

Supporting Information

Polypyridyl Ru(II)-Derivatized Polypropylacrylate Polymer with a Terminal Water Oxidation Catalyst. Application of Reversible Addition-Fragmentation Chain Transfer Polymerization

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EXPERIMENTAL

Materials. 2-(Dodecylthiocarbonothioylthio)-2-methylpropanoic acid (DDMAT) was synthesized using literature method.¹ Methacryloyl chloride, 3-chloropropan-1-ol, *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA), bis(triphenylphosphoranylidene)ammonium chloride (PPNCl), *N,N*-diisopropylethylamine (DIPEA) and sodium azide were received from

¹ Liu, Z.; Hu, J.; Sun, J.; Liu, G. *J. Polym. Sci. Part A Polym. Chem.* **2010**, 48, 4922-4928.

Sigma-Aldrich without further purification. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Copper (I) bromide was freshly treated with acetic acid, ethanol and acetone before use. $[\text{Ru}(4-(2,2':6',2'\text{-terpyridine-4'-yl)benzoic chloride})(\text{bpy})(\text{Cl})]^+$ was synthesized based on our reported method.² Triethylamine (Et_3N) and methylene chloride (CH_2Cl_2) were refluxed over calcium hydride and distilled. Other solvents were used as received from Fisher Scientific.

The solutions for photophysical measurements were prepared in HPLC grade propylene carbonate and degassed with argon for 20 mins. Standard tris(2,2'-bipyridine)ruthenium(II) hexafluorophosphate $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ was synthesized via a counter ion exchange from $\text{Ru}(\text{bpy})_3\text{Cl}_2$.

General Methods and Instrumentation. NMR spectra were obtained on a Bruker instrument operating at 400 MHz utilizing deuterated chloroform and/or DMF as solvents. Gel permeation chromatography (GPC) analyses were conducted with THF as the eluent on a Waters Alliance system comprised of a 2695 Separations Module and Waters 2414 Refractive Index Detector (Waters Associates Inc., Milford, MA). The molecular weight was calibrated using poly(methyl methacrylate) (PMMA) standards. UV-vis absorption spectra were recorded on a Hewlett Packard 8453 spectrometer. Steady-state emission spectra were recorded on an Edinburgh Instruments FLS920 emission spectrometer, equipped with a Xenon light source. Excitation was at 460 nm, with inclusion of a 495-nm long-pass optical filter before the detector. Emission intensities at each wavelength were corrected for system spectral response. Time-correlated single photon counting data were obtained by the same instrument equipped with a pulsed, 445

² Ashford, D.L.; Stewart, D.J.; Glasson, C.R.; Binstead, R.A.; Harrison, D.P.; Norris, M.R.; Concepcion, J.J.; Fang, Z.; Templeton, J.L.; Meyer, T.J. *Inorg. Chem.* **2012**, 51, 6428.

nm LED excitation source (Edinburgh Instruments EPL-445, fwhm \sim 1.5 ns, repetition rate = 50,000 Hz). Emission from Ru(II) complex was observed at 610 or 650 nm. Decay traces were fitted by using the Edinburgh F900 or Origin 8.1 software package.

Electrochemistry was probed using cyclic voltammetry on a computer-controlled CHI660D electrochemical workstation, where a glassy carbon electrode served as the working electrode, a platinum electrode as the counter electrode, and an AgNO₃/Ag electrode as the reference. A solution of tetrabutylammonium hexafluorophosphate (0.1 M) in degassed dry propylene carbonate was used as the supporting electrolyte, and the scan rate was 50 mV·s⁻¹.

Synthesis. 3-Chloropropyl methacrylate (1). To a solution containing 3-chloropropan-1-ol (8.38 mL), hydroquinone (0.1 g) and anhydrous triethylamine (18.3 mL) in dry CH₂Cl₂ (60 mL) cooled in ice bath, methacryloyl chloride (11.7 mL) was added dropwise. The mixture was stirred at 0°C for 1 hr, and then warmed to room temperature for another 12 hrs. CH₂Cl₂ (50 mL) was added and washed with diluted HCl, water and NaOH (10 wt %). Hydroquinone (0.1 g) was added to the solution, which was dried over MgSO₄. The solvent was distilled out under reduced pressure to yield a yellowish liquid. The crude was distilled in vacuum to afford a colorless liquid (7.6 g, 47%). ¹H NMR (400 MHz, CDCl₃) δ 6.07 (s, 1H), 5.53 (s, 1H), 4.26 (t, 2H, J = 6.2 Hz), 3.60 (t, 2H, J = 6.4 Hz), 2.11 (p, 2H, J = 6.2 Hz), 1.90 (s, 3H).

