

# **A Novel Copper Containing Photoinitiator, Copper (II) Acylphosphinate, and Its Application in Both the Photomediated CuAAC Reaction and in Atom Transfer Radical Polymerization**

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## **SUPPORTING INFORMATION**

### **General Information**

All chemical reagents were purchased from commercial sources and used as received. NMR spectra were recorded on Bruker Avance-III 400 spectrometers. Mass spectral and analytical data were obtained via the PE SCIEX/ABI API QSTAR Plusar Hybrid LC/MS/MS, Applied Biosystems operated in the central analytical laboratory, University of Colorado at Boulder. Triple-detection gel permeation chromatography (GPC; Viscotek, Westborough, MA) with differential refractive index (RI, Viscotek VE 3580), viscosity and light scattering detectors (Viscotek 270 dual detector) was employed for the analysis of poly (methyl methacrylate) molecular weight and polydispersity index (PDI).

### **Synthesis of Cu(AP)<sub>2</sub>/PMDETA**

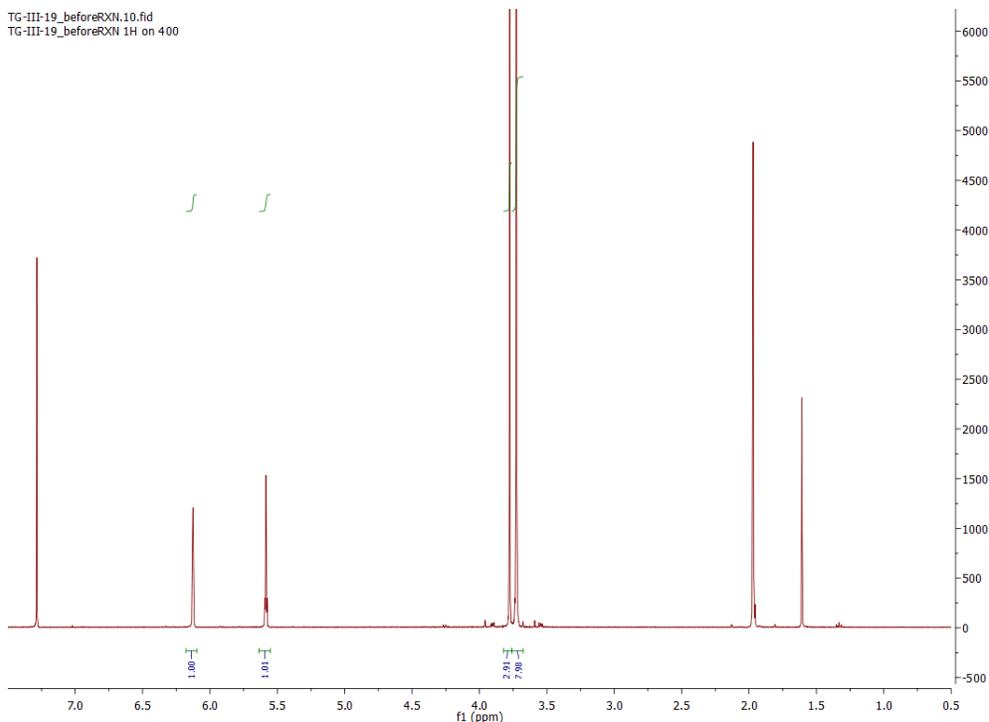
Lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP) was synthesized in a two step process according to the literature with only a slight modification.<sup>1</sup> At room temperature and under argon, 2,4,6-trimethylbenzoyl chloride (4.5 g, 25 mmol) was added dropwise to continuously stirred dimethyl phenylphosphonite (4.2 g, 25 mmol). The reaction mixture was then stirred for 24 hours whereupon an excess of lithium bromide (2.4 g, 28 mmol) in 50 mL of 2-butanone was added to the reaction mixture from the previous step which was then heated to 50 °C. After 10 min, a solid precipitate formed. The mixture was then cooled to room temperature, allowed to rest overnight and then filtered. The filtrate was washed with 2-butanone (3 x 25 mL) to remove unreacted lithium bromide and dried under vacuum to give LAP (6.2 g, 22 mmol, 88%) as a white solid.

