Electronic Supplementary Information (ESI):

Towards understanding the kinetic behavior and limitations in photo-induced copper(I) catalyzed azide-alkyne cycloaddition (CuAAC) reactions

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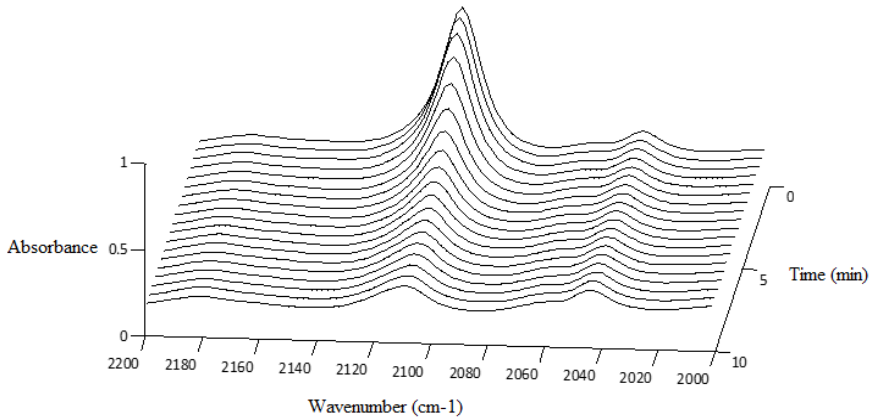

Figure S1. The change in absorbance of the azide peak at between 2080 and 2150 cm^{-1} over the first 10 minutes of a photo-CuAAC reaction using FTIR spectroscopy. The area under a reference peak at 2044 cm^{-1} from the DMF solvent used is constant throughout the reaction.