PCPM. A Schlenk flask containing **1** (2 g, 12.3 mmol), DDMAT (0.224 g, 0.615 mmol), AIBN (10 mg, 0.0615 mmol) was conducted a freeze-vacuum cycle for three times, and put in 80 °C oil bath. After 3 hrs, the mixture was diluted with THF (10 mL) and precipitated from methanol (200 mL). After isolated, the solid was dissolved in THF and precipitated again. The re-dissolve/precipitation process was conducted for three times to yield a light yellow solid (1.21 g,

54%). $M_n = 3530$, $M_w/M_n = 1.3$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.11, 3.67, 2.12, 1.93, 1.86, 1.25, 1.07, 0.91.

PNPM. To a solution of PCPM (0.4 g) in DMF (80 mL), NaN_3 (1.0 g) was added. The mixture was stirred for 2 days in nitrogen. The mixture was filtered and concentrated carefully in vacuum. The solution was poured into methanol to yield a white solid (0.28 g, 70 %). $M_n = 3090$, $M_w/M_n = 1.3$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.05, 3.43, 1.92, 1.84, 1.05, 0.89.

P1. A round bottom flask charged with **PNPM** (12 mg), (4-CC-bpy) $\text{Ru}(\text{bpy})_2(\text{PF}_6)_2$ (100 mg), CuBr (11 mg), PMEDTA (20 μL) and DMF (3 mL) was degassed with argon for 30 mins and stirred at room temperature overnight. The solution was dropped into ethanol to yield an orange solid. The solid was isolated by centrifuge and dissolved in a small amount of acetone, followed by precipitation in ethanol. This dissolve-precipitation process was repeated from three times and finally yielded a deep orange solid (65 mg, 78 %). The polymer product as metathesized to the chloride salt by precipitation from acetone upon the addition of PPNCl . The solid was dissolved in water and purified by dialysis with a 3500 cutoff membrane. $^1\text{H NMR}$ (400 MHz, D_2O) δ 8.89, 8.54, 8.01, 7.75, 7.62, 7.37, 7.22, 4.54-3.93, 2.33-0.75.

P2. To a flask charged with $[\text{Ru}(4-(2,2':6',2''\text{-terpyridine-4'-yl)benzoic chloride})(\text{bpy})(\text{Cl})]^+(\text{Cl})_2$, a solution containing **P1** (10 mg), DIPEA (0.3 mL) and DMF (3 mL), $[\text{Ru}(4-(2,2':6',2''\text{-terpyridine-4'-yl)benzoic chloride})(\text{bpy})(\text{Cl})]^+$ was added at 0°C . The mixture was stirred at 100°C overnight under argon, cooled and precipitated from acetone. The precipitate was dissolved in water and dialyzed with a 3500 cutoff membrane. After water was distilled out, the residue was dissolved in methanol with added AgOTf and stirred under argon overnight. The mixture was filtered and added with a saturated aqueous solution of LiClO_4 to yield a red solid (8 mg, 81%).

^1H NMR (400 MHz, D_2O) δ 9.51, 8.91, 8.49, 8.03, 7.75, 7.62, 7.37, 7.22, 7.15, 4.52-3.91, 2.31-0.75.

