

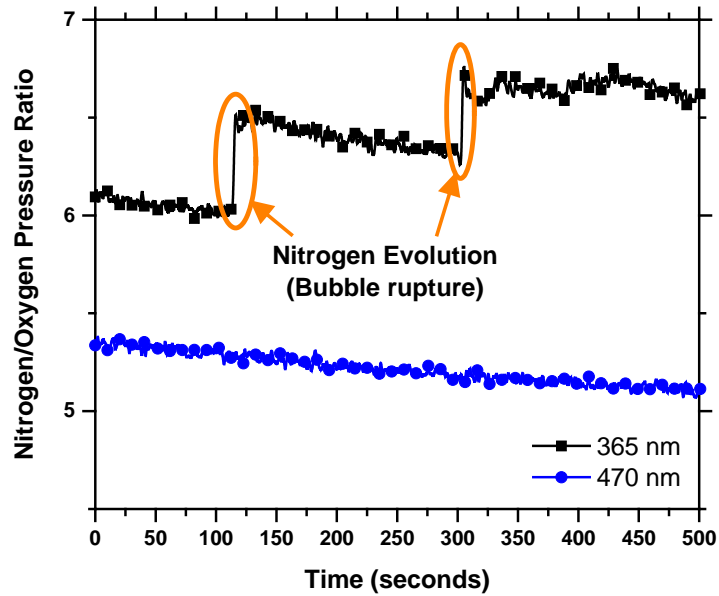
## †Electronic Supplementary Information (ESI)

### Blue-light activated rapid polymerization for defect-free bulk Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) crosslinked networks

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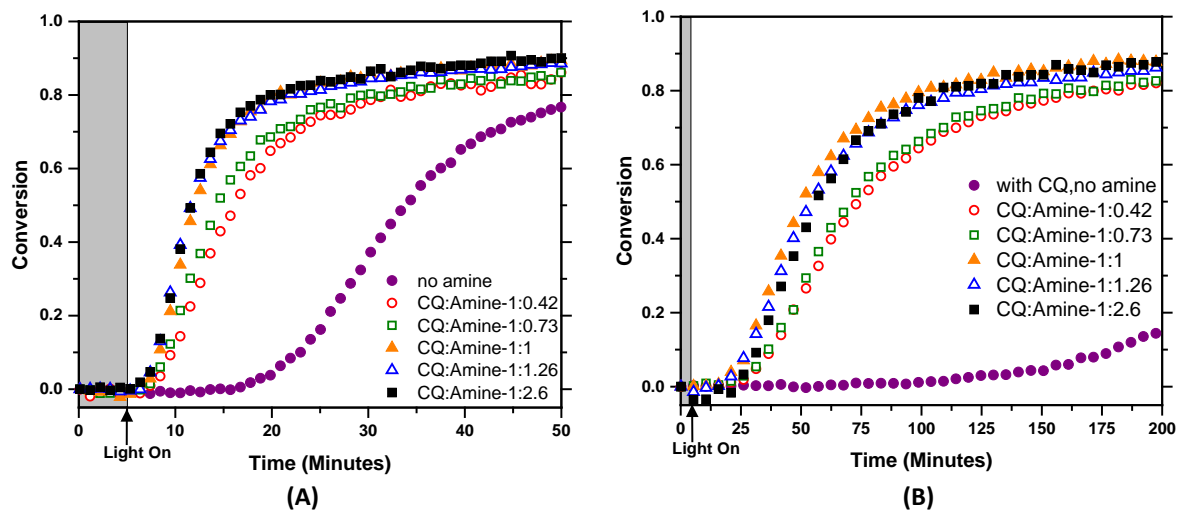
#### Table of Contents:

<b>Figure S1. Gas chromatography (GC) mass analysis for irradiation of bis(6-azidohexyl)(1,3-phenylenebis(propane-2,2-diyl))dicarbamate. ....</b>	<b>2</b>
<b>Figure S2. Amine concentration effects at high and low intensities. ....</b>	<b>3</b>
<b>Figure S3. Intensity and photo-initiator concentration effect on the photo-CuAAC polymerization kinetics. ....</b>	<b>4</b>
<b>Figure S4. Intensity effects in photo-CuAAC polymerization reaction. ....</b>	<b>5</b>
<b>Figure S5. Bulk photo-CuAAC kinetics using different amines ....</b>	<b>6</b>
<b>Figure S6. Dark polymerization of the photo-CuAAC reaction using different amines and time intervals. ....</b>	<b>7</b>
<b>Figure S7. Effect of defects on clarity of photo-CuAAC network films. ....</b>	<b>8</b>



