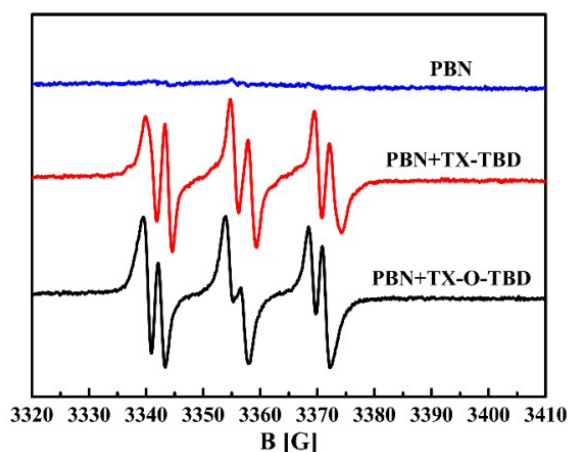


## Supplementary Information

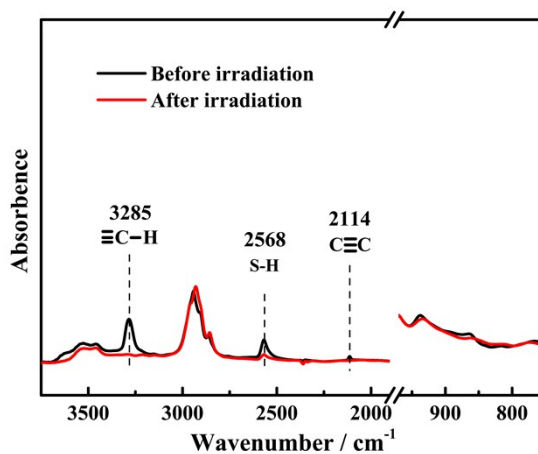
### Efficient Unimolecular Photoinitiators for Simultaneous Hybrid Thiol-Yne-Epoxy Photopolymerization under Visible LED Light Irradiation

Zhiquan Li, Weizhen Shen, Xiaoya Liu and Ren Liu\*

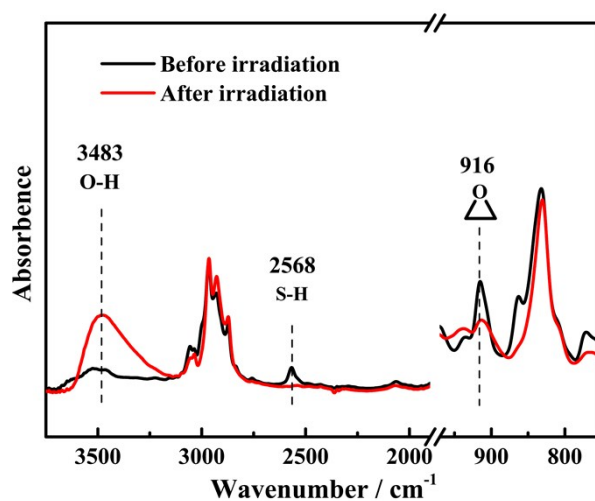
\* The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu 214122, P. R. China. E-mail: liuren@jiangnan.edu.cn;



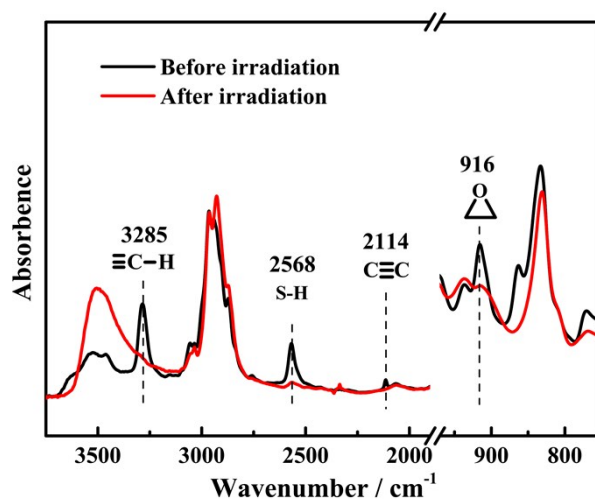
**Figure S1** experimental ESR spectra of control (blue curve), TX-TBD (red curve), and TX-O-TBD (black curve) in benzene with PBN under visible (405 nm) LED light irradiation for 30s.



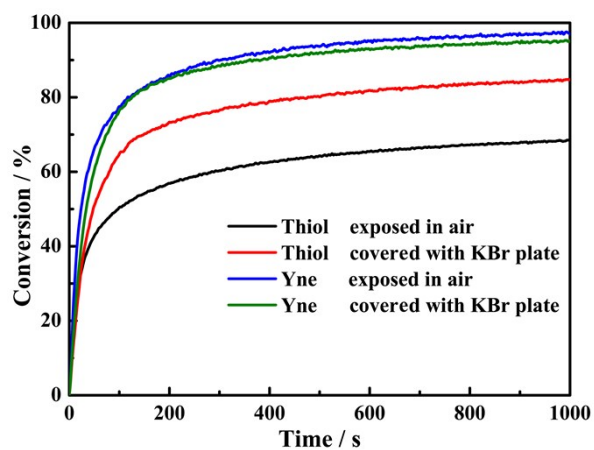
**Figure S2.** IR spectra of thiol-yne binary system TE0 before and after irradiation (light intensity: 168mW/cm<sup>2</sup>, 1000s).



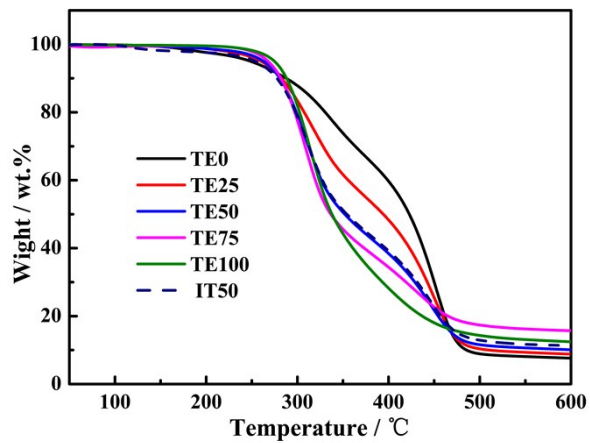
**Figure S3.** IR spectra of thiol-epoxy binary system TE100 before and after irradiation (light intensity: 168mW/cm<sup>2</sup>, 1000s).



**Figure S4.** IR spectra of thiol-yne-epoxy hybrid system TE50 before and after irradiation (light intensity: 168mW/cm<sup>2</sup>, 1000s).



**Figure S5.** Kinetics study of thiol-yne reaction exposed in air or covered with KBr plate.



**Figure S6.** TGA curves of different thiol-yne/thiol-epoxy hybrid network with various compositional ratios.