Copper phenyl-2,4,6-trimethylbenzoylphosphinate ( $\text{Cu}(\text{AP})_2$ ) was synthesized by reacting LAP with  $\text{Cu}_2\text{SO}_4$  in water.  $\text{Cu}_2\text{SO}_4$  (0.76 g, 3.0 mmol) was slowly added to LAP (0.84 g, 2.9 mmol) in 20 mL water. A white-blue precipitate was instantly formed and the reaction mixture was then stirred at room temperature overnight. The reaction mixture was filtered and washed with water (3 x 5 mL) and dried over vacuum to give  $\text{Cu}(\text{AP})_2$  (1.15 g, 1.86 mmol, 64.0%) as a white-blue solid.

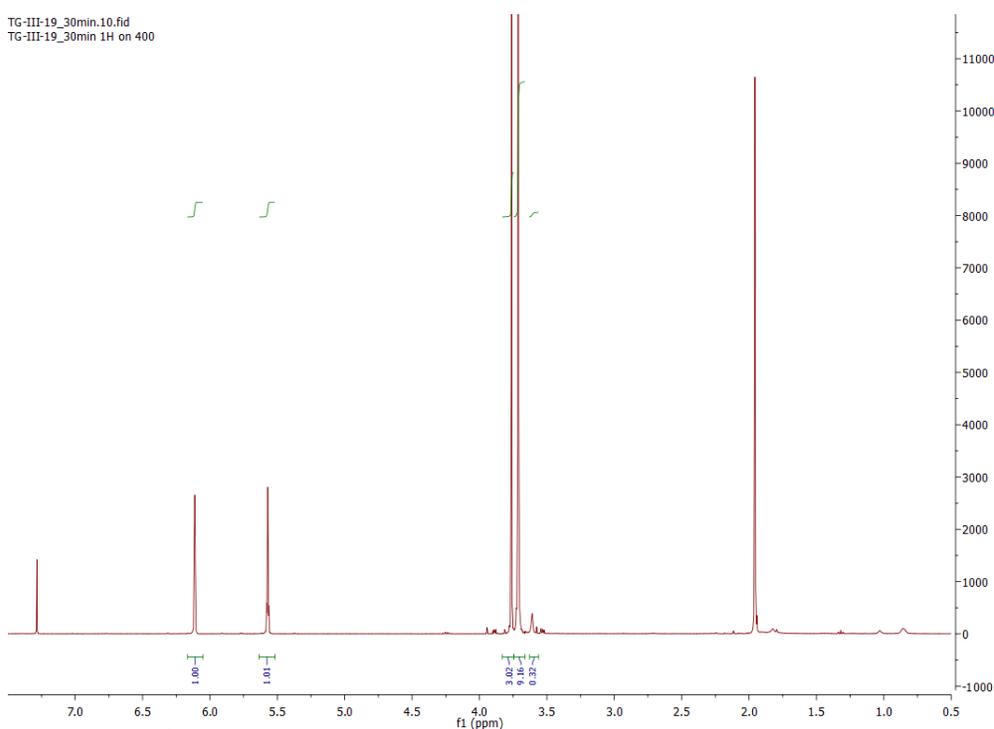
The  $\text{Cu}(\text{AP})_2/\text{PMDETA}$  complex was synthesized using a procedure similar to the synthesis of  $\text{CuCl}_2/\text{PMDETA}$  with a slight modification.<sup>2</sup>  $\text{Cu}(\text{AP})_2$  (0.75 g, 1.17 mmol) was suspended in 150 mL of acetonitrile under argon. Then, PMDETA (246  $\mu\text{L}$ , 1.18 mmol) was added dropwise and subsequently generated a deep blue color. The reaction mixture was then stirred at room temperature overnight and the solvent was removed in vacuo to form the  $\text{Cu}(\text{AP})_2/\text{PMDETA}$  (0.94 g, 1.16 mmol, 99%) complex as a deep blue crystalline solid. MS (ESI)  $m/z$ :  $[\text{M}-\text{C}_{16}\text{H}_{16}\text{PO}_3]^+$ , calcd for  $\text{CuC}_{41}\text{H}_{55}\text{N}_3\text{P}_2\text{O}_6$ , 523.2 ; found, 523.2.

