# Well-Defined Polymers Containing a Single Mid-Chain Viologen Group:

Synthesis, Environment-Sensitive Fluorescence, and Redox Activity

Zhaoxu Wang and Nicolay V. Tsarevsky*

Department of Chemistry and Center for Drug Discovery, Design, and Delivery at Dedman College,

Southern Methodist University, 3215 Daniel Avenue, Dallas, TX 75275, USA

* Corresponding author. Email: nvt@smu.edu; tel.: +1-214-768-3259

Supporting Information
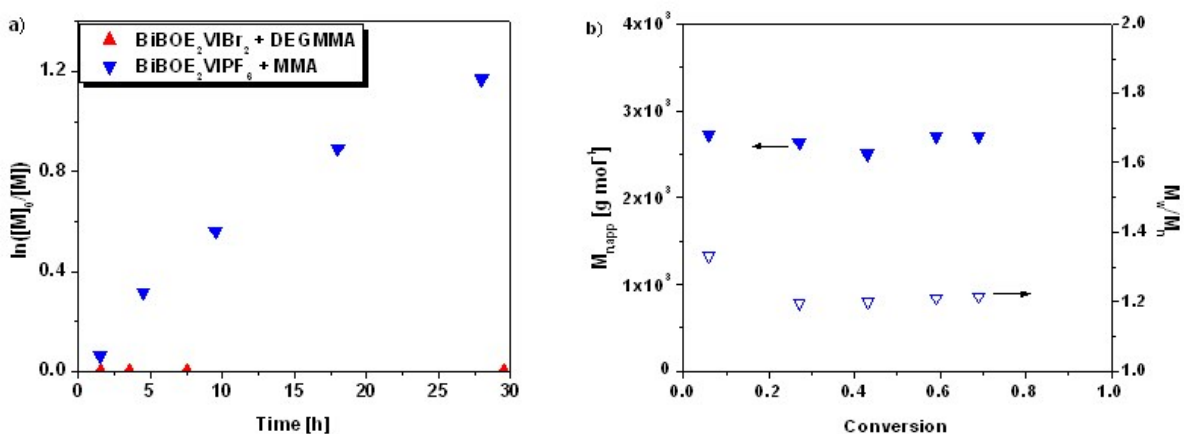
Figure S1. a) Kinetics of the ICAR ATRP of DEGMEMA and MMA mediated by Cu/TPMA complexes initiated by viologen-based bis(2-bromoisobutyrates) with different counterions; and b) Evolution of apparent molecular weights and MWD dispersities with monomer conversion during the ATRP reaction of MMA. Reaction conditions: $[DEGMMA]_0$ / $[(BiBOE)_2Vl(Br)_2]_0$ / $[CuBr_2]_0$ / $[TPMA]_0$ / $[AIBN]_0 = 400$: 1 : 0.06 : 0.12 : 0.2; DEGMMA / DMSO=1 / 1 (v / v), and $[MMA]_0$ / $[(BiBOE)_2Vl(PF_6)_2]_0$ / $[CuBr_2]_0$ / $[TPMA]_0$ / $[AIBN]_0 = 400$: 1 : 0.06 : 0.12 : 0.2; MMA / DMF=1 / 1 (v/v). Both reactions were carried out at 65 °C.
