Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Upconversion nanoparticle-assisted cationic and radical/cationic hybrid photopolymerization using sulfonium salts

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1. Experimental Section

Materials

Lanthanide-doped UCNPs β-$NaYF_4$:18%Yb, 0.5%Tm nanoparticles were purchased from Shanghai Keyan Phosphor Technology Co., Ltd. Sulfonium salts GR55 and GR61 were provided by Hubei Gurun Technology Co., Ltd as gifts. 1,2-Epoxycyclohexane (CHO, 98%), 9-vinylcarbazole (NVC, 98%), n-butyl vinyl ether (BVE, 98%), benzyltriethylammonium chloride (TEBAC) and all the other reagents were purchased from Adamas (China) Co., Ltd. CHO and BVE was purified by the neutral alumina column and other reagents was used without any further purification. Trimethylolpropane triacrylate (TMPTA) and 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (TTA21) were provided by Jiangsu Kailin Ruiyang Chemical Co., Ltd and Jiangsu Tetra New Material Technology Co., Ltd, respectively. The conjugated sulfonium salt CSS was synthesized according to the literature[1]. Chemical structures of the monomers were shown in Figure S1

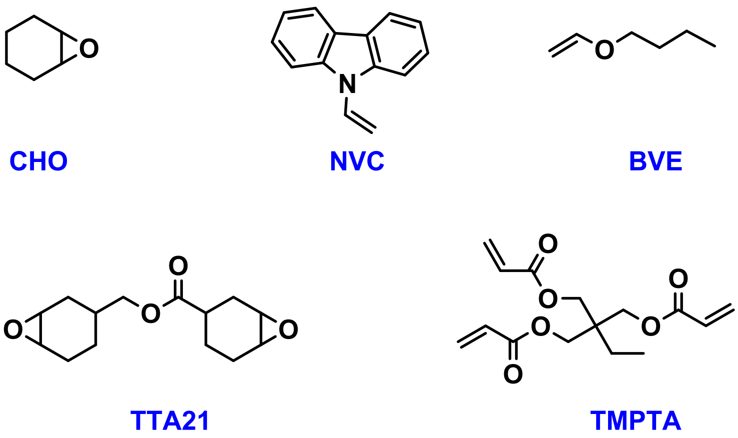

Figure S1. Chemical structures of the monomers

Characterization:

UV-Vis absorption spectra of sulfonium salts 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. The conversions of the cationic photopolymerization using different cationic photoinitiators and monomers under different irradiation conditions were measured using a gravimetric method. The conversions of vinyl and epoxy groups in the hybrid photopolymerization at different depths were measured using an ATR Fourier-transform infrared (ATR-FTIR) spectroscopy (Thermal Fisher Nicolet iS10 series). The thermal stability of the samples obtained under different irradiation conditions was investigated by thermogravimetric analysis (TGA1100SF, Mettler Toledo International Trading Co. Ltd., Switzerland). The samples were heated from 30 to 600 °C under a continuous N_2 flow of 50 mL/min and with a heating rate of 10 °C/min.

Preparation and photocuring of the photopolymerizable samples

General procedure for cationic photopolymerization: The sulfoniums salt GR55 (2×10^{-2}

mmol) and UCNPs (1 wt.%) were dispersed in 1 mL of dry CH_2Cl_2 in the Schlenk tube. With stirring, 1 mL 1, 2-expoxycyclohexane (CHO) was added into the mixed solution. Before the irradiation, the solution was degassed by purging dry nitrogen and the whole photopolymerizations were carried out under the nitrogen atmosphere. After a certain irradiation time of 980 nm NIR laser with a light intensity of 11.6 W (the shape of the laser spot is a circle with a 7 mm diameter), the polymer was then precipitated in methanol (20 mL) before removing the UCNPs via centrifugation. After that, the polymer was separated from the mixture after 3 times centrifugation and dried in vacuum for more than 24h and then weighed. All other polymerizations were performed under the same conditions. The conversion is calculated using the following formula:

$$Convesion\ (\%) = \frac{W_t}{W_0} \times 100\%$$

Where W_t is the weight of the dried sample, and W_0 is the weight of the two monomers before irradiation.

General procedure for hybrid photopolymerization: The photocurable formulations were prepared by mixing UCNPS (0.4 wt%) with 0.3 wt% of photoinitiator sulfoniums salt GR55 and trimethylolpropane triacrylate (TMPTA) / 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (TTA21) (1:1 wt%). The mixture was stirred for 30 min. The photoinitiator was completely dissolved and the UCNPS were evenly distributed in the formulation. Then 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), and then the glass tube was vertically exposed to a fiber coupled laser system (980 nm, Changchun New Industries Optoelectronics Techno logy). The output power was adjusted to 12 W for the activation of the UCNPS. The cured samples obtained with different irradiating time were transferred out of the tube.