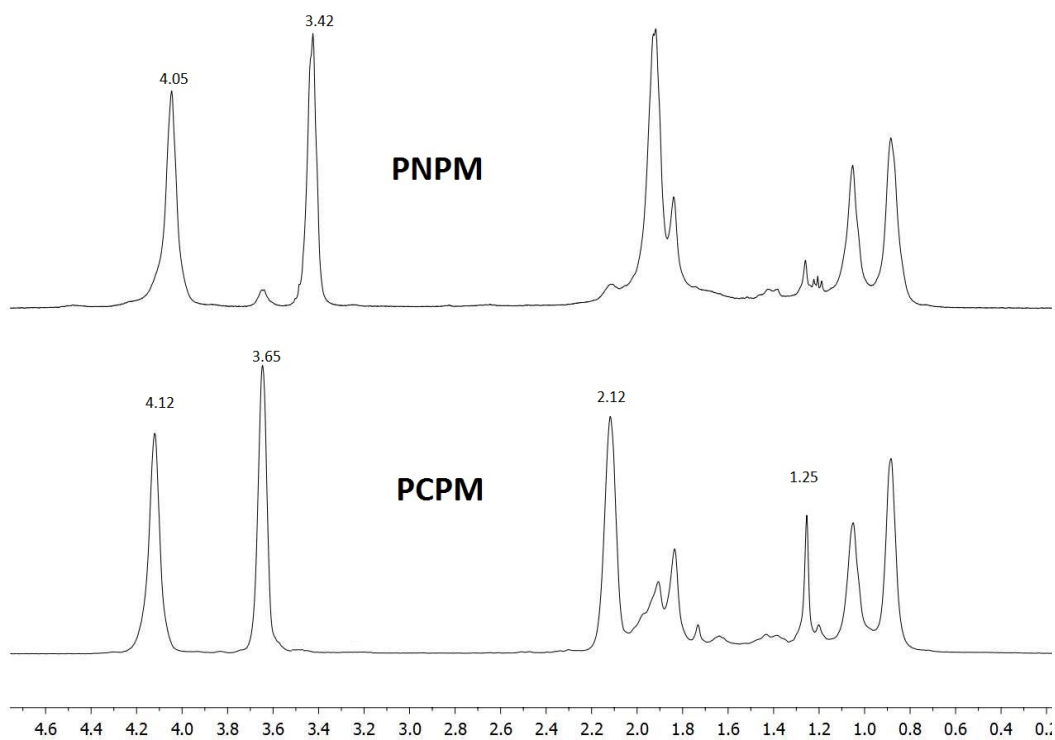


Figure S1. ^1H -NMR of PCPM and PNPM in CDCl_3 solutions

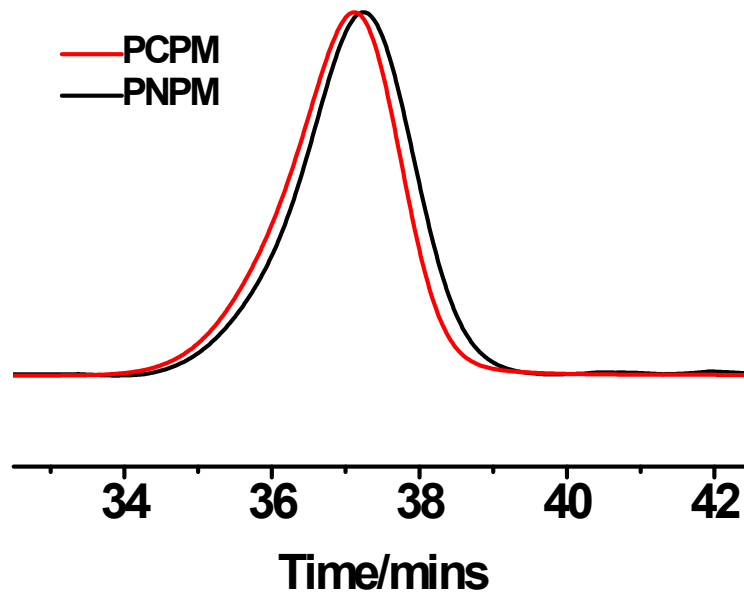


Figure S2. GPC curves of PCPM and PNPM

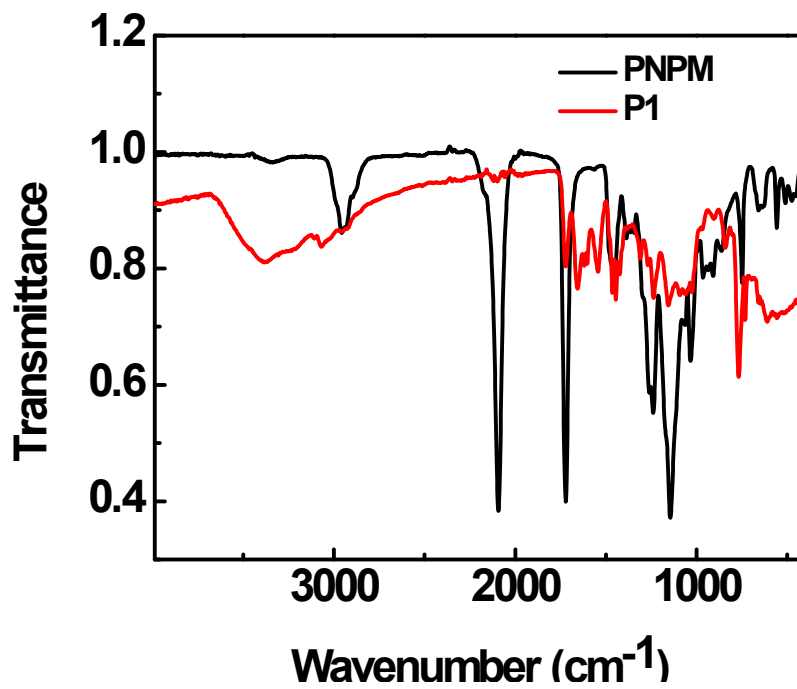


Figure S3. FTIR of PNPM and P1

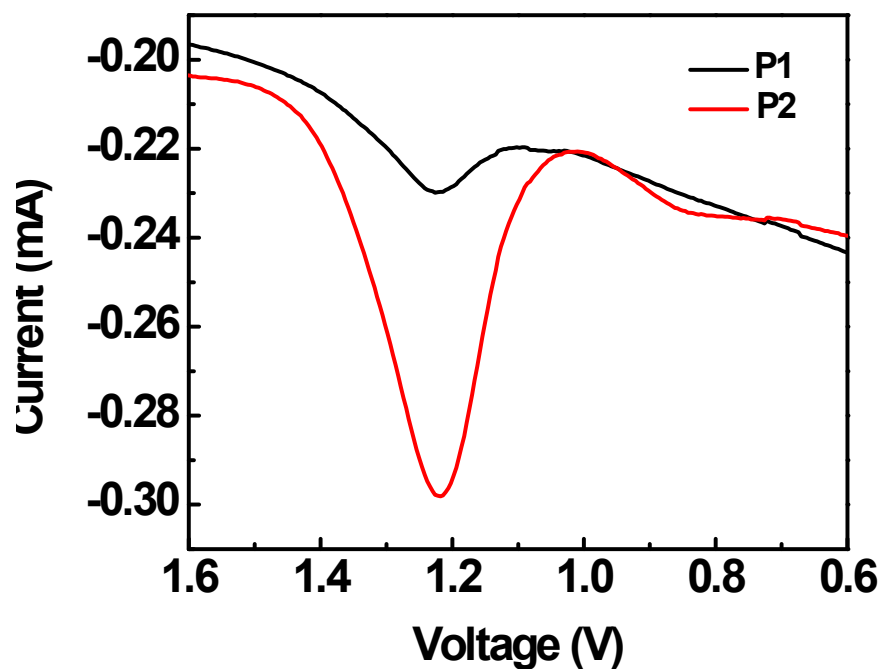


