Supporting Information for the Manuscript:

Role of Cu^0 in Living Radical Polymerization

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I. Comproportionation and Disproportionation Experiments: Electronic Spectra

A. Solvent Effect

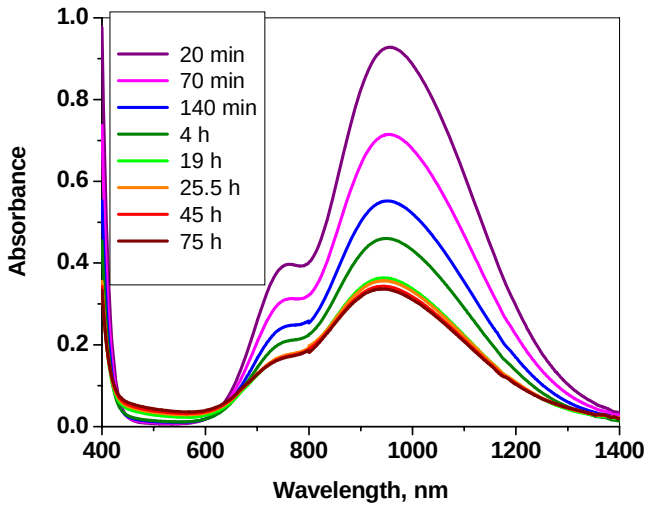

Figure S1. Evolution of the electronic spectra of $CuBr_2$/Me_6TREN in the presence of Cu metal in DMSO. Conditions: $[CuBr_2]_0$ = 2.5 mM, $[Cu^0]_0$ = 2.75 mM, $[Me_6TREN]_0$ = 5.25 mM, 25 ^oC.

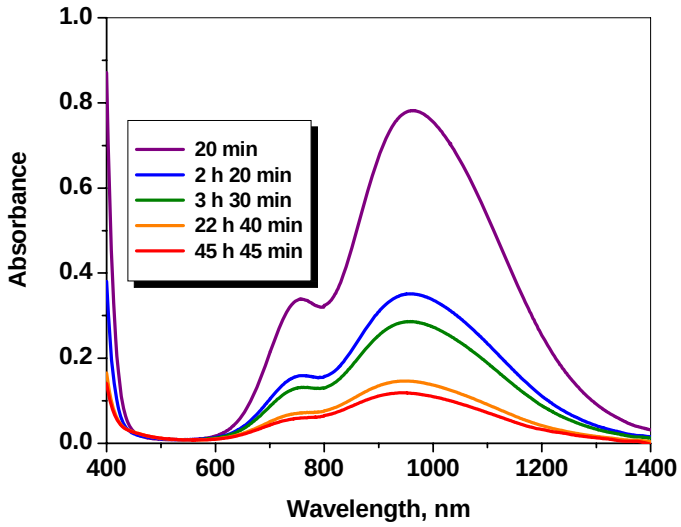

Figure S2. Evolution of the electronic spectra of $CuBr_2$/Me_6TREN in the presence of Cu metal in DMF. Conditions: $[CuBr_2]_0$ = 2.5 mM, $[Cu^0]_0$ = 2.75 mM, $[Me_6TREN]_0$ = 5.25 mM, 25 ^oC.

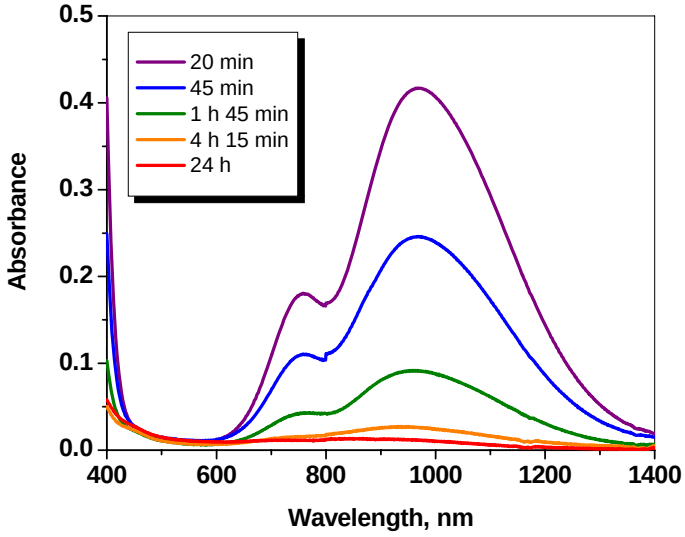

Figure S3. Evolution of the electronic spectra of $CuBr_2$/Me_6TREN in the presence of Cu metal in MeCN. Conditions: $[CuBr_2]_0$ = 2.5 mM, $[Cu^0]_0$ = 2.75 mM, $[Me_6TREN]_0$ = 5.25 mM, 25 ^oC.