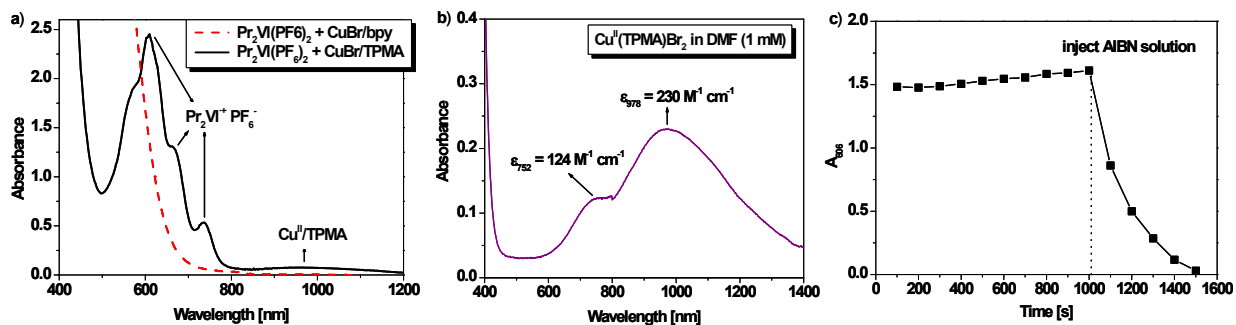
Figure S2. a) UV-vis spectra of mixtures of *N,N'*-dipropyl-4,4'-dipyridinium hexafluorophosphate (Pr$_2$Vl(PF$_6$)$_2$) with the CuBr complexes of TPMA and bpy in DMF at 45 °C, ca. 1 min after mixing (3.75 mM). b) UV-vis spectrum of Cu^{II}(TPMA)Br$_2$ (1 mM in DMF); the extinction coefficients at the absorption maxima are shown. c)Evolution of the intensity of the absorbance peak of the viologen radical cations (Pr$_2$Vl$^{\bullet+}$) generated from Pr$_2$Vl(PF$_6$)$_2$ (2 mM in DMF) at 606 nm in the presence of dissociating AIBN (6 mM in DMF) at 65 °C. Pr$_2$Vl(PF$_6$)$_2$ was first reduced using a Mg ribbon in deoxygenated Schlenk flask fitted with a cuvette, and the solution of Pr$_2$Vl$^{\bullet+}$ was transferred into the Schlenk flask attached to the cuvette for UV-vis measurement. Then, solution of AIBN was injected though the side arm of the Schlenk flask. The absorbance after the addition of the AIBN solution was adjusted to reflect the dilution.
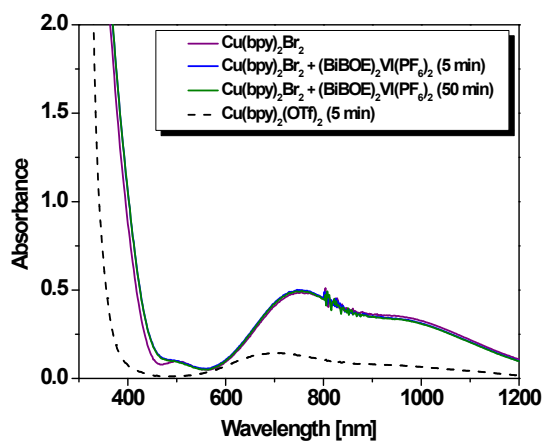

