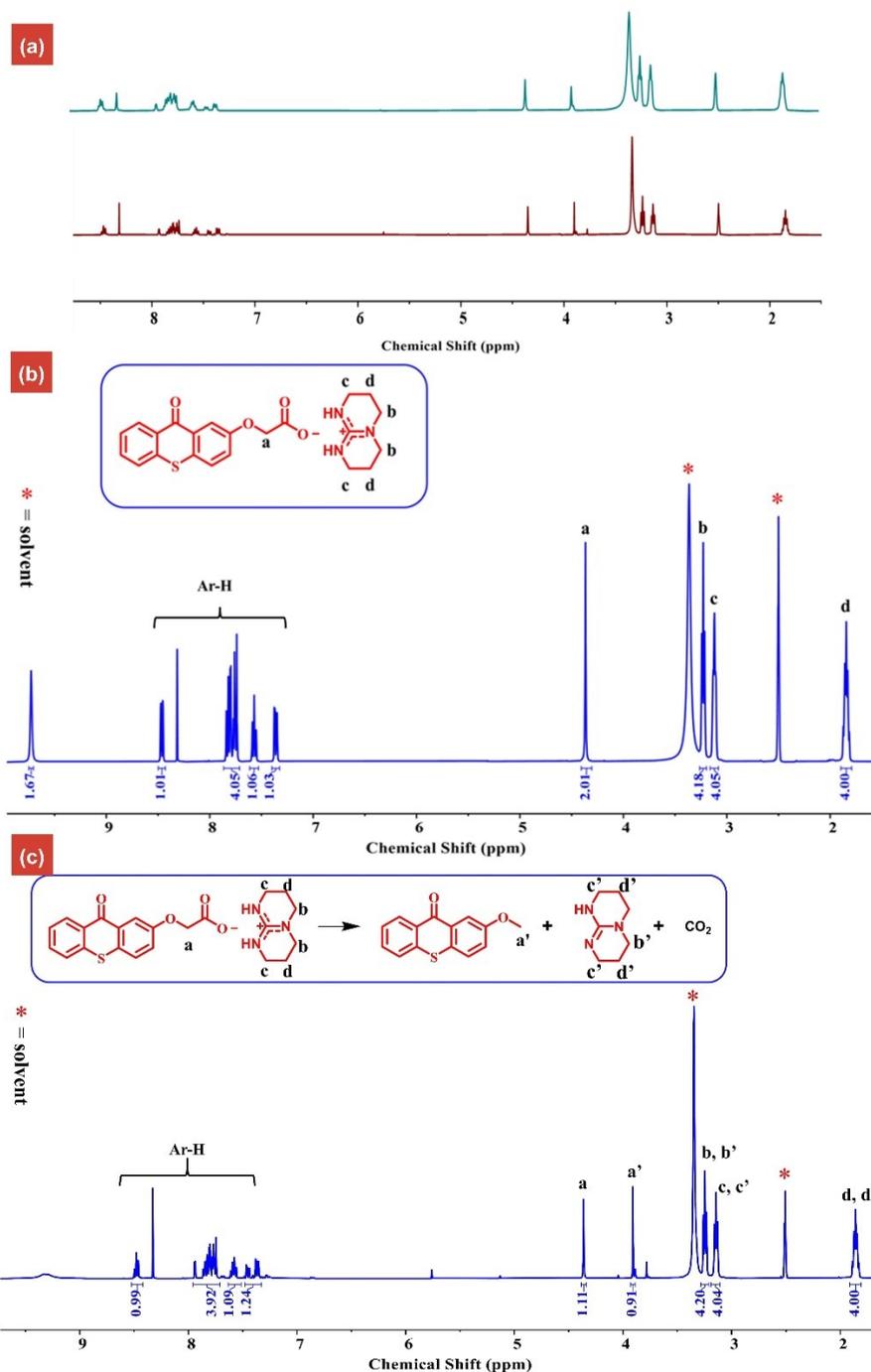


Fig S4. $^1\text{H-NMR}$ spectra of TX-TBD (a) irradiated under 365 nm UV light (120 mW cm^{-2}) for 10 min (up) and under upconversion illuminance (excited by a 980 nm NIR laser with an intensity of 17.85 W cm^{-2}) for 1h (down); analysis of $^1\text{H-NMR}$ spectra of TX-TBD (b) before irradiation and (c) under upconversion illuminance for 1h.