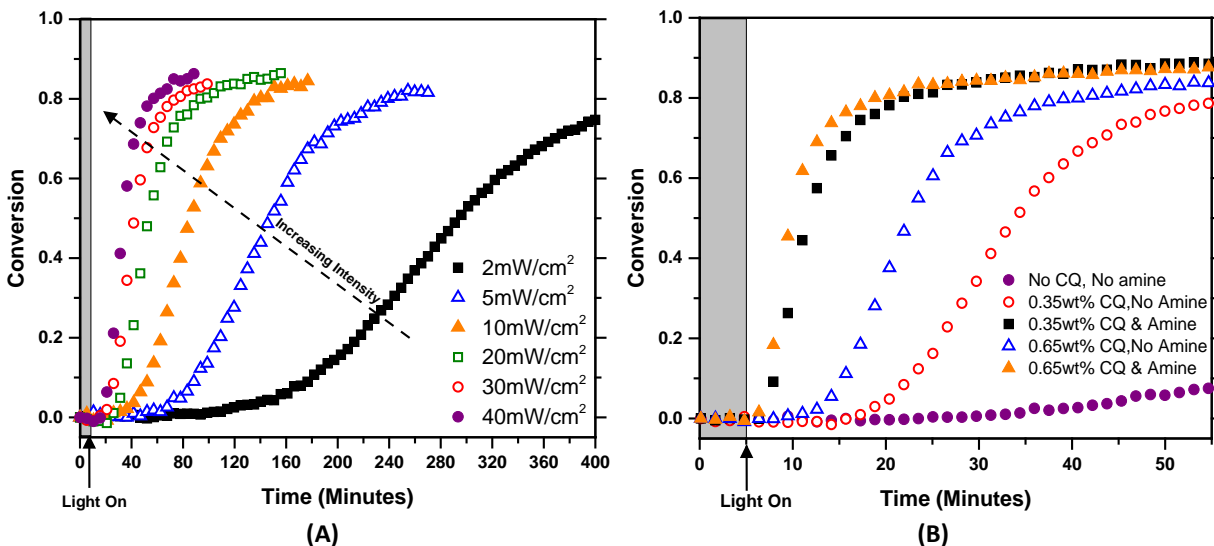
**Figure S1. Gas chromatography (GC) mass analysis for irradiation of bis(6-azidohexyl)(1,3-phenylenebis(propane-2,2-diyl))dicarbamate.**

The decomposition of the azide monomer (**1**) was tracked using GC-mass analysis. Upon irradiation of the sample with UV light (365 nm wavelength) at an intensity of  $40 \text{ mW cm}^{-2}$ , the production of bubbles were observed and the rupture of which led to a spike in the nitrogen to oxygen ratio in the environment above the surface of the monomer detected by probe. In contrast, no bubbles were observed in the sample irradiated with blue-light (470 nm wavelength) of same intensity, and consequently no spike in the nitrogen to oxygen ratio was observed. This experiment further supports that bubbles in the polymer films were mainly caused by nitrogen formation from azide decomposition under UV-light.



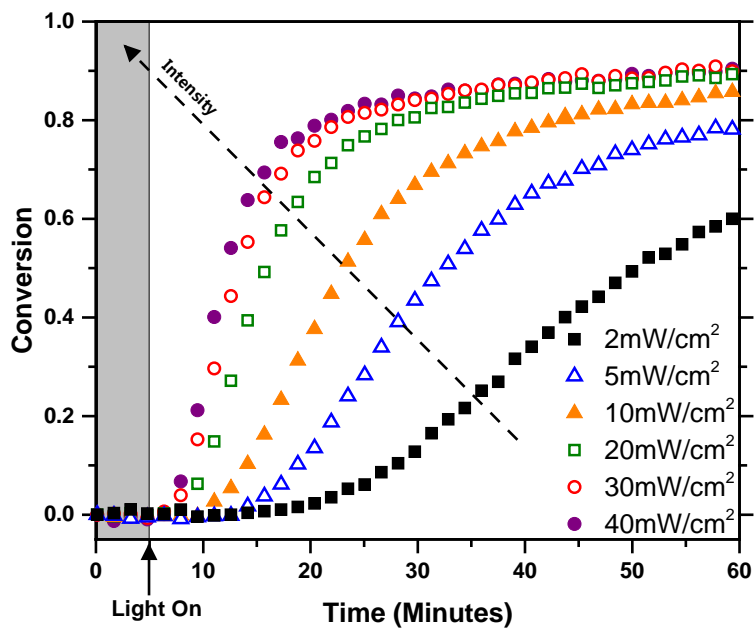
**Figure S2. Amine concentration effects at high and low intensities.**