B. Effect of Me_6TREN Concentration

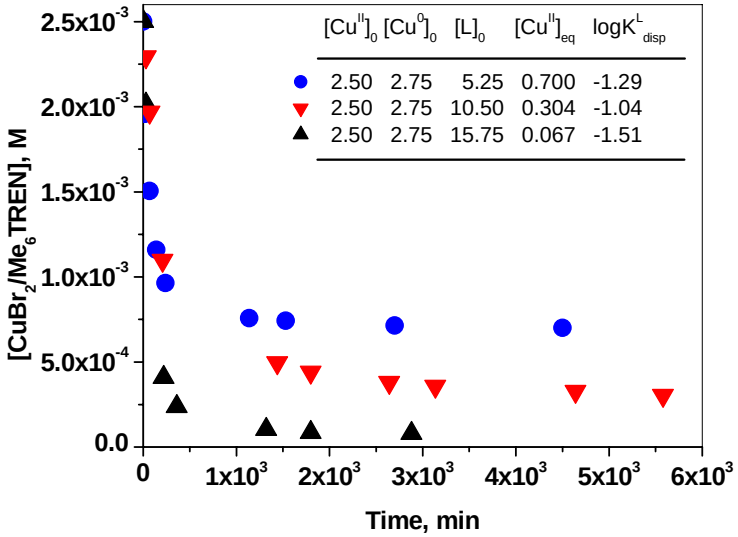

Figure S4. Comproportionation of $CuBr_2/Me_6$TREN (initial concentration 2.5 mM) in the presence of Cu^0 (10 % excess) and various amounts of ligand in DMSO at 25 °C. All concentrations in the inserted table are in mM.

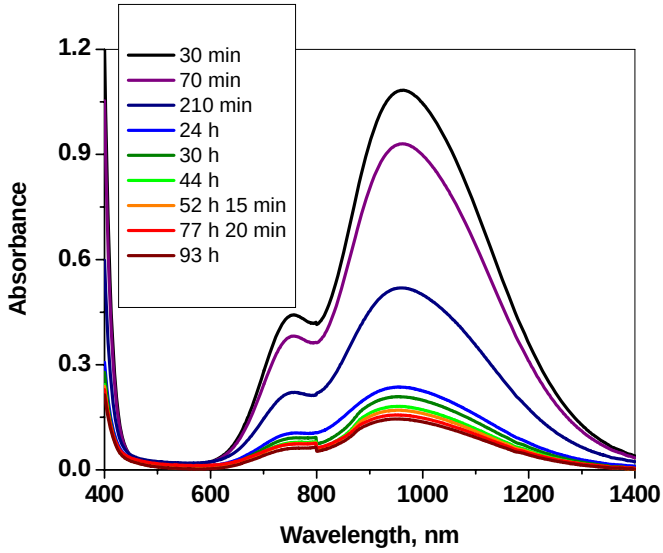

Figure S5. Evolution of the electronic spectra of $CuBr_2/Me_6$TREN in the presence of Cu metal in DMSO. Conditions: $[CuBr_2]_0$ = 2.5 mM, $[Cu^0]_0$ = 2.75 mM, $[Me_6TREN]_0$ = 10.5 mM, 25 °C.