#### **Synthesis of Poly (methyl methacrylate) (PMMA) using reverse atom transfer radical polymerization (Reverse ATRP) with $\text{Cu}(\text{AP})_2/\text{PMDETA}$**

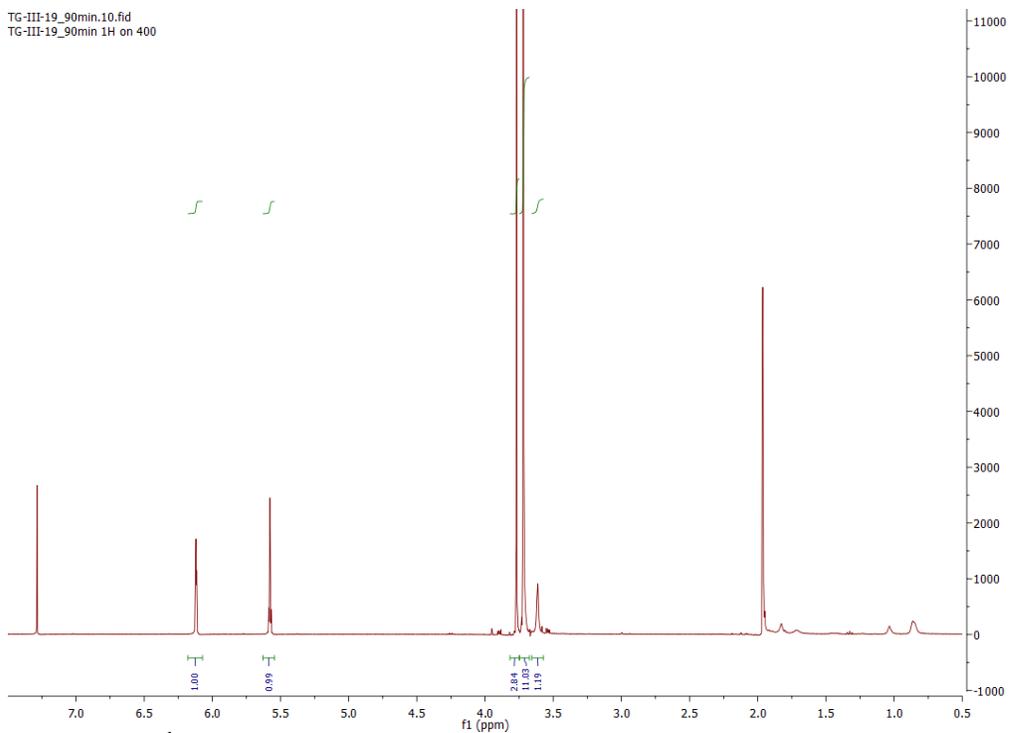
Methyl methacrylate (2 mL, 18.8 mmol), ethyl  $\alpha$ -bromoisobutyrate (13.8  $\mu\text{L}$ , 0.094 mmol),  $\text{Cu}(\text{AP})_2/\text{PMDETA}$  (76 mg, 0.094 mmol), and 1,4-dioxane (1.6 mL, 18.8 mmol) were added into a Schlenk tube and the reaction mixture was degassed by three freeze/pump/thaw cycles and backfilled with argon. The mixture was then stirred at room temperature with light irradiation using 10  $\text{mW}/\text{cm}^2$  light intensity from an Acticure 4000 lamp with a 400-500 nm bandgap filter. A small fraction of the sample was taken out for NMR measurement to determine the monomer conversion (as shown in **Figure S1**, **Figure S2**, **Figure S3** and **Figure S4**) and GPC measurements to determine the molecular weight and molecular weight distribution. Then, the reaction mixture was opened to air at approximately 53% monomer conversion, and the resulting polymers were precipitated in hexane and dried under vacuum overnight to give a white powder.  $M_n = 10900$  g/mol,  $M_w/M_n = 1.36$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 3.58 (s, 1H), 1.93-1.79 (m, 2H), 1.00 (bs, 1H), 0.83 (bs, 2H). All the other polymerization/control reactions were performed under identical experimental conditions.



