Supporting Material to

Methyl Acrylate Polymerizations in the Presence of a Copper/N₃S₃ Macrobicyclic Cage in DMSO at 25 °C.

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**Scheme S1.** Mechanism for AMME-N$_3$S$_3$sar mediated initiation and RAFT mediated polymerizations.
Figure S1. Redox potentials of CuBr$_2$/AMME-N$_3$S$_3$sar, CuBr$_2$/Me$_6$TREN and Ferrocene in both dimethyl sulfoxide and acetonitrile. All complex concentrations are 1 mM, contain 0.1 M Et$_4$NClO$_4$ and are referenced to Fe$^{+/0}$. 

\[ E_{1/2}, \text{V (vs Fe}^{+/0}) \]
Figure S2. Cyclic voltammograms of [Cu(AMME-N₃S₃sar)]²⁺⁺ (a) without EBiB and (b) with EBiB (100 mM) in DMSO. Complex concentrations are 1 mM and all voltammograms are recorded at 50 mV/s scanning rate in 0.1 M Et₄NClO₄ and are referenced to Ag/AgNO₃.
Figure S3: Cyclic voltammograms of [Cu(Me₆TREN)]²⁺ with varying concentrations of EBiB (0 - 10 mM) in DMSO. Complex concentrations are 1 mM and all voltammograms are recorded at 100 mV/s scanning rate in 0.1 M Et₄NCIO₄ and are referenced to Ag/AgNO₃.
Figure S4: Kinetic data for the polymerization of methyl acrylate (3.67 M) in DMSO (9.36 M) at 25 °C with EBiB (1.83 x 10^{-2} M), CuBr (1.83 x 10^{-2} M) and AMME-N₃S₃sar. (A) conversion versus time, (B) ln[M]₀/[M] versus time (C) number-average molecular weight (Mₙ,SEC) versus conversion, and (D) polydispersity index versus conversion. The concentration ratios of reactants [MA]/[EBiB]/[CuBr]/[AMME-N₃S₃sar] are (a) 200/1/1/1, (b) 200/1/1/2, and (c) 200/1/1/3
Figure S5: Kinetic data for the polymerization of methyl acrylate (3.67 M) in DMSO (9.36 M) at 25 °C with EBiB, MCEBTTC, CuBr and either AMME-N₃S₃sar or Me₆TREN where [MA]/[RAFT]/[EBiB] = 200/1/0.1. For all reactions, [EBiB]/[CuBr]/[ligand] = 1/1/1. (A) conversion vs time, (B) number-average molecular weight (Mn,SEC) vs conversion, and (C) polydispersity index vs conversion. Curves (a) CuBr/AMME-N₃S₃sar (b) CuBr/Me₆TREN.
Figure S6: Dual detector Size Exclusion Chromatograms of MCEBTTC mediated polymerization of methyl acrylate (3.67 M) in DMSO (9.36 M) at 25 °C with EBiB, MCEBTTC, CuBr and Me₆TREN at various ratios of initiator (— represents refractive index, --- represents UV absorbance at 306.6 nm). The concentration ratios of reactants [MA]/[EBiB]/[CuBr]/[Me₆TREN]/[MCEBTTC] are (A) 200/0.1/0.1/0.1/1, (B) 200/1/1/1/1, (C) 200/1/1/1/0.5, and (D) 200/1/1/1/0.1
Figure S7: Kinetic data for the polymerization of methyl acrylate (3.67 M) in DMSO (9.36 M) at 25 °C with EBiB (1.83 x 10^{-2} M), CuBr, [Cu(AMME-N3S3sar)]Br2 and AMME-N3S3sar. (A) conversion versus time, (B) ln[M0/[M] versus time (C) number-average molecular weight (Mn,SEC) versus conversion, and (D) polydispersity index versus conversion. The concentration ratios of reactants [MA]/[EBiB]/[CuBr]/[AMME-N3S3sar]/[[Cu(AMME-N3S3sar)]Br2] are (a) 200/1/1/1/0, (b) 200/1/1/1/0.05, (c) 200/1/1/1/0.1, and (d) 200/1/1/1/0.3