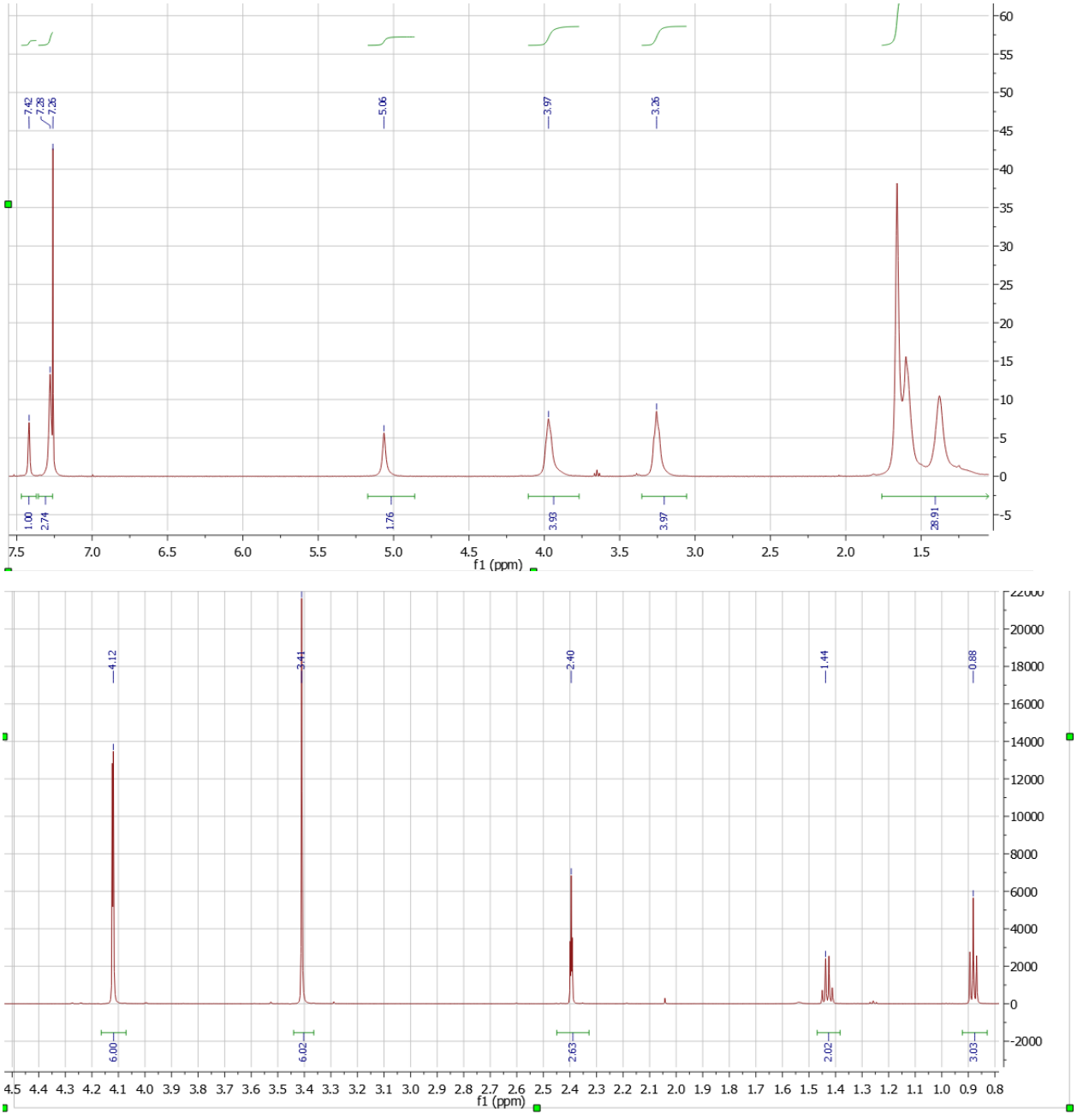

Figure S2. H-NMR for monomer **1** (top) and monomer **2 (**bottom).

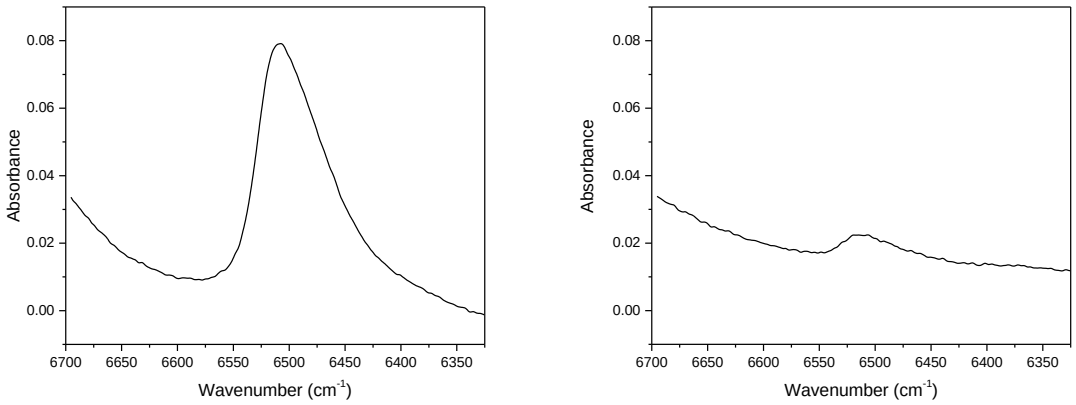

Figure S3. The change in absorbance of the near-IR alkyne peak at 6509 cm^{-1} for the CuAAC polymer system before (left) and after irradiation (right).

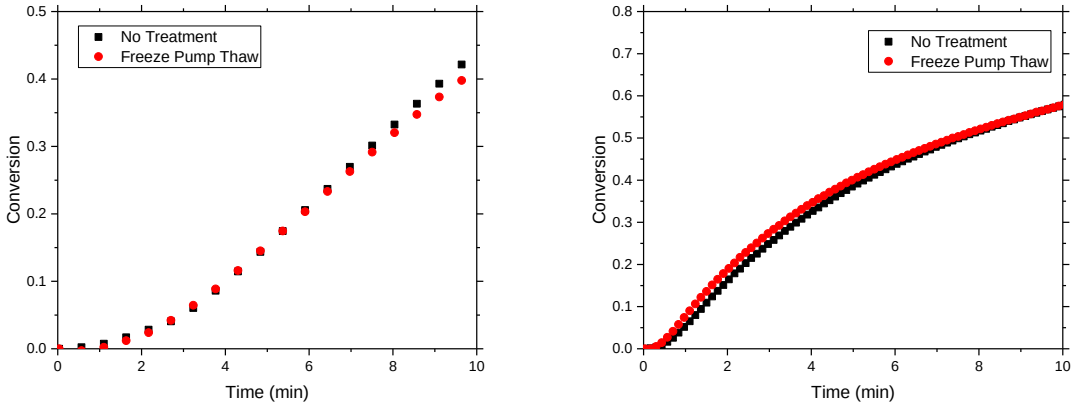

Figure S4. Oxygen inhibition effects. Conversion of a system of 110 mM methyl 2-azidoacetate, 110 mM 1-dodecyne, 10 mM copper and 10 mM Irgacure 819 in DMF after subjected to a freeze pump thaw cycle and 30 min of argon purging and without freeze pump thaw (none) at 2 mW/cm^2 (left) 20 mW/cm^2 (right). At both intensities, there is little difference between the conversions of these systems, indicating that oxygen inhibition does not play a significant role in the photo-CuAAC reaction.