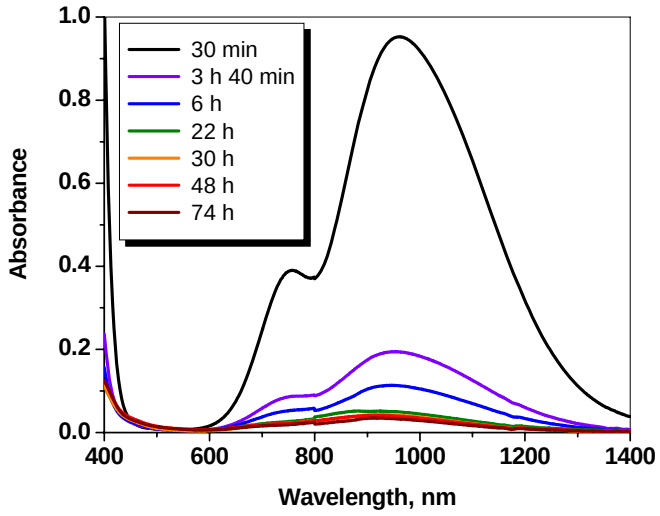

Figure S6. Evolution of the electronic spectra of $CuBr_2/Me_6TREN$ in the presence of Cu metal in DMSO. Conditions: $[CuBr_2]_0$ = 2.5 mM, $[Cu^0]_0$ = 2.75 mM, $[Me_6TREN]_0$ = 15.75 mM, 25 ^oC.

C. Counterion Effect

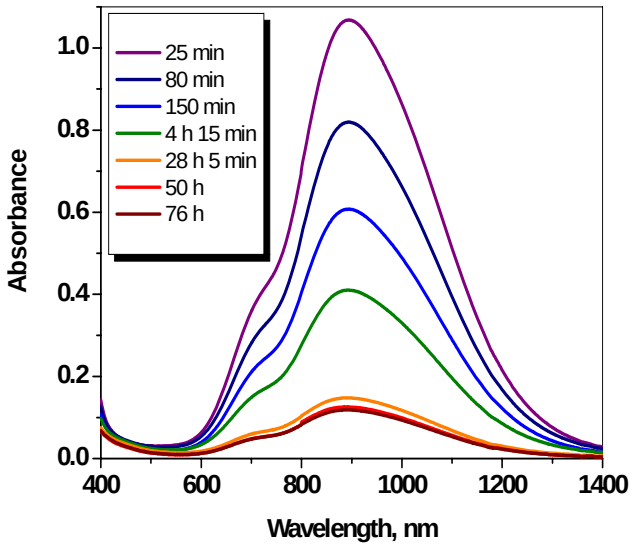

Figure S7. Evolution of the electronic spectra of $Cu(OTf)_2/Me_6TREN$ in the presence of Cu metal in DMSO. Conditions: $[Cu(OTf)_2]_0$ = 2.5 mM, $[Cu^0]_0$ = 2.75 mM, $[Me_6TREN]_0$ = 5.25 mM, 25 ^oC.

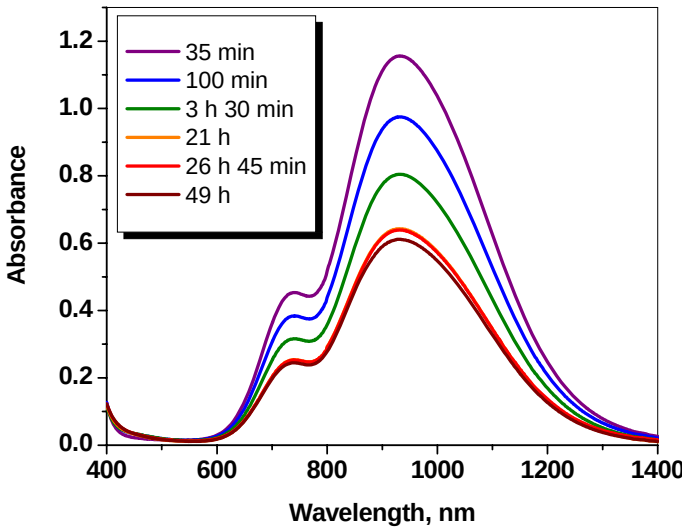

Figure S8. Evolution of the electronic spectra of $CuCl_2$/Me_6TREN in the presence of Cu metal in DMSO. Conditions: $[CuCl_2]_0$ = 2.5 mM, $[Cu^0]_0$ = 2.75 mM, $[Me_6TREN]_0$ = 5.25 mM, 25 ^oC.

