# Supplementary Materials: Carbanion as a Superbase for Catalyzing Thiol–Epoxy Photopolymerization

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## **Experimental Section**

## Electron Spin Resonance Spin-Trapping

The electron spin resonance (ESR) experiments were carried out using an EMXplus-10/12 X-band spectrometer (Bruker, Karlsruhe, Germany) at 100 kHz magnetic field modulation, which was used to adjust the power intensity to 20 mW. The mixture of PBGs (photobase generators, 1 mol%) and Phenyl-N-tert-butyl-nitrone (PBN, TCI Chemicals, Shanghai, China, 2 mol%) was dissolved in benzene and deoxygenated with nitrogen for 5 min before irradiation. The radicals were generated through photolysis at room temperature (LED source emitting 365 nm light, UV Pro, Shanghai, China, irritation for 30 s).

## Laser Flash Photolysis

Laser flash photolysis (LFP) experiments employed the Edinburgh Analytical Instruments F900 (Edinburgh Instruments, Livingston, United Kingdom) which used an Nd/YAG laser (355 nm, 25 mJ per 8 ns pulse) and a multichannel scaler. PBGs samples at concentrations ranging from 0.1 to 0.3 mM were prepared in acetonitrile, which were purged with the appropriate gas (i.e., N<sub>2</sub>, Ar<sub>2</sub>) for 30 min before, and during, the acquisition of the transient spectrum.

## Figures



Figure S1. UV-VIS absorbance spectrum of PBGs in acetonitrile solution.



**Figure S2.** UV-VIS spectra changes of TX-NEt (9-Oxo-9H-thioxanthen-2-yl)-acetatetetraethyl-ammonium) solution (10<sup>-4</sup> M) without (**a**) and with (**b**) the addition of phenol red irradiated with an Hg lamp at different light doses.



**Figure S3.** Photos of generated CO<sub>2</sub> detection: (**a**) before and (**b**) for 20 min UV irradiation solution of TX-NEt and TX (thioxanthone acetic acid,  $5.0 \times 10^{-3}$  M), solutions of Na<sub>2</sub>CO<sub>3</sub> ( $2.0 \times 10^{-4}$  M) using an IWATA UV-100 LED irradiating 365 nm light.



Figure S4. <sup>1</sup>H NMR spectrum of TX-NEt in CDCl<sub>3</sub> with D<sub>2</sub>O under 30 s irradiation.



**Figure S5.** Ring-opening polymerization <sup>1</sup>H NMR spectra (DMSO-d6) of BADGE (a diglycidyl ether ), and mixtures of TX and BADGE irradiated by an LED lamp (**a**); and the conversion degree of BADGE ring-opening under irradiation (**b**).



**Figure S6.** Transient optical absorption spectrum following laser excitation (355 nm) of TX-NEt in nitrogen saturated acetonitrile solution at 25 °C.



**Figure S7.** Transient optical absorption spectrum following laser excitation (355 nm) of TX in nitrogen-saturated acetonitrile solution at 25 °C.



Figure S8. ESR spectrum of TX-NEt (left) and TX (right).



Figure S9. TG cures of photocured films catalyzed by different PBGs.