Supporting Information: Copper Ligand and Anion Effects: Controlling the Kinetics of the Photoinitiated Copper(I) Catalyzed Azide—Alkyne Cycloaddition Polymerization

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Table of Contents

Section 1: Experimental Data	S2
Section 2: Monomer Synthesis	S16
Section 3: H NMR Spectra	S18
Section 4: UV-Vis Spectra of Copper(II) Catalysts	S20
Section 5: References	S25





Figure S1. Near-IR alkyne peak before (red) and after (blue) irradiation.



Figure S2. Conversion profile of the CuAAC reaction between AZD and YNE monomers using 1.5wt% copper(II) bromide or chloride pre-ligated to BPY or DPA, respectively, under 470 nm light at 30 mW/cm² in the presence of 1 wt% camphorquinone. Negligible reaction was observed in these systems over 2 hours.



Figure S3. Cyclic voltammetry of copper(II) bromide with different polydentate ligands in a 0.1 M potassium phosphate buffer. Ag/AgCl was the reference electrode and the scan speed was 0.02 V/s.



Figure S4. Conversion profile between AZD and YNE using equimolar amounts of copper(II) concentrations with different anions ligated to Me6TREN in the presence of 0.7 wt% camphorquinone under 470 nm light at 30 mW/cm². The halides (bromide and chloride) exhibited the fastest reaction kinetics compared to triflate ions.



Figure S5. Conversion profile between AZD and tripropargyl amine using equimolar amounts of copper(II) concentrations with different anions ligated to Me_6TREN in the presence of 1 wt% camphorquinone under 470 nm light at 30 mW/cm². The halides (bromide and chloride) exhibited the fastest reaction kinetics compared to triflate and bistriflimide ions.



Figure S6. Conversion profile between AZD and YNE using equimolar amounts of copper(II) concentrations with different anions (chloride, bistriflimide) ligated to Me_6TREN in the presence of 1 wt% Irgacure-819 under 405 nm light at 30 mW/cm². The halide anion, chloride, exhibited the faster kinetics than TFSI (bistriflimide).



Figure S7. UV vis spectra of a 10 mM of CuBr2/TMEDA solution in methanol at t = 0 mins and t = 1000 mins.



Figure S8. UV-vis spectra over 900 minutes of a 10 mM of $CuBr_2/TMEDA$ solution with 100 mM of 1-dodecyne in chloroform. A decrease in the copper(II) absorbance peak at 730 nm and a change in color from brown to green is observed at t=0 and t=900 minutes, indicating a change in the copper(II) structure and/or oxidation state.



Figure S9. Change in ¹³CNMR spectra at time=0 (blue) to time=18 hours (red) for a solution of 100 mM 1-dodecyne and 10 mM copper(II) bromide TMEDA in deuterated methanol. The blue box indicates the peaks corresponding to the C=C triple bond.



Figure S10. Change in ¹H NMR spectra at time=0 (blue) to time=18 hours (red) for a solution of 100 mM 1-dodecyne and 10 mM copper(II) bromide PMDETA in deuterated methanol. The NMR showed no change over time.



Figure S11. Change in ¹H NMR spectra at time=0 (blue) to time=18 hours (red) for a solution of 100 mM 1-dodecyne and 10 mM copper(II) bromide Me6TREN in deuterated methanol. The NMR showed no change over time.



Figure S12. Change in ¹HNMR spectra at time=0 (blue) to time=18 hours (red) for a solution of 100 mM 1-dodecyne and 10 mM copper(II) TFSI ligated to TMEDA in deuterated methanol. The NMR showed a decrease in the peak at 2.15 ppm and an appearance of a peak at 2.63 ppm.



Figure S13. Conversion as a function of time for an equimolar solution of YNE and AZD in the presence of $CuBr_2/Me6TREN$ and 30 mW/cm² of 470nm light. No reaction occurred during 2 hours of irradiation in the absence of a photoinitiator.

#	AZD	YNE	Copper(II)	Ligand	Pre-ligated	CQ/amine	Polymerization?
1	+	+	+ CuBr2	-	-	+	No
2	+	+	-	+ PMDETA	-	-	No
3*	+	+	+ CuBr2	+ PMDETA	-	-	Yes
4*	+	+	+ CuBr2	+ PMDETA	-	-	Yes
5	+	+	+ CuBr2	+ HMTETA	-	-	Yes
6	+	+	+ CuCl2	+ PMDETA	-	-	Yes
7	+	+	+ CuBr2	+ PMDETA	+	-	No
8	+	+	+ CuCl2	+ PMDETA	+	-	No
9	-	+	+ CuBr2	+ PMDETA	-	-	No
10	+	+	+ CuBr2	+ PMDETA	-	+	Yes - rapid

Table S1. Polymerization results in the presence or absence of: AZD, YNE, copper(II) source, an amine ligand, pre-ligation, and camphorquinone with accelerating amine. These specimens were not irradiated with an external light source.