Figure S3. UV-vis-NIR spectra of Cu(bpy)$_2$Br$_2$ (2 µM), Cu(bpy)$_2$(OTf)$_2$ (2 µM) and the mixture of Cu(bpy)$_2$Br$_2$ (2 µM) and (BiBOE)$_2$Vl(PF$_6$)$_2$ (2 µM), DMF, 45 °C.

2
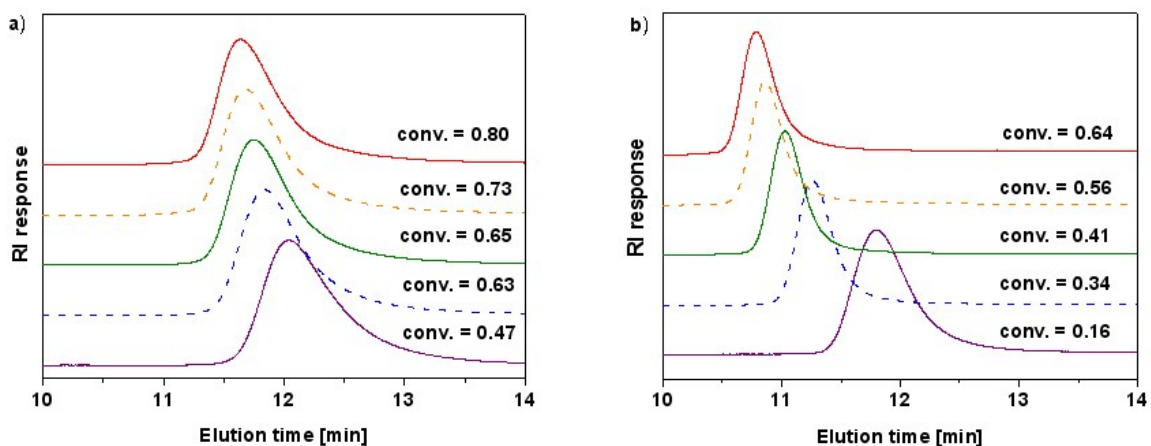
Figure S4. Evolution of SEC traces of polymers prepared by the ATRP of MMA initiated by $(BiBOE)_2Vl_2(PF6)_2$ and mediated by Cu/bpy complexes at 45 ^{o}C in DMF at $DP_{n,targ} = 200$ (a) and 1,200 (b). The monomer conversions are shown at each of the SEC traces.
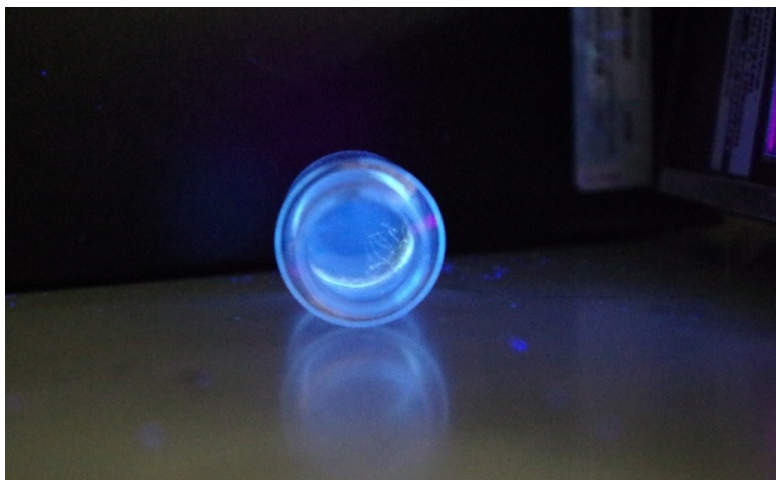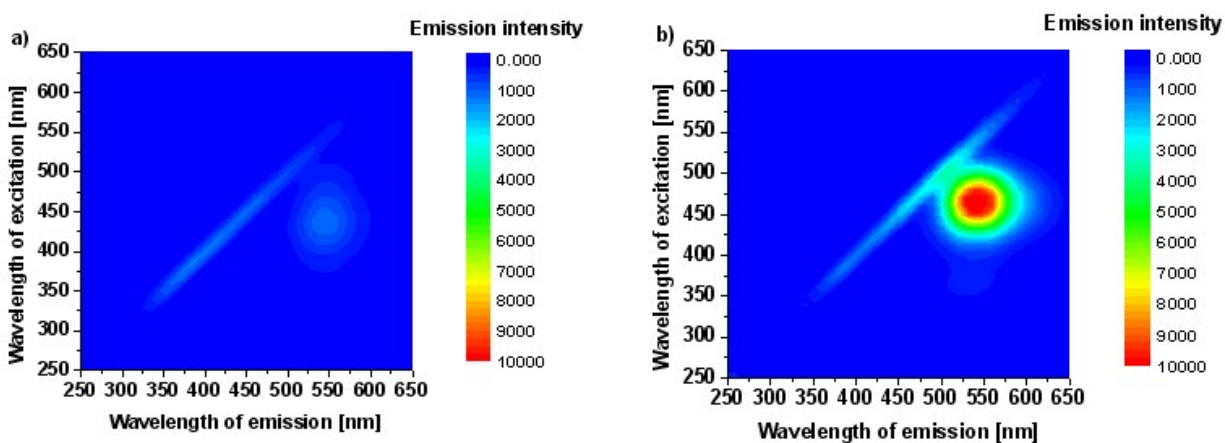