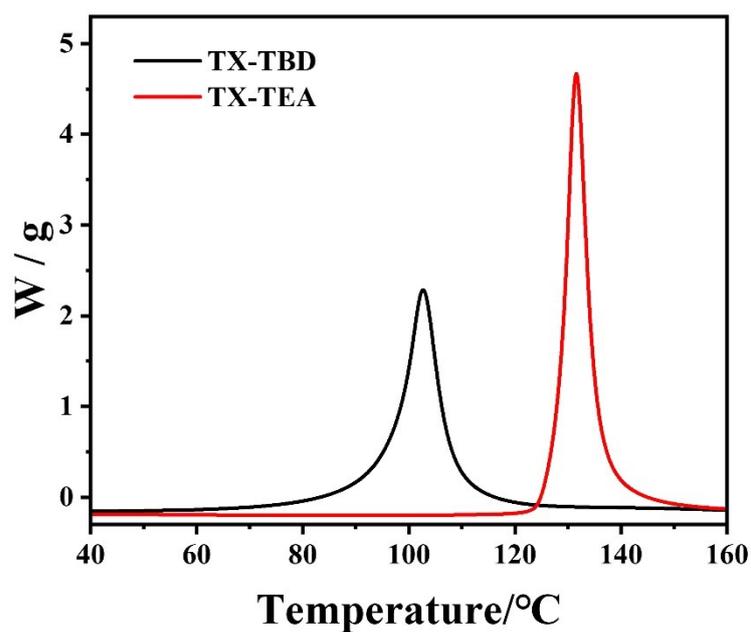


Fig S5. DSC curves of the thiol-epoxy samples after 10 min upconversion fluorescence irradiation with different PBGs.

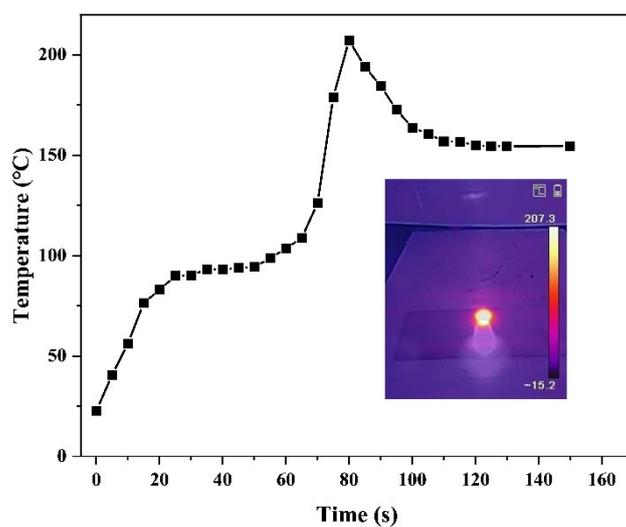


Fig S6. Temperature profiles of the sample under 980 nm NIR irradiation with different irradiation time. The insert shows the thermal graphic of the samples with maximum temperature during irradiation.

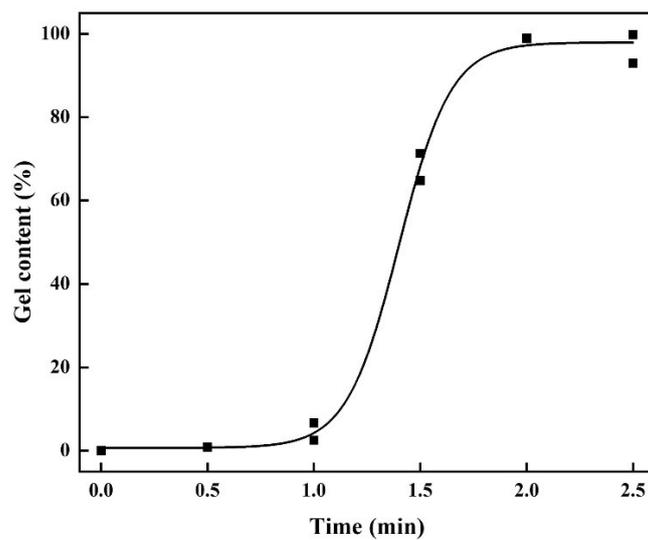


Fig S7. The gel content of the thiol-epoxy polymeric networks obtained with different NIR irradiation time.