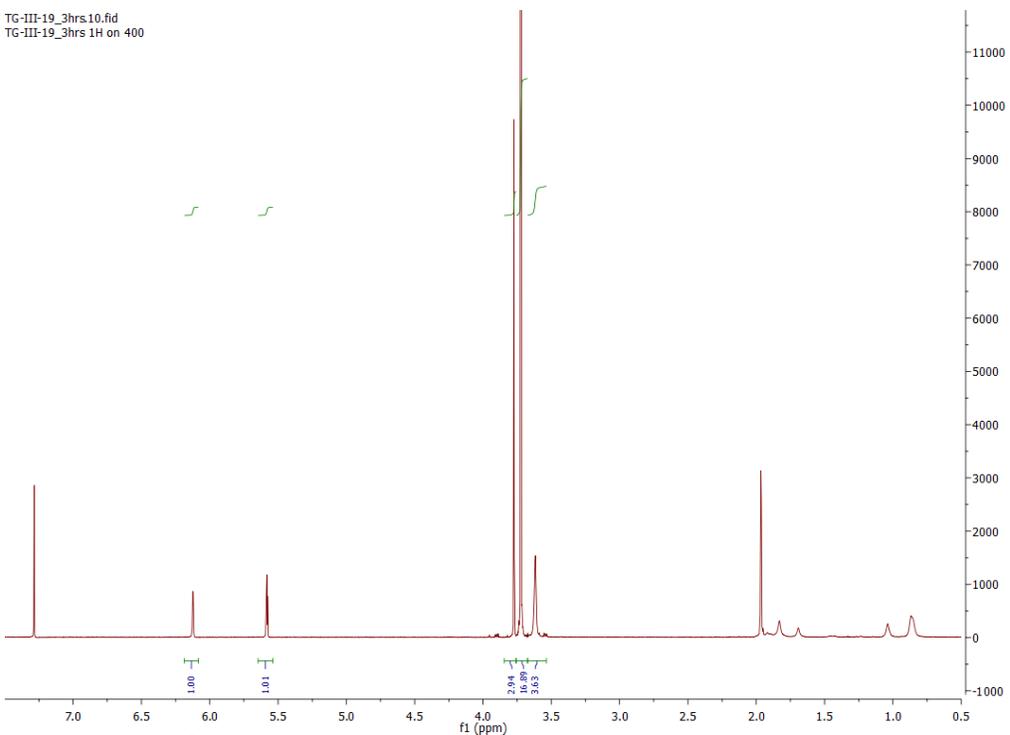
**Figure S1.** <sup>1</sup>H NMR spectrum of ATRP reaction mixture before light irradiation, the ratio of internal standard, 1,4-dioxane and MMA monomer is 1.0



**Figure S2.** <sup>1</sup>H NMR spectrum of ATRP reaction mixture after 30 minutes of light irradiation, the ratio of internal standard, 1,4-dioxane and MMA monomer is 1.15



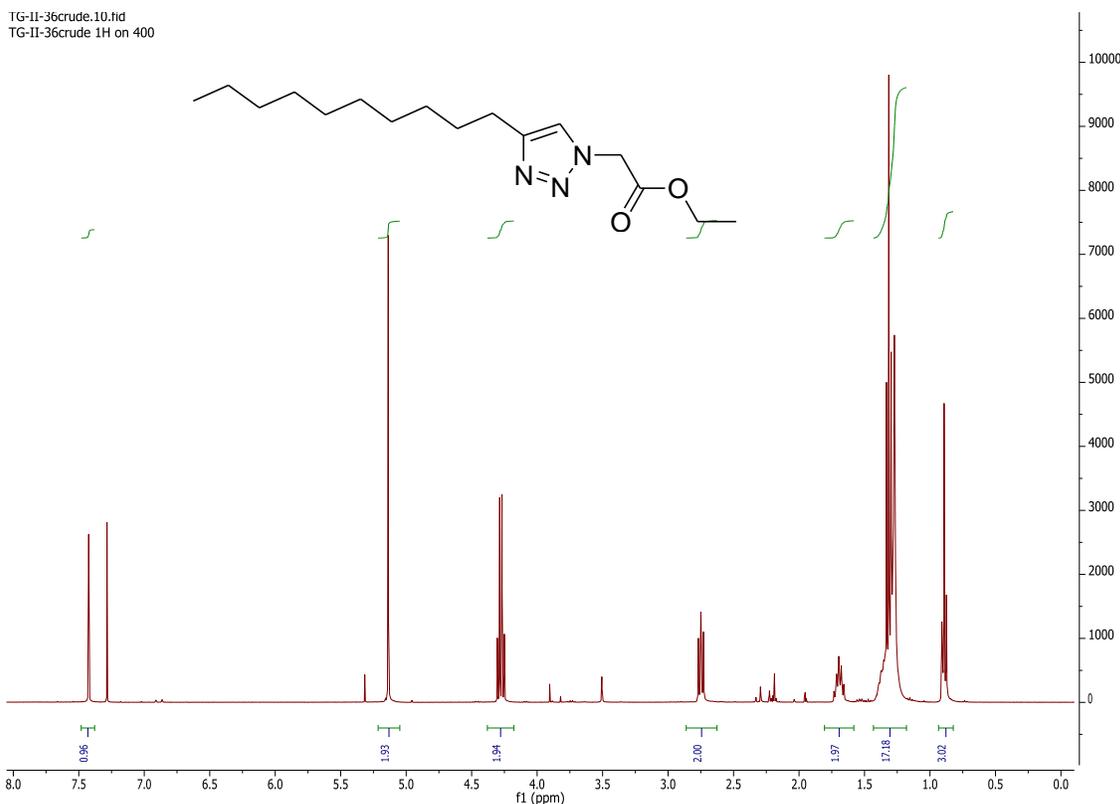
**Figure S3.**  $^1\text{H}$  NMR spectrum of ATRP reaction mixture after 90 minutes of light irradiation, the ratio of internal standard, 1,4-dioxane and MMA monomer is 1.38



