

Copper (photo)redox catalyst for radical photopolymerization in shadowed areas and access to thick and filled samples

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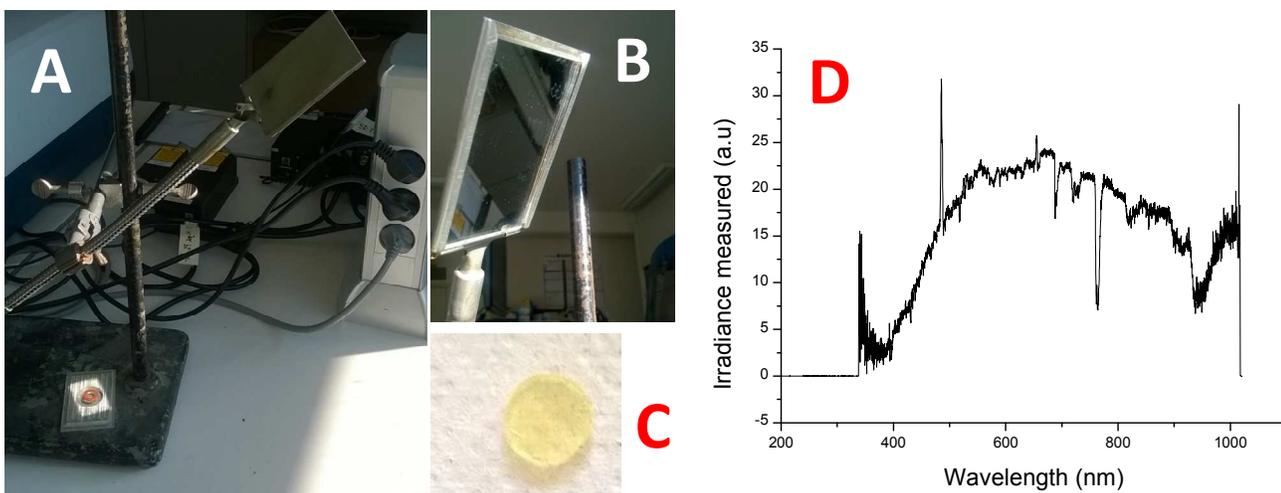


Figure S1: A,B: Experimental set-up for sunlight induced photopolymerization. C: Photopolymer obtained under sunlight exposure. D: Emission spectra of the sun on the day of the experiment (behind glass window)



Figure S2: A: Experimental set-up used for the photopolymerization of the model resin (thickness = 9 cm) (LED@405 nm); Pasteur pipette **wrapped in black tape** with polymerizable medium containing: 0.13 wt% of Cu(I) / 2.0 wt% Iod / 6 wt% Tin(II). B: **9 cm cured polymer after breaking the glass (Pasteur Pipette) surrounding the polymer**

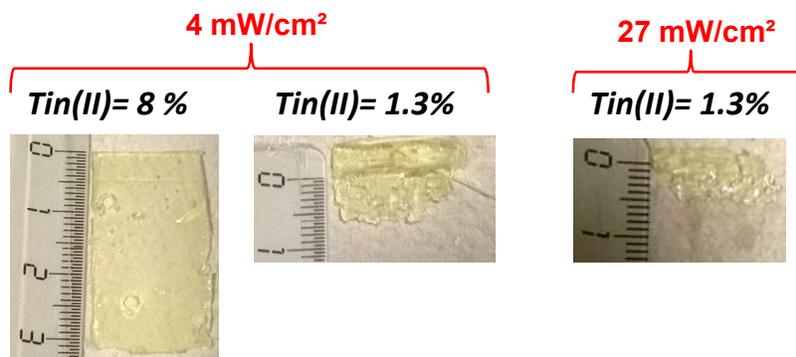


Figure S3: Photopolymers obtained for the model resin, under air, with 3 mm of the sample irradiated by a LED@405 nm (as illustrated in Figure 6). Initiating system: 0.17 wt% Cu(I); 2.0 wt% Iod. Upon 4 mW/cm² irradiance with Tin(II)=8.0 wt% and Tin(II)=1.3 wt% and upon 27 mW/cm² with Tin(II)=1.3 wt%.