D. Disproportionation of CuBr / Me6TREN in DMF

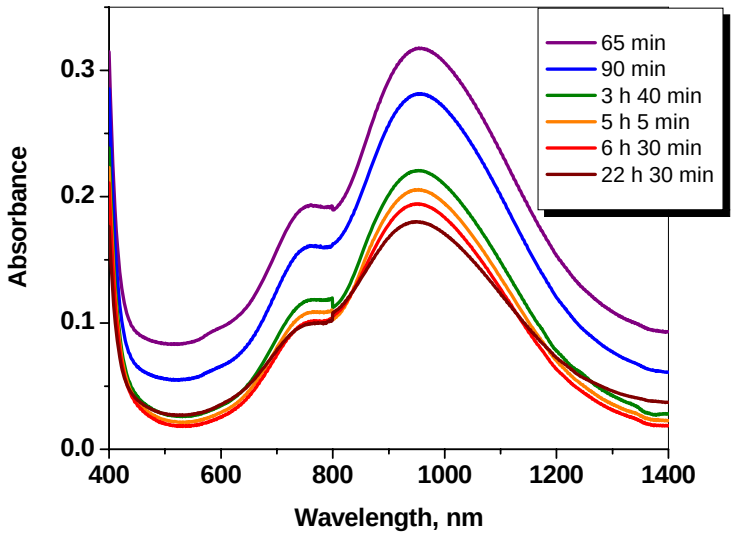

Figure S9. Evolution of electronic spectra during the disproportionation of CuBr/Me_6TREN in DMF. Conditions: $[CuBr]_0$ = 5 mM, $[Me_6TREN]_0$ = 5 mM, 25 ^oC.

II. Polymerization Results

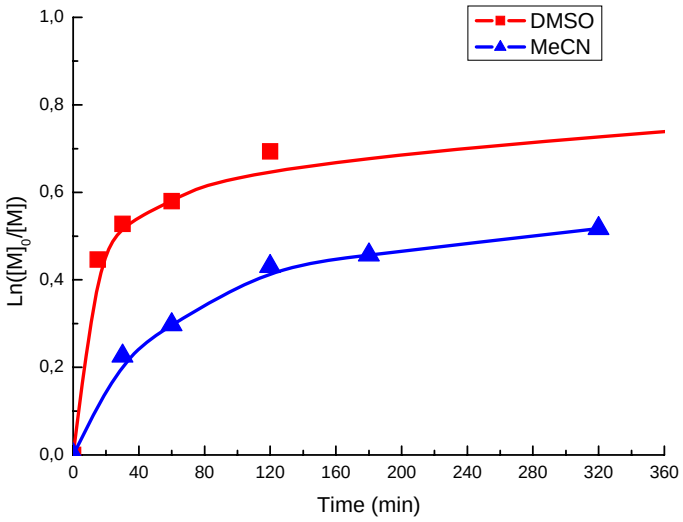

Figure S10. Kinetic plot for MA polymerization with CuBr/Me_6TREN: [MA]/[MBP]/[CuBr]/[Me_6TREN] = 222/1/1/1; 25°C, MA/DMSO or MeCN = 1/1 v/v.