The conversion of alkyne functional groups was monitored via real-time near infrared (NIR) spectroscopy during the irradiation of the CuAAC formulation used in the accompanying communication. All samples contained a 1:1 azide:alkyne functional group ratio, 1.5 wt% CuCl<sub>2</sub>-PMDETA catalyst and 0.35 wt% camphorquinone while increasing the concentration of amine (4,N,N-trimethyl aniline) between 0.42 wt% and 2.6 wt% relative to camphorquinone at **(A)** 40 mW cm<sup>-2</sup> and **(B)** 2 mW cm<sup>-2</sup> of 470 nm incident light. All samples were irradiated after 5 minutes in the dark (marked by (■) shaded region). The results suggest that threshold value exists for the camphorquinone to amine ratio above which the reaction kinetics are no longer increased. In this case, the 1:1 CQ:amine ratio is the threshold value.



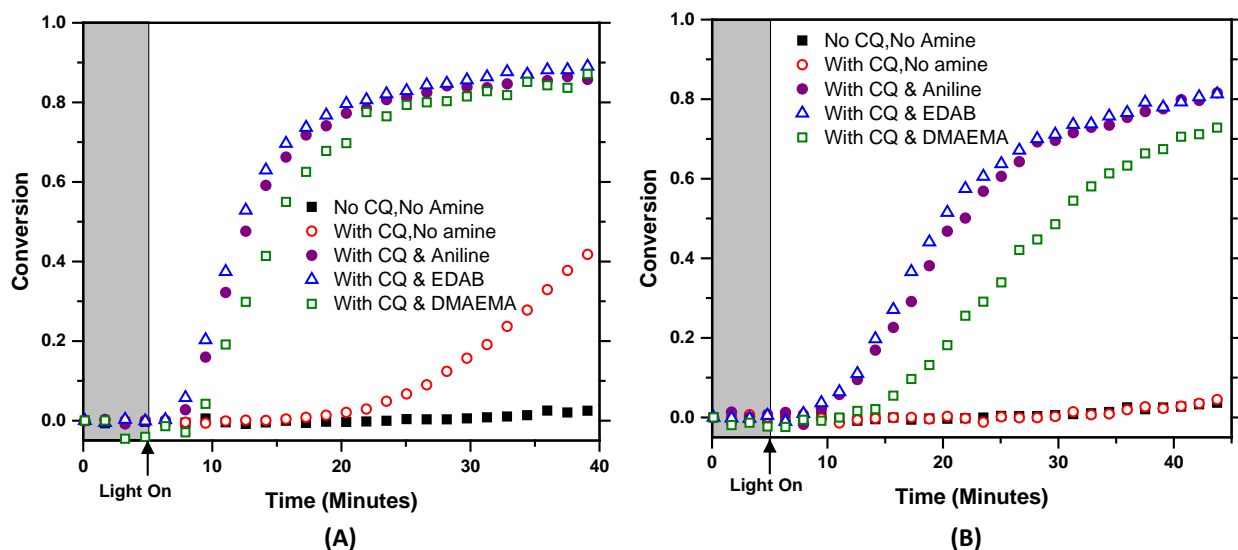
**Figure S3. Intensity and photo-initiator concentration effect on the photo-CuAAC polymerization kinetics.**

The conversion of the alkyne functional groups in a photo-CuAAC polymerization tracked via real-time near infrared (NIR) spectroscopy. All samples contained a 1:1 azide: alkyne functional group ratio, 1.5 wt% CuCl<sub>2</sub>-PMDETA catalyst. All samples were irradiated starting after 5 minutes in dark with 470 nm light. **(A)** depicts that the polymerization kinetics is increased by increasing the light intensity (470 nm) with presence of camphorquinone (0.35 wt%) only, without any addition of any amine. **(B)** shows that the reaction kinetics can alternatively be increased by increasing the relative ratio of camphorquinone and amine at a constant intensity of 40 mW cm<sup>-2</sup>. The final monomer conversions plateau at approximately 90 % in the amine containing samples irrespective of the CQ and amine ratio owing to vitrification in the crosslinked network.