**Figure S4.**  $^1\text{H}$  NMR spectrum of ATRP reaction mixture after 3 hours of light irradiation, the ratio of internal standard, 1,4-dioxane and MMA monomer is 2.11

## Photo CuAAC Reaction of Ethyl Azidoacetate and 1-Dodecyne

Ethyl azidoacetate (25wt% in ethanol) (480 mg, 0.94 mmol), 1-dodecyne (116 mg, 0.94 mmol), and Cu(AP)<sub>2</sub>/PMDETA (15.3 mg, 0.019 mmol) in 5 mL of ethanol were added to a small reaction vial and the reaction was stirred rapidly at room temperature and under argon. The sample was then irradiated for 3 hours using 10 mW/cm<sup>2</sup> light from an Acticure 4000 lamp using a 400-500 nm bandgap filter. The resulting mixture was diluted with dichloromethane and subsequently washed with saturated ethylenediaminetetraacetic acid (EDTA) solution (3 x 10 mL). The organic layer was then separated, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated to give triazole product as a white solid (0.27 g, 0.91 mmol, 97%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, δ): 7.40 (s, 1H), 5.11 (s, 2H), 4.25 (q, 2H, J = 8.0 Hz), 2.72 (t, 2H, J = 8.0 Hz), 1.67 (p, 2H, J = 8.0 Hz), 1.40-1.15 (m, 17H), 0.87 (t, 3H, J = 8.0 Hz) as shown in **Figure S5**. HRMS (ESI) m/z: [2M-Na]<sup>+</sup>, calculated for C<sub>16</sub>H<sub>29</sub>N<sub>3</sub>O<sub>2</sub>, 613.4412 ; found, 613.4409.



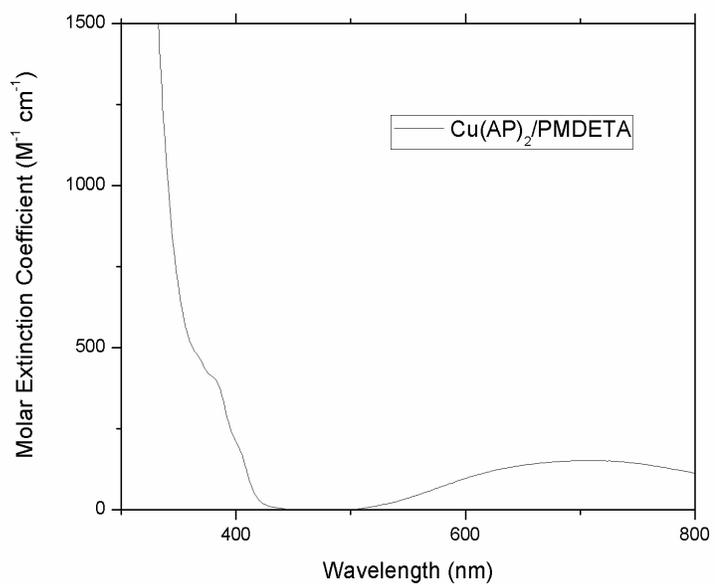
## Fourier Transform Infrared (FTIR) Spectroscopy

A Nicolet Magna-IR 750 Series II FTIR spectrometer, outfitted with a horizontal transmission stage, was used in conjunction with a variable pathlength liquid cell with calcium fluoride windows (International Crystal Laboratories). A pathlength of 50  $\mu\text{m}$  was used for all experiments to enable greater than 90% transmission of light. The samples were irradiated by an EXFO Acticure high pressure mercury vapor short arc lamp equipped with a 400-500 nm bandgap filter. Light intensities were measured using an International Light IL1400A radiometer equipped with a GaAsP detector and a quartz diffuser.