Figure S4. DPV curves of **P1** and **P2** on nano-ITO, soaked in 0.1 mM TBAH in propylene carbonate

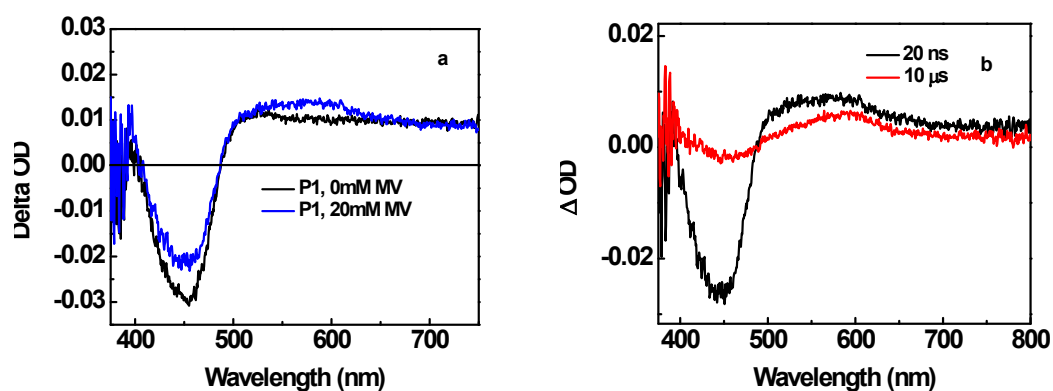


Figure S5. Nanosecond transition absorption difference spectra of **P1** with and without MV^{2+} in deaerated DMF obtained at ~ 20 ns (a), and the spectra at different time (b) following excitation by 425 nm laser. $[Ru] = 20 \mu M$