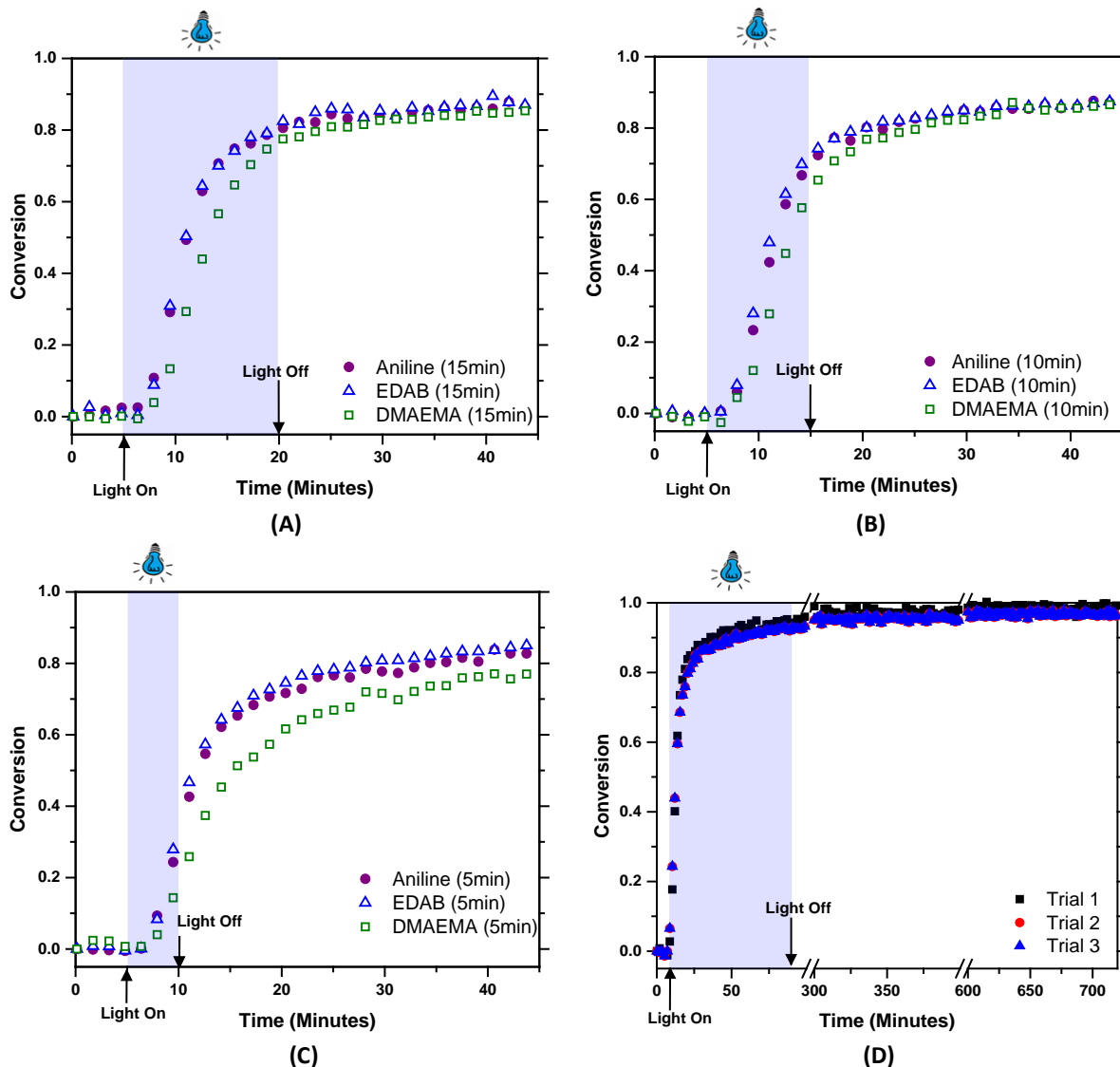
**Figure S4. Intensity effects in photo-CuAAC polymerization reaction.**

The conversion of the alkyne functional groups in a photo-CuAAC polymerization tracked via real-time near infrared (NIR) spectroscopy. All samples contained a 1:1 azide: alkyne functional group ratio, 1.5 wt% CuCl<sub>2</sub>-PMDETA catalyst, 0.35 wt% camphorquinone, and 0.35 wt% of 4,N,N-trimethyl aniline. The intensity was increased from 2 to 40 mW cm<sup>-2</sup> of 470 nm wavelength light. The light intensity was found to scales to I<sup>0.5</sup>.