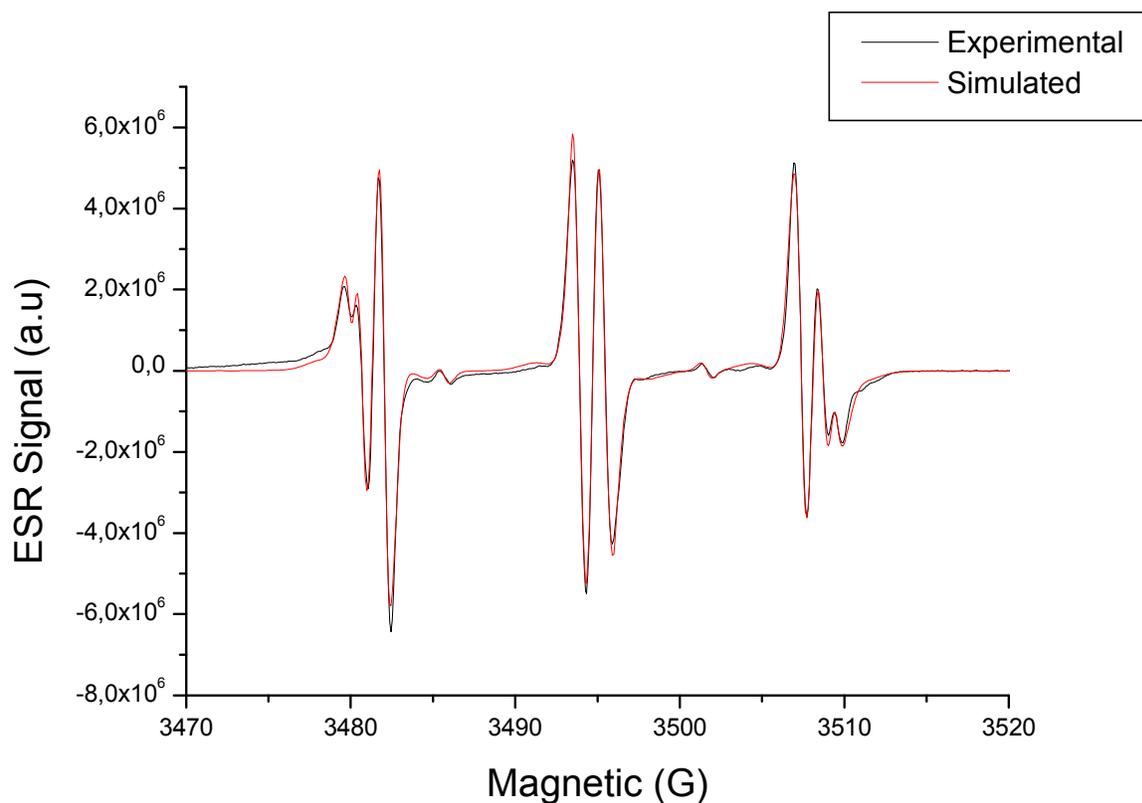


Figure S4. ESR spectra in toluene/DCM (85/15 v/v) under air, without light activation when mixing 0.5 mM Cu(I) with 2 mM R''OOH. Red curve: simulation fitting.

Proposed interpretation for Figure S4: Two species corresponding to oxygen-centered radicals

R''OO^{•1} (Simulated: 30 % for $a_N = 13.2$ G and $a_H = 1.3$ G) and R''O^{•2} (Simulated: 44 % for $a_N = 14.3$ G

and $a_H = 2.0$ G). The hyperfine coupling constants of R''O[•] are lower than the one in figure 8B as a

result of a lower polarity (no Tin(II)) as demonstrated by Beckwith et al.³ The carbon-centered

radicals (two species) might be related to hydrogen abstraction (Simulated: 4 % for $a_N = 14.2$ G and $a_H = 3.9$ G; 22 % for $a_N = 14.7$ G and $a_H = 3.5$).

References:

- (1) Niki, E.; Yokoi, S.; Tsuchiya, J.; Kamiya, Y. Spin Trapping of Peroxy Radicals by Phenyl N-(Tert-Butyl) Nitron and Methyl N-Duryl Nitron. *J. Am. Chem. Soc.* **1983**, *105* (6), 1498–1503.
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- (3) Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. Kinetics of Nitroxide Radical Trapping. 1. Solvent Effects. *J. Am. Chem. Soc.* **1992**, *114* (13), 4983–4992.