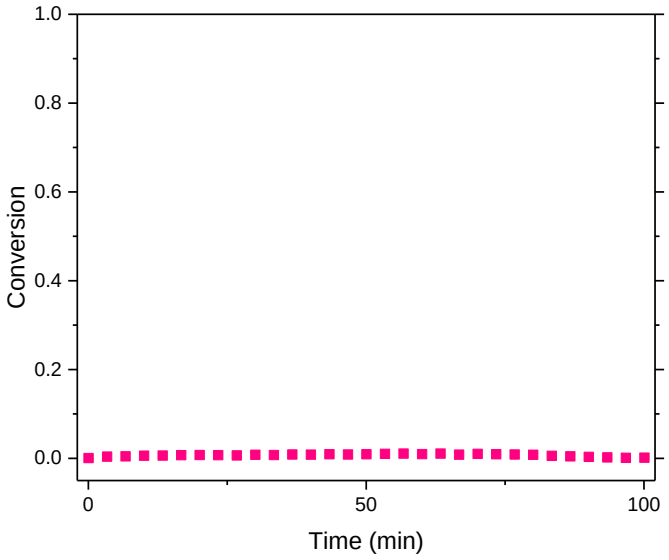

Figure S5. Kinetics of methyl 2-azidoacetate decomposition in DMF over 100 minutes of reaction time using 10 mW/cm^2 of 405 nm light. The results show no significant decrease in the concentration of the azide, indicating that negligible azide decomposition occurred.

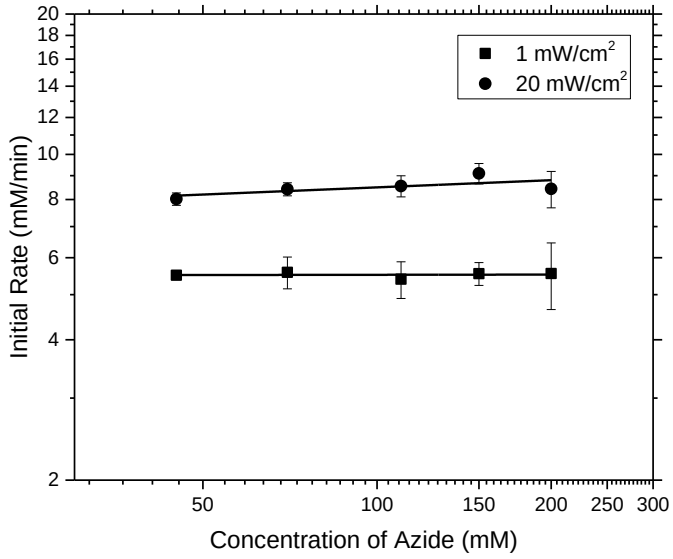

Figure S6. The effect of varying methyl 2-azidoacetate concentrations on the initial rate of the reaction with constant photoinitiator and copper(II) concentrations of 10 mM and 1-dodecyne of 110 mM at 1 mW/cm^2 and 20 mW/cm^2 of 405 nm light. The methyl 2-azidoacetate scaling was found to be (0.00 ± 0.01) and (0.05 ± 0.03) at 1 and 20 mW/cm^2 respectively

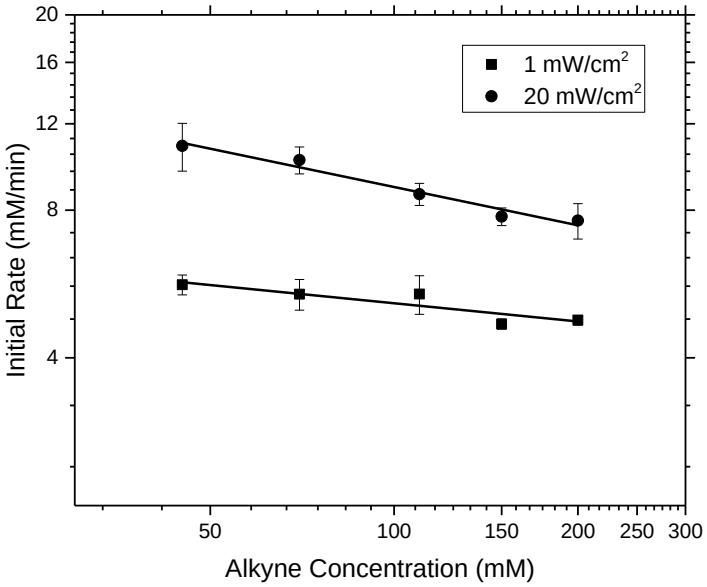

Figure S7. The effect of varying 1-dodecyne concentrations on the initial rate of the reaction with constant photoinitiator and copper(II) concentrations of 10 mM and 1-dodecyne of 110 mM at 1 mW/cm^2 and 20 mW/cm^2 of 405 nm light. The 1-dodecyne scaling was between -0.1 and -0.26.