* #3 used methanol as the solvent, whereas #4 used acetonitrile.

No polymerization takes places in the absence of a ligand or a copper(II) species (entries 1-2). If the ligand species was not pre-ligated to the copper(II) before adding to the resin formulation, polymerization occurs with both PMDETA and HMTETA in the presence of both copper(II) bromide and chloride (entries 3-6). If the copper catalyst is pre-ligated, no polymerization occurs (entries, 7-8). These results further demonstrate the importance of pre-ligation of the amine with the copper(II) salt in photo-CuAAC polymerizations to maintain the latency of initiation in the absence of light.

Section 2: Monomer Synthesis

Bis(6-azidohexyl)(1,3-phenylenebis(propane-2,2-diyl))dicarbamate (AZD monomer) was synthesized using a 2-step synthesis¹.



(1) 1,3-Bis(2-isocyanato-2-propanyl)benzene (10.0 g; 0.041 mol) was added to an argon purged round bottom flask to which dibutyltin dilaurate (a few drops) in 50 mL of THF was added. The reaction mixture was then placed in an ice bath where 2 equivalents of 6-chloro-1-hexanol (11.5 g; 0.084 mol) was added dropwise. After addition, the reaction flask was removed from the ice bath and left to react overnight at room temperature. Excess THF (100 mL) was added and the mixture was passed through a silica plug. The product was dried under high pressure to yield to a translucent oil.

(2) The crude product from (1) (10.0 g; 0.021 mol) was dissolved in 150 mL of DMF. Sodium azide (5.5 g; 0.084 mol) was added in aliquots to the reaction mixture. The flask was then heated to 80°C under reflux for 24 hours. The product was extracted with ethyl acetate (3 × 200 mL) and washed with water (3 × 200 mL) to remove any remaining DMF. Column chromatography (1:1 ethyl acetate:hexanes) yielded a clear viscous oil (8.8 g; 78% yield). 1H NMR (400MHz, CDCl₃) δ 7.42 (1H, s), 7.28 (2H, s), 5.06 (2H, s), 3.97(4H, t), 3.26 (4H, t), 1.25-1.80 (28H, m). 1-(Prop-2-ynyloxy)-2,2-bis(prop-2-ynyloxymethyl)butane² (YNE monomer): Trimethylolpropane (7.50g, 0.056 mol) was added to a solution of KOH (26.00g, 0.46 mol) in 100 mL of DMSO. The reaction mixture was then placed in an ice bath for 30 minutes. Propargyl bromide (80% in toluene; 22.0g, 0.15 mol) was filtered from MgO and added dropwise to the slurry. The reaction was then allowed to equilibrate to room temperature and reacted for an additional 48 hours. The resulting mixture was added to 1000 mL of water and extracted with a 50:50 vol% mixture of ethyl acetate and diethyl ether (3 × 500 mL). The organic layer was then washed with brine (4 × 500 mL) and dried over MgSO₄. The mixture was concentrated under reduced pressure and separated using column chromatography (hexanes/ethyl acetate). The product was obtained as a slightly yellow oil (6.0 g, 43% yield). ¹H NMR (400 MHz, CDCl₃): δ 4.12 (d, 6H), 3.41 (s, 6H), 2.40 (t, 3H), 1.42 (q, 2H), 0.88 (t, 3H).

Section 3: H NMR spectra



Figure S14. ¹H NMR spectra of Bis(6-azidohexyl)(1,3-phenylenebis(propane-2,2diyl))dicarbamate (AZD) in CDCl₃



Figure S15. ¹H NMR spectra of (Prop-2-ynyloxy)-2,2-bis(prop-2-ynyloxymethyl)butane (YNE) in CDCl₃

Section 4: UV-VIS SPECTRA OF COPPER(II) CATALYSTS

All UV-vis spectra were taken using an Evolution 260 Bio UV-Visible Spectrophotometer from Fisher Scientific. The samples contained 10 mM of the copper(II) ligand and were dissolved in methanol. They were placed in a quartz cuvette with a constant pathlength of 1 cm.



Figure S16. CuBr₂/HMTETA UV-vis spectra



Figure S17. CuBr₂/PMDETA UV-vis spectra



Figure S18. CuBr₂/TMEDA UV-vis spectra



Figure S19. Cu(TFSI)₂/TMEDA UV-vis spectra



Figure S20. Cu(OAc)₂/TMEDA UV-vis spectra



Figure S21. CuBr₂/Me6TREN UV-vis spectra



Figure S22. CuCl₂/PMDETA UV-vis spectra



Figure S23. Cu(OAc)₂/PMDETA UV-vis spectra



Figure S24. Cu(TFSI)₂/PMDETA UV-vis spectra

Section 5: References

- 1 H. B. Song, A. Baranek and C. N. Bowman, *Polym. Chem.*, 2016, **7**, 603–612.
- 2 T. Gong, B. J. Adzima, N. H. Baker and C. N. Bowman, *Adv. Mater.*, 2013, **25**, 2024–2028.