Figure S5. Photograph of solid viologen-containing polyMMA under UV light.
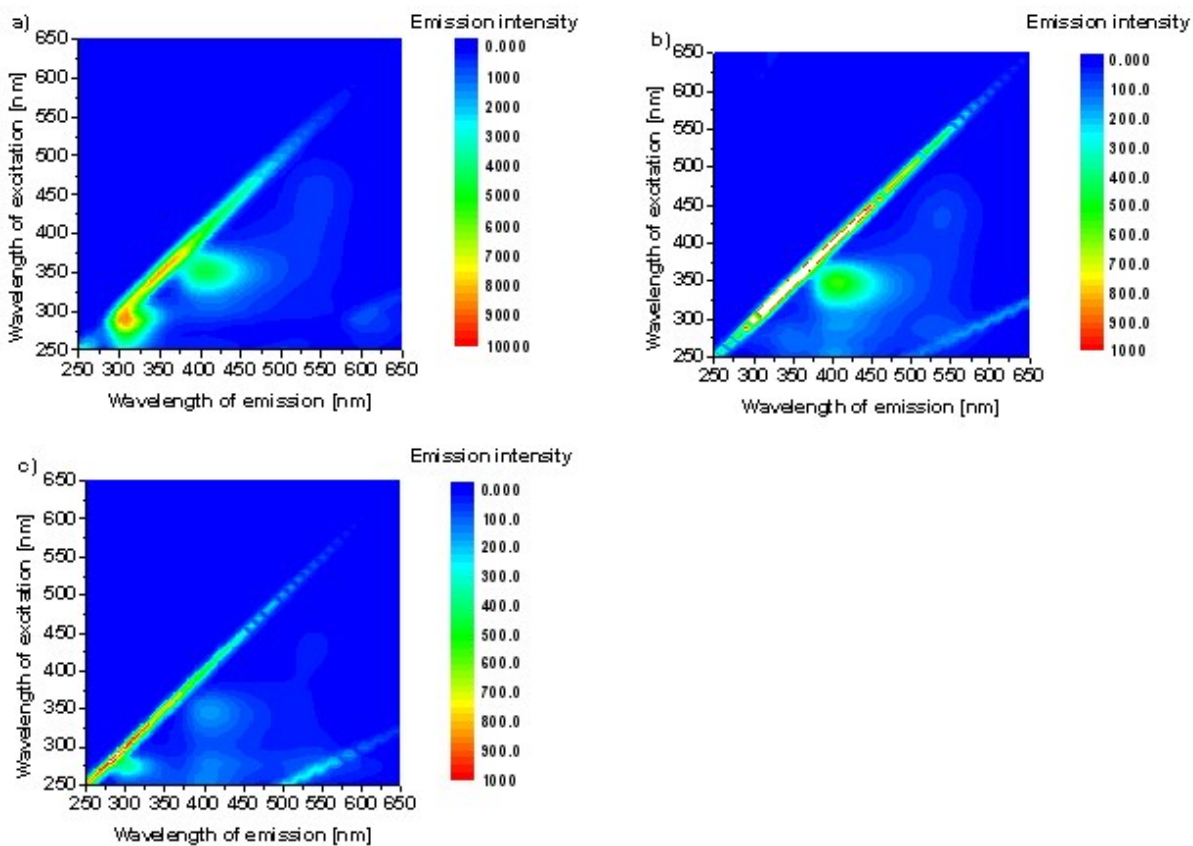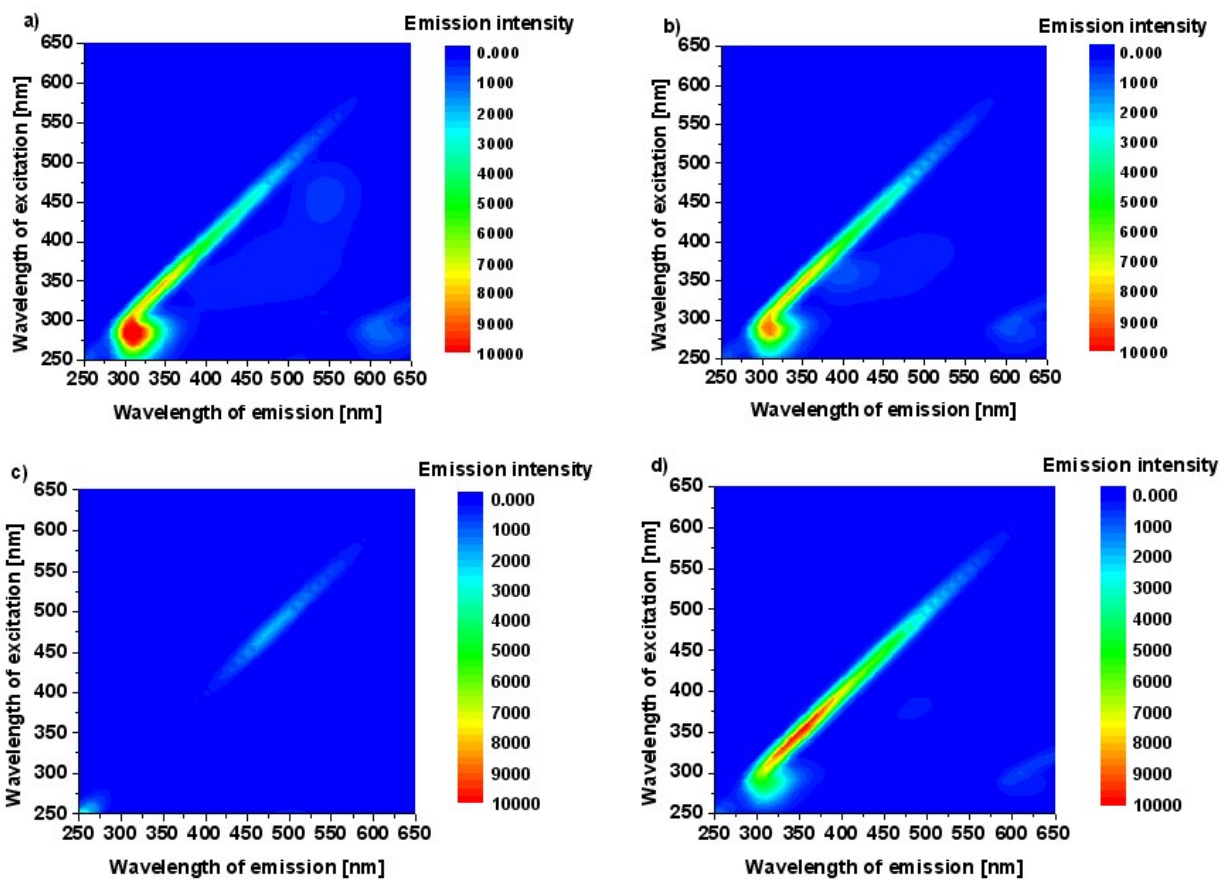
Figure S6. Fluorescence excitation–emission matrix of acetonitrile solution of a) viologen-containing polyMMA (6.7 mg mL^{-1}, $M_{n, app}$ = 31,760 g mol^{-1}, slit widths = 20 nm), b) viologen-containing polyMMA (12 mg mL^{-1}, $M_{n, app}$ = 31,760 g mol^{-1}, slit widths = 10 nm), c) viologen-containing polyMMA (1.2 mg mL^{-1}, $M_{n, app}$ = 31,760 g mol^{-1}, slit widths = 10 nm).
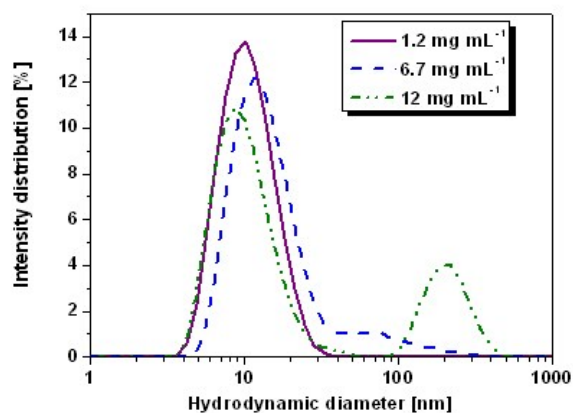
Figure S7. Intensity size distribution of aggregates formed by dissolving viologen-containing polyMMA ($M_{n, app}$ = 31762 g mol^{-1}) in acetonitrile at different concentrations (1.2 mg mL^{-1}, 6.67 mg mL^{-1}, or 12 mg mL^{-1}).

Figure S8. Fluorescence excitation–emission matrix of DMF solution of Pr$_2$Vl(PF$_6$)$_2$ (1.9 mM, 1.5 mL) a) before, b) after treating with Mg (ribbon, 40 mg) under air at room temperature (ca. 21 °C) for 20 h.

Figure S9. Fluorescence excitation–emission matrix of acetonitrile solution of viologen-containing polyMMA (6.7 mg mL^{-1}, $M_{n, app}$ = 31762 g mol^{-1}) in the presence of 50 mM a) Bu$_4$NCl, b) Bu$_4$NBr, c) NH$_4$I, d) NH$_4$SCN.