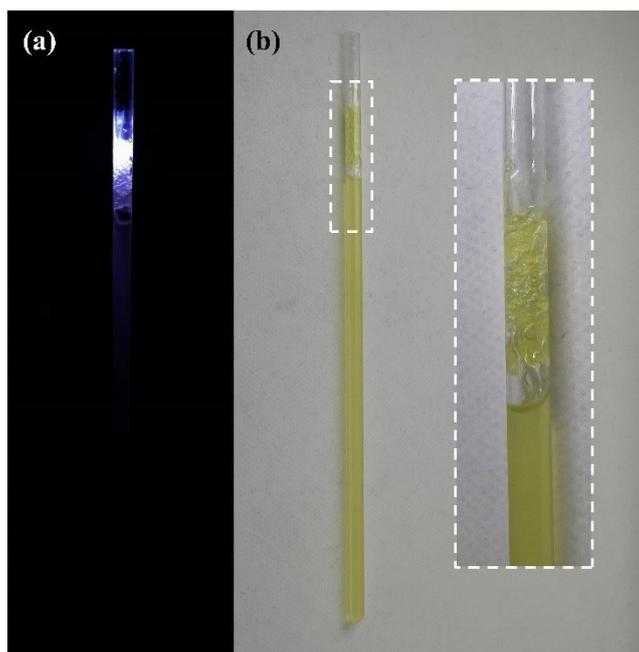


Fig S8. The digital photographs of the photopolymerizable sample (a) during and (b) after the continuous irradiation under a 980 nm laser. The insert shows the magnification view of the designated part.

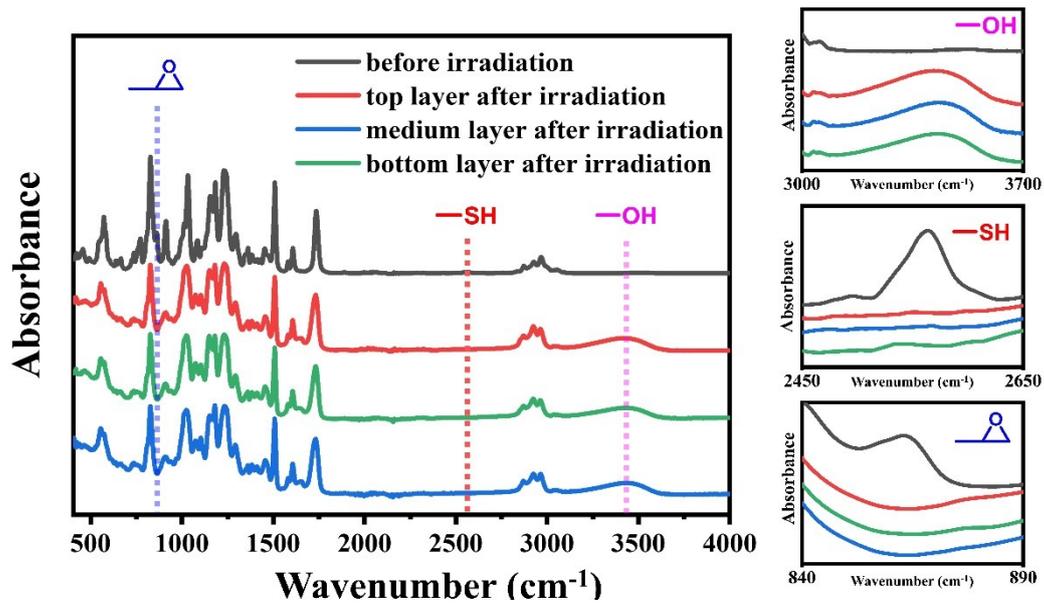


Fig S9. The FI-IR spectra with targeting bands before and after UCNPs-assisted photopolymerization

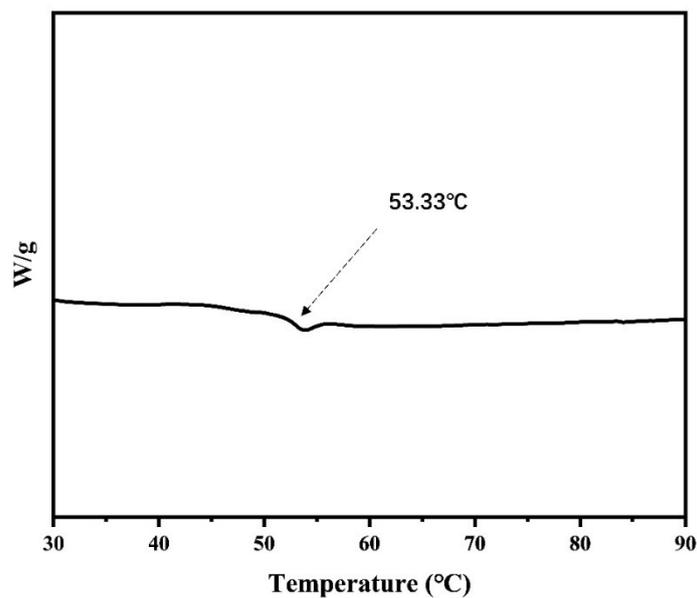


Fig S10. DSC curves of the thiol-epoxy polymeric network obtained under upconversion fluorescence irradiation

3. References

1. Z. Li, W. Shen, X. Liu and R. Liu, *Polym. Chem.*, 2017, 8, 1579–1588.