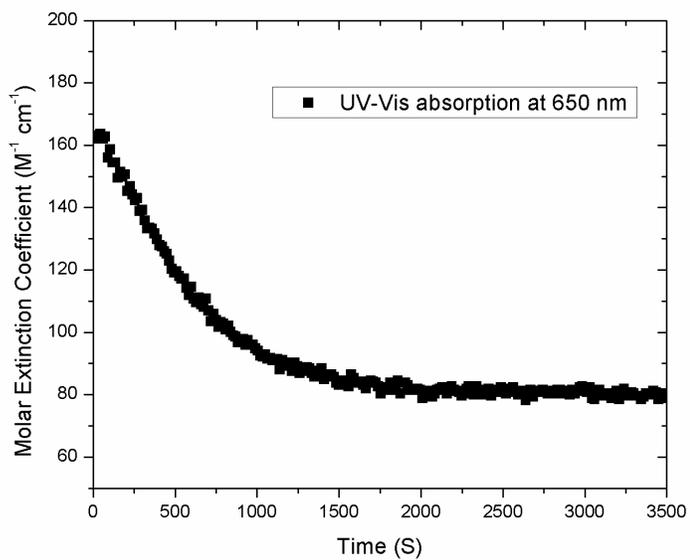
In a typical experiment, a solution of dimethylformamide (DMF) or absolute ethanol with 200 mM ethyl azidoacetate, 200 mM 1-Dodecyne, and 10 mM of  $\text{Cu}(\text{AP})_2/\text{PMDETA}$  was injected into the liquid cell. Irradiation was commenced for a time between 5 and 10 minutes. Approximately 3.6 scans per minute were performed. This delay time enabled the initial peak areas to be determined, which are subsequently used to calculate conversion.

## Real Time UV-Vis Spectroscopy

Real time  $\text{Cu}(\text{II})$  concentration was monitored using a UV-Vis spectrophotometer (Thermo-Fischer Scientific) with remote sampling capability. Sample solutions of  $\text{Cu}(\text{AP})_2/\text{PMDETA}$  (8.3 mg in 3.4 mL of acetonitrile) were analyzed in a glass cylindrical tube with a 5 mm diameter. Visible light was used to irradiate from the top of the sample at an intensity of 5  $\text{mW}/\text{cm}^2$  using a mercury gas-discharge lamp (Acticure) with 400-500 nm bandgap filter. Fiber optics (1000 and 600  $\mu\text{m}$  inner diameter) were utilized to remotely obtain the absorbance decay with time. Complete scans were taken from 550-800 nm with a time-resolution of  $\sim 1$  min. Data was collected in absorbance mode with a bandwidth of 2 nm and a speed of 240 nm/min. Photobleaching experiments took approximately 10 minutes. The broad peak centered at  $\sim 650$  nm decayed with time corresponding to the reduction of  $\text{Cu}(\text{II})$  to  $\text{Cu}(\text{I})$ . The absorbance of  $\text{Cu}(\text{II})$  at these concentrations is within the Beer-Lambert region. The resolution of the spectrophotometer is 0.0025 AU. Absorbance was then normalized to obtain the fractional conversion of  $\text{Cu}(\text{II})$  to  $\text{Cu}(\text{I})$ . The UV-Vis spectrum of  $\text{Cu}(\text{AP})_2/\text{PMDETA}$  in  $\text{CH}_3\text{CN}$  and real time absorbance at 650 nm for  $\text{Cu}(\text{AP})_2/\text{PMDETA}$  in  $\text{CH}_3\text{CN}$  upon 5  $\text{mW}/\text{cm}^2$  irradiation of 400-500 nm light are shown in **Figure S6** and **Figure S7**.



**Figure S6.** UV-Vis spectrum of Cu(AP)<sub>2</sub>/PMDETA in CH<sub>3</sub>CN.



**Figure S7.** Real time absorbance at 650 nm of Cu(AP)<sub>2</sub>/PMDETA in CH<sub>3</sub>CN upon 5 mW/cm<sup>2</sup> irradiation of 400-500nm light.

**Reference:**

1. T. Majima, W. Schnabel and W. Weber, *Makromol Chem*, 1991, **192(10)**, 2307-2315.
2. G. Margraf, J. W. Bats, M. Wagner and H. W. Lerner, *Inorg Chim Acta*, 2005, **358(4)**, 1193-1203.