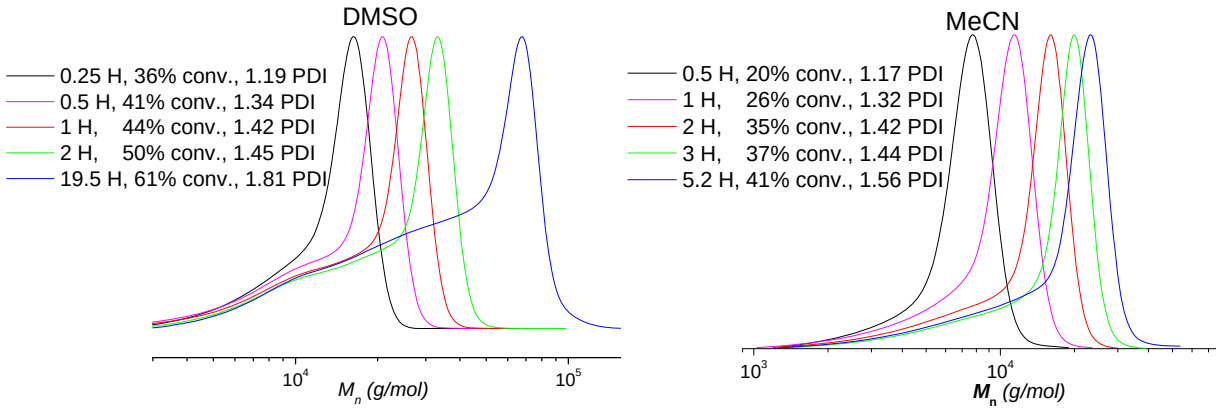

Figure S11. GPC traces illustrating molecular weight evolution during MA polymerization with CuBr/Me_6TREN: [MA]/[MBP]/[CuBr]/[Me_6TREN] = 222/1/1/1 ; 25°C, MA/DMSO or MeCN = 1/1 v/v.

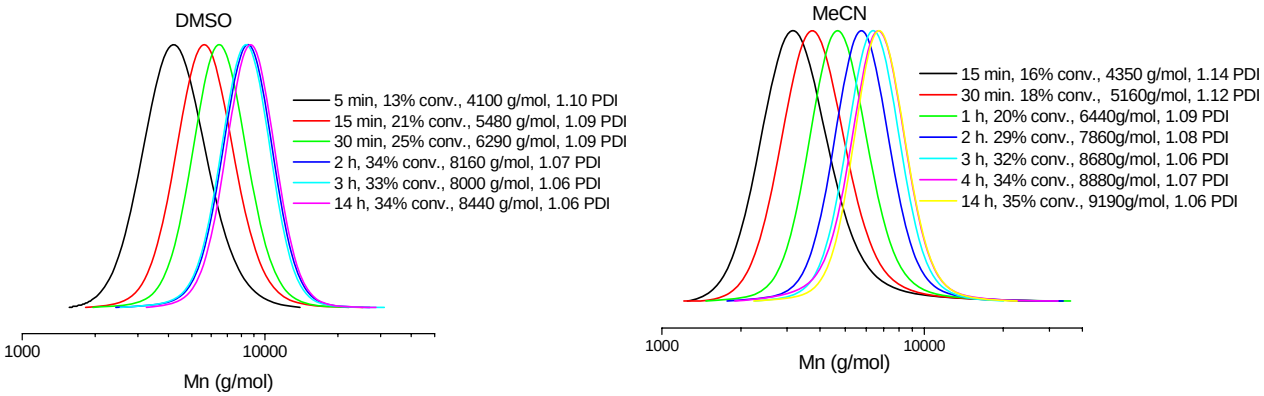

Figure S12. GPC traces illustrating molecular weight evolution during MA polymerization with CuBr/Me_6TREN: [MA]/[MBP]/[CuBr]/[Me_6TREN] = 222/1/0.1/0.1 ; 25°C, MA/DMSO or MeCN = 1/1 v/v.

III. "Ultra-high" molar mass PMA using stock suspensions

Experimental. 8 parallel reactions were carried out at room temperature in a 12 position parallel synthesizer (Carousel Reaction Station). In a typical experiment, seven 1 mL aliquots of an 8 mL suspension of Me_6TREN (17 μL, 0.064mmol) and Cu^0 (4.1 mg, 0.064mmol) in DMSO or MeCN were injected into seven different reactors, while the eighth (remaining) aliquot was left in the original reactor. Nitrogen purged MA (8 mL, 89 mmol) and DMSO or MeCN (7 mL) were added to the tubes. Finally 0.1 mL of MBP (0.008 mmol) was taken from a stock solution (18 μL (0.16 mmol) in 2 mL solvent) and added to the polymerization mixture.

Targeting ultra-high molecular weight PMA can be challenging on a laboratory scale when microgram quantities of reagents must be accurately dispensed. Stock solutions are typically employed under such conditions, but given the heterogeneous nature of a Cu^0 stock suspension, flawless reproducibility of polymerizations targeting ultra-high molecular weights cannot be

achieved on a relatively small scale. To minimize any error, seven aliquots of a Cu^0/Me_6TREN suspension in either DMSO or MeCN were injected into seven different reactors, and the eighth (remaining) aliquot was left in the original reactor. After monomer was added to each reactor, initiator was injected. Parallel reactions were all run for the same length of time. Results of these polymerizations are summarized in Figure S13.