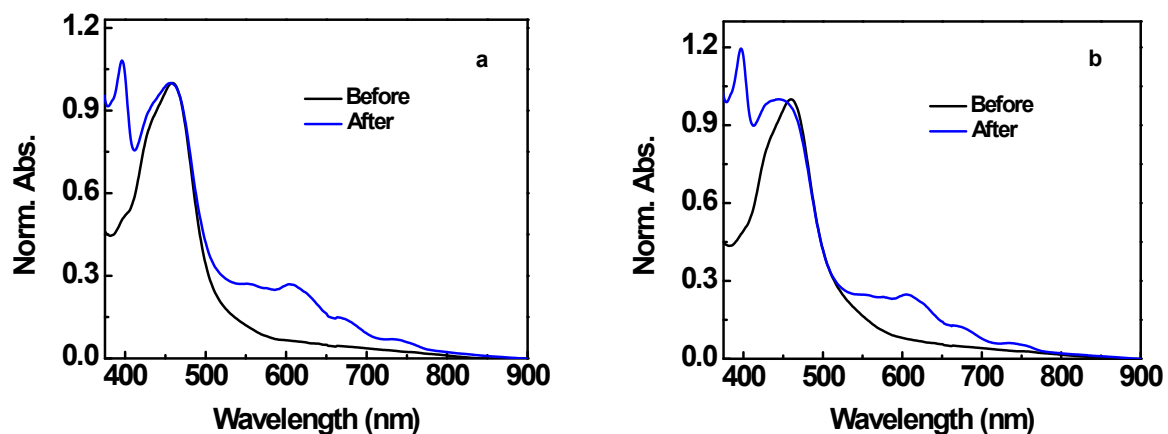


Figure S6. P1 (a) and P2 (b) solutions in the presence of MV^{2+} before and immediately after laser irradiation; $[Ru] = 20 \mu M$ in deaerated DMF; $[MV^{2+}] = 20 mM$.

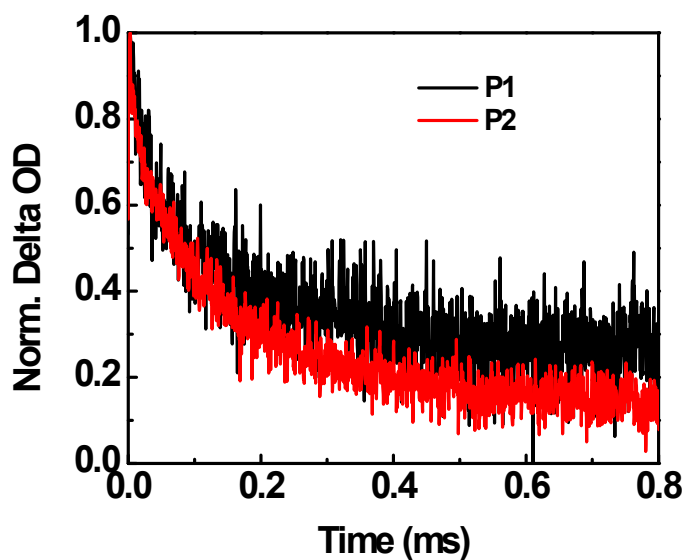


Figure S7. Normalized transition absorption-time traces at 600 nm for back electron transfer from $MV^{\bullet+}$ to P1 and P2 following 425 nm excitation in DMF. Ruthenium concentration: 20 μM .

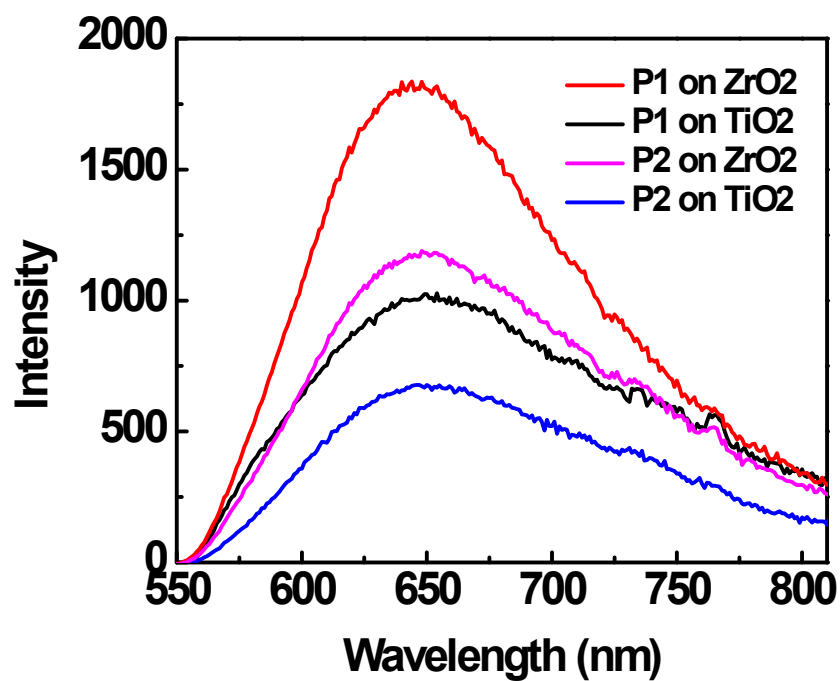


Figure S8. Corrected emission spectra of **P1**, **P2**, on ZrO₂ and TiO₂ films. The intensity represents the relative quantum yields.