### **Supplementary Information**

## Visible-light Induced Controlled Radical Polymerization of Methacrylates with Cu(dap)<sub>2</sub>Cl as Photoredox Catalyst

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### 1. Setup of the polymerization



Fig. S1 The setup for the photo-induced polymerizationss.

# 2. On/off light experiment about polymerization of PEGMA with Cu(dap)<sub>2</sub>Cl as photoredox catalyst

The reaction was performed in a dry one-necked round-bottom Pyrex flask (25 mL) and the operation procedure was similar to that of homopolymerization of PEGMA with Me<sub>6</sub>TREN as both ligand and reducing agent. The ratio of [PEGMA]/[EBPA]/[Cu(dap)<sub>2</sub>Cl]/[Me<sub>6</sub>TREN] was 28/1/0.015/0.20, and the concentration of PEGMA in methanol (4.00 g) and DCM (1.00 g) mixed solvent was set to be about 35 wt%.



**Fig. S2** Polymerization of PEGMA using catalyst  $Cu(dap)_2CI$  while cycling the reaction's exposure to visible light. (a) conversion versus time, (b) evolution of  $M_n$  and PDI with conversion, and (c) GPC curves of PPEGMA initiated with [PEGMA]:[EBPA]:[Cu(dap)\_2CI]:[Me\_6TREN]=28:1:0.015:0.20 catalyst system.

#### 3. One-pot synthesis of PPEGMA-b-PMMA

The diblock copolymer PPEGMA-*b*-PMMA was synthesized by one-pot process with sequential monomer addition. The produce was similar to the homopolymerization of PEGMA with Me<sub>6</sub>TREN as both ligand and reducing agent. The ratio of [PEGMA]/[EBPA]/[Cu(dap)<sub>2</sub>Cl]/[Me<sub>6</sub>TREN] was 28/1/0.015/0.20 and the concentration of PEGMA in methanol (4.00 g) and DCM (1.00 g) mixed solvent was set to be about 35 wt%. After 119 h of irradiation under LED light lamp, a small portion of the reactant was sampled to determine the conversion of PEGMA (88%) and the  $M_n$  and PDI of the polymer PPEGMA ( $M_{n,GPC}$ =11500; PDI=1.13). Then, deoxygenated MMA (2.0056 g, MMA/PEGMA=1/1 in volume) and Me<sub>6</sub>TREN (11  $\mu$ L) were introduced into the reactant. The reaction was stopped after 80 h of visible light irradiation and the polymers were precipitated in excess methanol. At last, the product was dried under vacuum at 40 °C to a constant weight.



**Fig. S3** GPC curves of the PPEGMA macroinitiator and the PPEGMA-*b*-PMMA block copolymer obtained by one-pot procedure.



Fig. S4 <sup>1</sup>H NMR spectra of PPEGMA-*b*-PMMA copolymer obtained by one-pot procedure.

## Photopolymerization of methacrylic acid (MAA) using Cu(dap)<sub>2</sub>Cl catalyst system

The concentration of MAA in deionized water (2.50 g) and methanol (2.50 g) mixed solvent was set to be about 25 wt%. The ratio of  $[MAA]/[EBPA]/[Cu(dap)_2CI]/[Me_6TREN]$  was 100/1/-/0.30 and 100/1/-0.015/0.30, respectively. In addition, the ratio of  $[MAA]/[EBPA]/[Cu(dap)_2CI]/[DMA]$  was 110/1/0.015/5. The other steps were similar to those of the PEGMA polymerization. At last, the reactant samples were withdrawn from the reaction mixture and purified by dissolution-precipitation twice with THF and acetone. Then the precipitates were dried at 40 °C in vacuum and analyzed by GPC. The GPC (Waters 1515 system with waters ultrahydrogel 250 and 2000 columns in series) was calibrated with poly(sodium-*p*-styrenesulfonate) standards and with deionized water as the eluent.

First, the polymerization of MAA using Me<sub>6</sub>TREN as both ligand and reducing agent was reported in this part. Even after 78 h, no polymerization was observed in the absence of Cu(dap)<sub>2</sub>Cl. When the ratio of [MAA]/[EBPA]/[Cu(dap)<sub>2</sub>Cl]/[Me<sub>6</sub>TREN] was 100/1/0.015/0.30, the monomer conversion of MAA reached 97.7% after 78 h. Meanwhile, poly(MAA) (PMAA) with high molecular weight and high molecular weight distribution ( $M_{n,GPC}$ =19600, PDI=2.41) was obtained. However, this process was not a living/controlled polymerization.

The polymerization of MAA using DMA as a reducing agent was also reported. When the molar ratio of  $[MAA]:[EBPA]:[Cu(dap)_2CI]:[DMA]$  was 110:1:0.015:5, plots of both  $ln([M]_0/[M])$  versus time (Fig. S5(a)) and  $M_n$  versus conversion (Fig. S5(b)) gave linear relationships, as direct evidence of the controlled polymerization of MAA. GPC traces of the corresponding PMAA are present in Fig. S6. GPC elution profiles are symmetrical and the peak of the final polymer product shifted to higher molecular weight end, indicating a controlled photopolymerization of PMAA. However, the experimental molecular weights were much higher than the theoretical values, indicating low initiation efficiency.



**Fig. S5** (a) The kinetic plots of  $\ln([M]_0/[M])$  as a function of time and (b) evolution of  $M_n$  and PDI with conversion for the polymerization of MAA using DMA as a reducing agent at ambient temperature irradiated with 420 nm light. Polymerization condition: [MAA]:[EBPA]:[Cu(dap)\_2Cl]:[DMA]=110:1:0.015:5.



Fig. S6 GPC curves of PMAA initiated with [MAA]:[EBPA]:[Cu(dap)<sub>2</sub>Cl]:[DMA]=110:1:0.015:5 catalyst system.

## Photopolymerization of N,N-dimethylacrylamide (DMAA) using Cu(dap)<sub>2</sub>Cl catalyst system

The concentration of DMAA in ACN (4.50 g) and methanol (0.50 g) mixed solvent was set to be about 28 wt%. The ratio of  $[DMAA]/[EBPA]/[Cu(dap)_2Cl]/[Me_6TREN]$  was 110/1/0.015/-, 110/1/0.015/0.30, and

110/1/0.015/0.60, respectively. In addition, the ratio of  $[DMAA]/[EBPA]/[Cu(dap)_2Cl]/[DMA]$  was 110/2/0.015/5. The other steps were similar to those of the PEGMA polymerization.

After 94 h, no detectable polymerization of DMAA occurred while using  $Me_6TREN$  as both ligand and reducing agent. The result indicated that the polymerization of DMMA using  $Cu(dap)_2Cl/Me_6TREN$  photoredox catalyst was less successful.

When the ratio of [DMAA]/[EBPA]/[Cu(dap)<sub>2</sub>Cl]/[DMA] was 110/2/0.015/5, the monomer conversion of DMMA reached as high as 80.9% after 30 h. The polymerization was found to proceed according to first order kinetics (Fig. S7(a)). It is clearly observed that the number average molecular weight increased slowly with monomer conversion and the PDI of resulted polymers were less than 1.2 (Fig. S7(b)). This result confirmed the living character of this photo-induced polymerization.



**Fig. S7** (a) The kinetic plots of  $ln([M]_0/[M])$  as a function of time and (b) evolution of  $M_n$  and PDI with conversion for the polymerization of DMMA using DMA as a reducing agent. Polymerization condition: [DMMA]:[EBPA]:[Cu(dap)\_2Cl]:[DMA]=110:2:0.015:5.