The conversions of vinyl and epoxy groups in the hybrid photopolymerization at different depths were measured using an ATR-FTIR (500-4000 cm^{-1} wavelength range, resolution 8 cm, 6 scans per sample). The vinyl and epoxy conversion were determined from the ratio of the absorbance intensities of C=C (for acrylate, peak at 1634 cm^{-1}) and C-O (for epoxy, peak at 810 cm^{-1}) to that of C=O as the reference (peak at 1717 cm^{-1}) before and after curing with the following formula:

$$Convesion\ (\%) = 1 - \frac{A_t/A_{ra}}{A_0/A_{rb}} \times 100\%$$

Where A_0, and A_t denote the absorbance intensities of C=C for acrylate (or C-O for epoxy) before and after curing, while A_{rb} and A_{ra} represent the absorbance intensities of C=O before and after curing, respective.

2. Figures

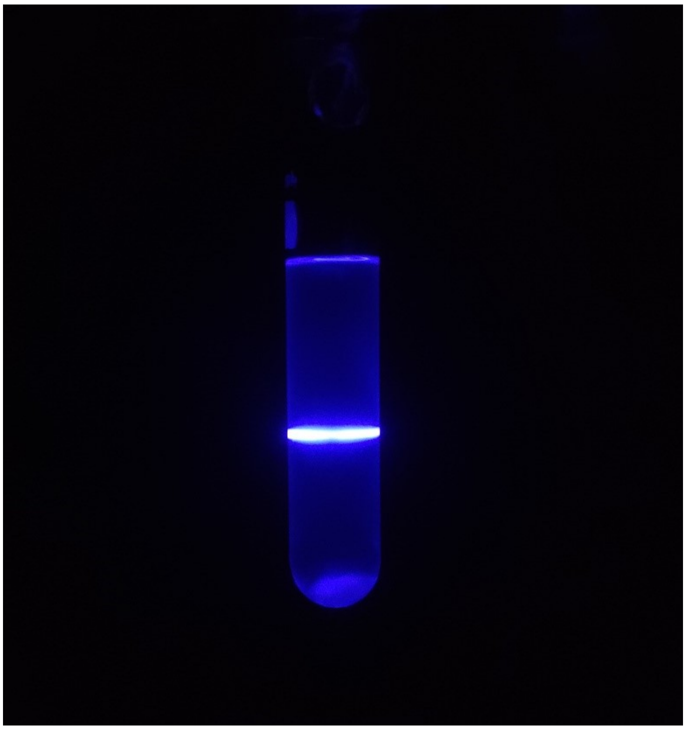

Fig S2. Blue fluorescence emitted from UCNPs under 980 nm NIR irradiation

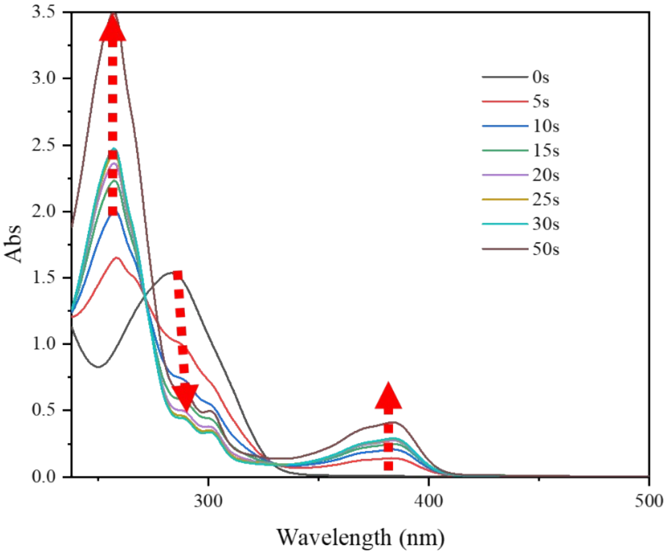

Fig S3. Photolysis of GR55 under 365 nm LED irradiation

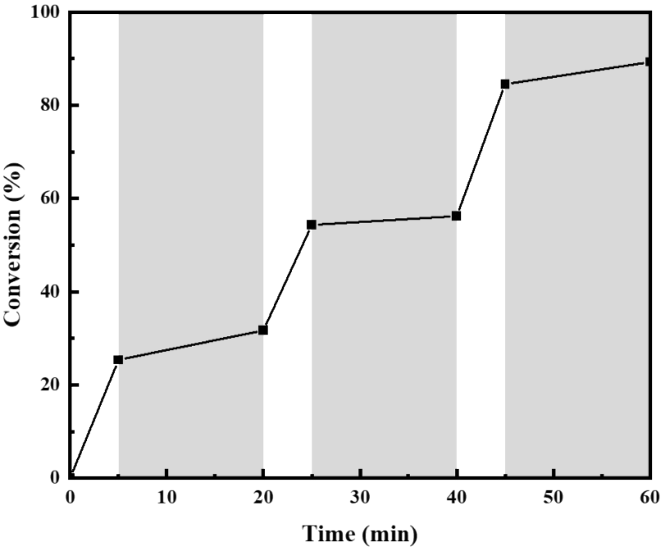

Fig S4. The conversion of epoxy group of **CHO** during the polymerization using **GR55** as an initiator in a turn on–off approach