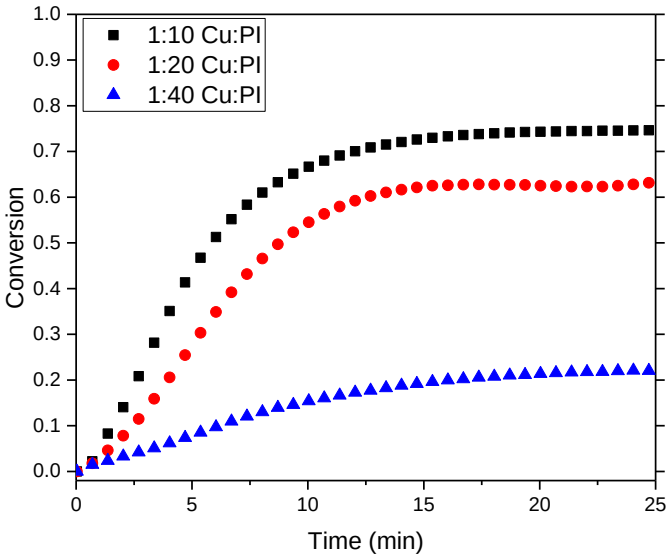

Figure S8. Increasing the concentration of photoinitiator beyond that of copper results in a decreased overall conversion of the photo-CuAAC reaction system.

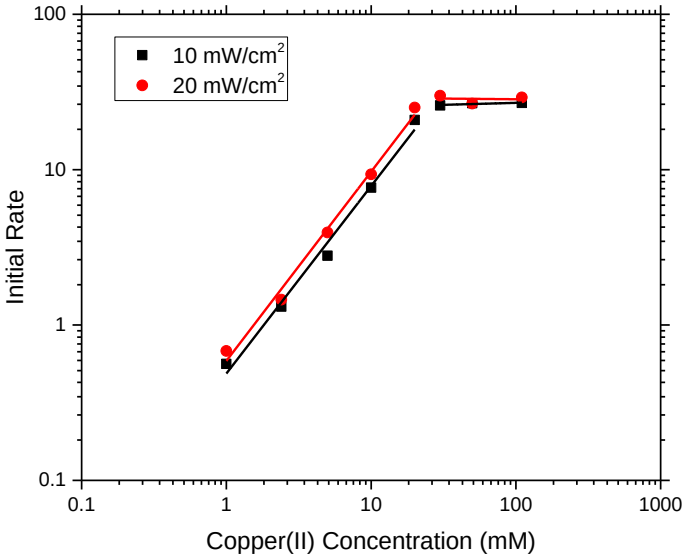

Figure S9. Initial rate of the photo-induced CuAAC reaction as a function of varying initial Cu(II) concentration using at 10 and 20 mW/cm^2 intensity of 405 nm light. The other components in the reaction system were 110 mM of methyl 2-azidoacetate and 1-dodecyne and 10 mM of Irgacure 819. Cu(II) initially scales to (1.20 ± 0.07) and (1.21 ± 0.06) at 10 and 20 mW/cm^2 respectively. After the concentration is increased above 20 mM of Cu(II), the scaling shifts to (0.03 ± 0.02) and (0.01 ± 0.09) at 10 and 20 mW/cm^2 respectively.