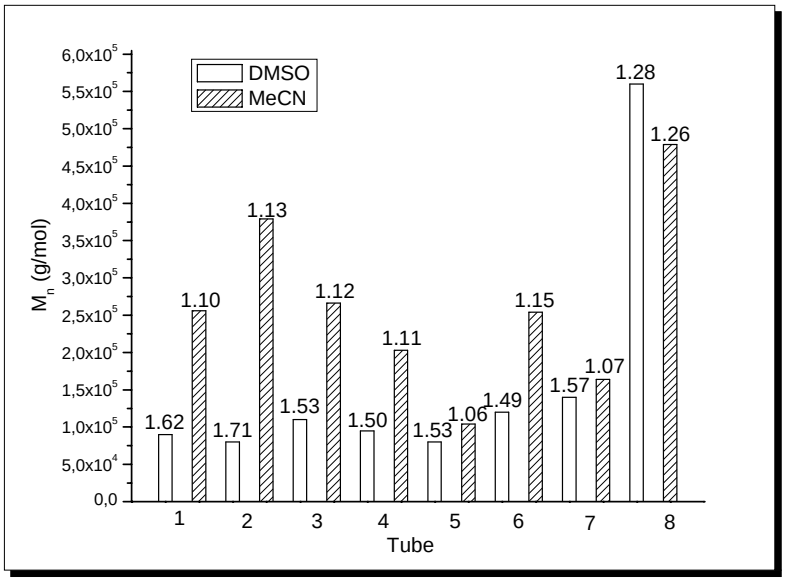

Figure S13. Final M_n and PDI of PMA with ultra-high molar mass targeted in several parallel reactors using the same stock solution. [MA]/[MBP]/[Cu^0]/[Me_6TREN]/[$CuBr_2$] = 11,100/1/1/1.1/0.1; 25°C; MA/DMSO or MeCN = 1/1 v/v. Catalyst was taken from the stock solution (tube 8) and distributed into 7 reaction tubes starting from tube 1 to 7. Reaction time: 23 h for tubes 1-7 in DMSO, 8 h for tube 8; 7.5 h for tubes 1-8 in MeCN.

The molecular weights attained ranged between M_n = 60,000 and 600,000 g/mol, and the polymerization rate (as deduced from molar masses) also varied by an order of magnitude, illustrating the difficulty in handling these heterogeneous systems at low catalyst concentrations.

IV. Model Studies: Reaction of MBP with Cu^0/Me_6TREN in the absence of a nitroxide radical trap

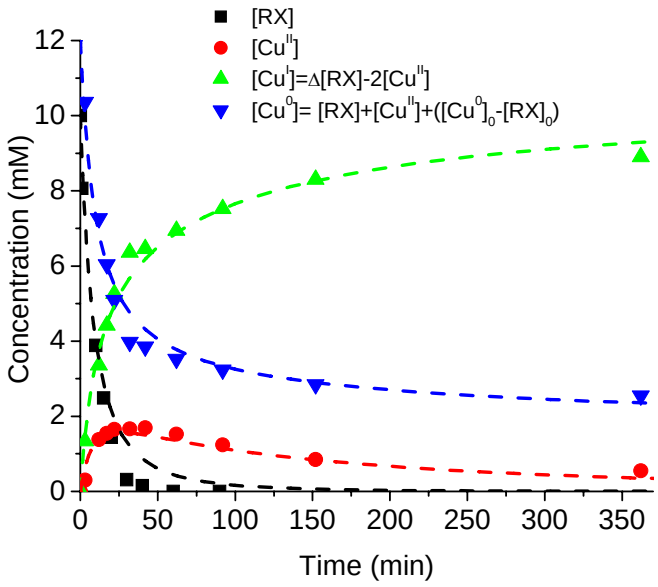

Figure S14. Time dependent concentration of Cu species and $PhCH_2Cl$ in MeCN as determined by gas chromatography and spectrophotometric measurements. $[Cu^0]/[Me_6TREN]/[PhCH_2Cl]/[trichlorobenzene]$ = 12/10/10/10 mM.