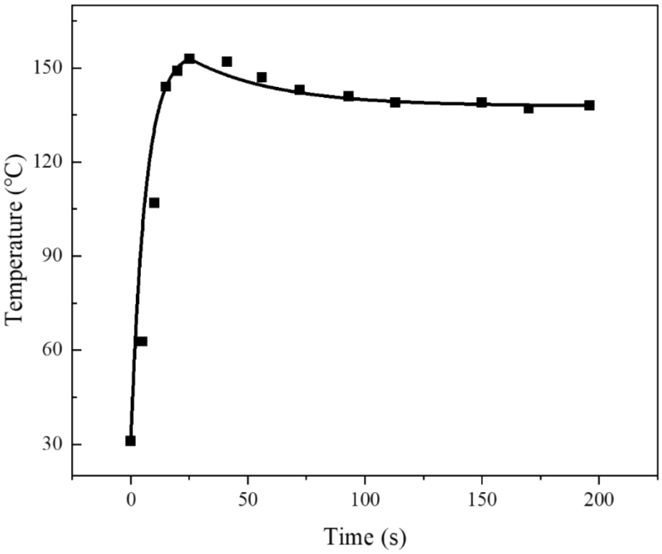

Fig S5. Temperature profiles of the hybrid sample under 980 nm NIR irradiation with different irradiation time.

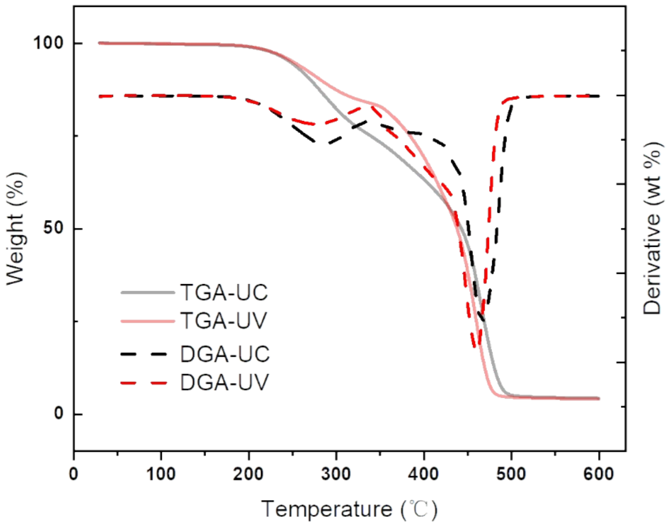

Fig S6. TGA and DTG curves of cured samples obtained under UCNP illuminance and 365 nm LED irradiation

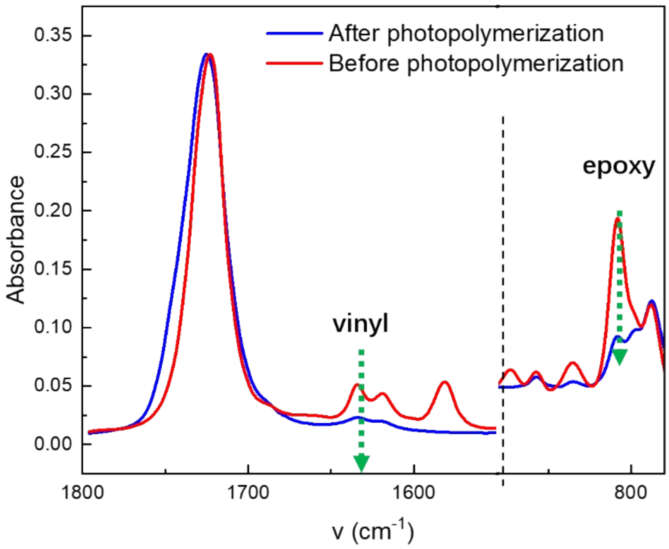

Fig S7. The FI-IR spectra with targeting bands before and after UCNPs-assisted photopolymerization

3. Reference

1. Jin, M.; Wu, X.; Malval, J. P.; Wan, D.; Pu, H. Journal of Polymer Science Part A: Polymer Chemistry 2016, 54, 2722-2730.