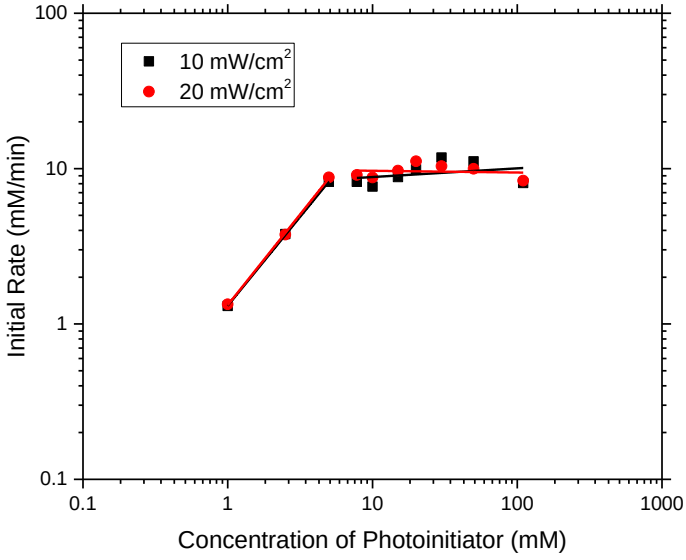

Figure S10. Initial rate of the photo-induced CuAAC reaction as a function of varying initial Irgacure 819 concentration using at 10 and 20 mW/cm^2 intensity of 405 nm light. The other components in the reaction system were 110 mM of methyl 2-azidoacetate and 1-dodecyne, and 10 mM of Cu(II). The photoinitiator initially scales to (1.14 ± 0.01) and (1.17 ± 0.03) at 10 and 20 mW/cm^2 respectively. After the concentration is increased above 20 mM of Cu(II), the scaling shifts to (0.06 ± 0.08) and (-0.01 ± 0.05) at 10 and 20 mW/cm^2 respectively.

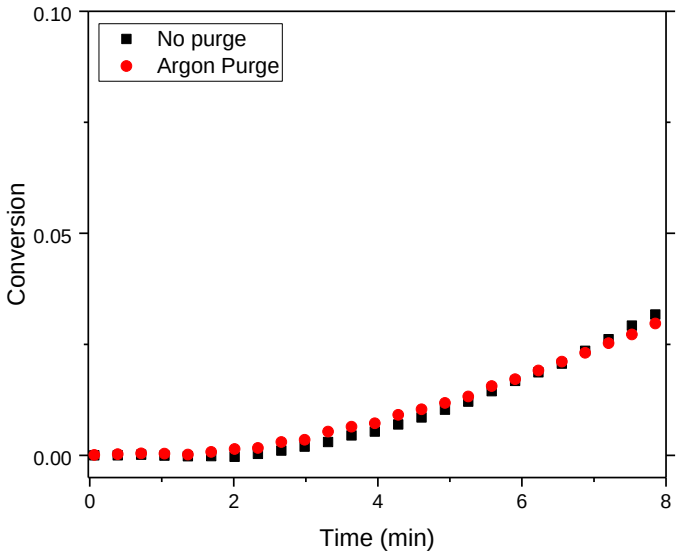

Figure S11. The induction period of photo-CuAAC chemistries is not due to oxygen inhibition effects: Conversion of a system of 110 mM methyl 2-azidoacetate, 110 mM 1-dodecyne, 10 mM copper and 10 mM Irgacure 819 in DMF after subjected to 15 minutes of argon purging was nearly identical after 8 minutes of reaction time. The inhibition time was not reduced after the reaction system was purged with argon.

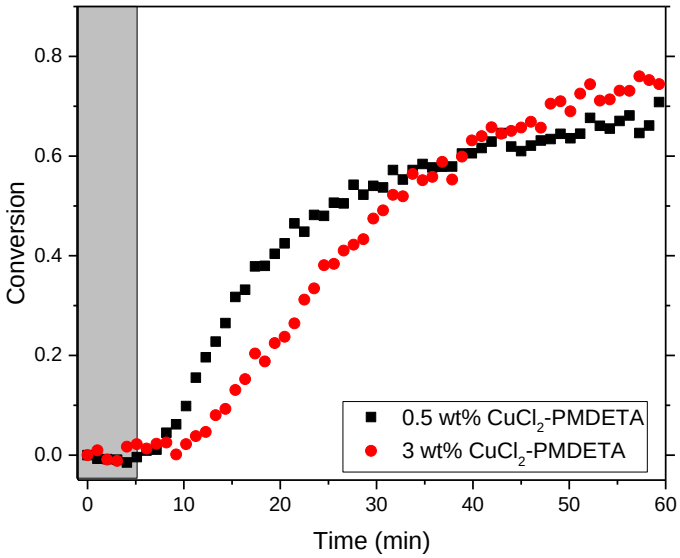

Figure S12. Increasing the concentration of copper in photo-CuAAC polymer networks. System consisted of an equimolar functional group concentration of monomer **1** and **2** and 1wt% of Irgacure 819 (405 nm filter bandgap: 1 mW/cm^2). Sample thickness was 0.12 mm. All samples contained 5wt% MeOH. As the concentration of copper(II) in increased in a photo-CuAAC polymerization, the induction time of the reaction increases.