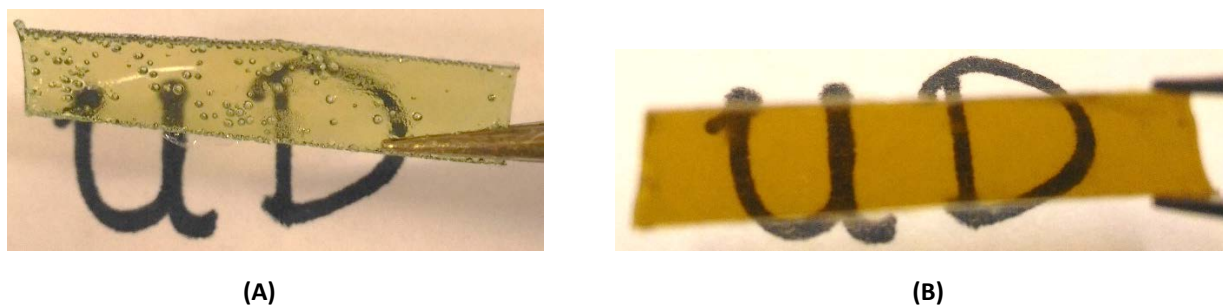
**Figure S5. Bulk photo-CuAAC kinetics using different amines**

The conversion of the alkyne functional groups in a photo-CuAAC polymerization tracked via real-time near infrared (NIR) spectroscopy. All samples contained a 1:1 azide: alkyne mol ratio, 1.5 wt%  $\text{CuCl}_2\text{-PMDETA}$  catalyst, and 0.35 wt% camphorquinone (when present). Different tertiary amines were used at 0.9 wt% and the kinetics were compared. The amines used were 4,N,N-trimethyl aniline (Aniline-●), ethyl-4-dimethylamino benzoate (EDAB -▲), and 2-dimethylaminoethyl methacrylate (DMAEMA -□). All samples were irradiated with 470 nm light starting after 5 minutes in dark (to assess stability): **(A)** at an intensity of  $30 \text{ mW cm}^{-2}$  and **(B)** at an intensity of  $10 \text{ mW cm}^{-2}$ . The control materials not containing camphorquinone or amine exhibit extremely slow kinetics. All three amines reached similar final conversions, but the polymerization rate of the resin containing DMAEMA was slower due to the presence of a double bond on the amine, which reactively competes with the initiated radicals.



**Figure S6. Dark polymerization of the photo-CuAAC reaction using different amines and time intervals.**

The conversion of the alkyne functional groups in a photo-CuAAC polymerization was tracked via real-time near infrared (NIR) spectroscopy. All specimens formulated with a 1:1 azide: alkyne functional group ratio, 1.5 wt% CuCl<sub>2</sub>-PMDETA catalyst, 0.35 wt% camphorquinone, and 0.9 wt% of the amine. The specimens were then irradiated with 470 nm light after 5 minutes at an intensity of 40 mW cm<sup>-2</sup> in the dark. To demonstrate assess dark polymerization, the light was ceased after different time intervals: **(A)** 15 minutes, **(B)** 10 minutes, and **(C)** 5 minutes (marked by ( ) shaded region). After 45 minutes, all the samples reached similar conversions (between 80 and 90%). The figure **(D)** demonstrates that continuous irradiation is not necessary to reach full conversion. All samples reached full conversion after 720 minutes owing to the stability of the Cu(I) oxidation state.



**Figure S7. Effect of defects on clarity of photo-CuAAC network films.**

The image **(A)** is of a defect containing film from bulk photo-CuAAC crosslinked network showing the unclear view of the letters “UD” behind the films making it ineffective for the applications requiring optical transparency/clarity. The formulation was photopolymerized under UV light (365 nm) of  $40 \text{ mW cm}^{-2}$  intensity for 15 minutes. The sample **(A)** contains 1:1 azide: alkyne functional group ratio, 1.5 wt%  $\text{CuCl}_2\text{-PMDETA}$  catalyst and 1 wt% Irgacure 819. Unlike **(A)**, the image **(B)** obtained by photopolymerization under blue-light (470 nm) of similar intensity of  $40 \text{ mW cm}^{-2}$  is defect-free and transparent without any obstruction in the clarity and the letters “UD” are clearly visible. The formulation for sample **(B)** contains 1:1 azide: alkyne functional group ratio, 1.5 wt%  $\text{CuCl}_2\text{-PMDETA}$  catalyst and 0.35 wt% camphorquinone, and 0.35 wt% of 4,N,N-trimethyl aniline irradiated for 15 minutes.