Supporting Information

Electrochemical Oxidation of Trivalent Americium Using a Dipyrazinylpyridine Modified ITO Electrode

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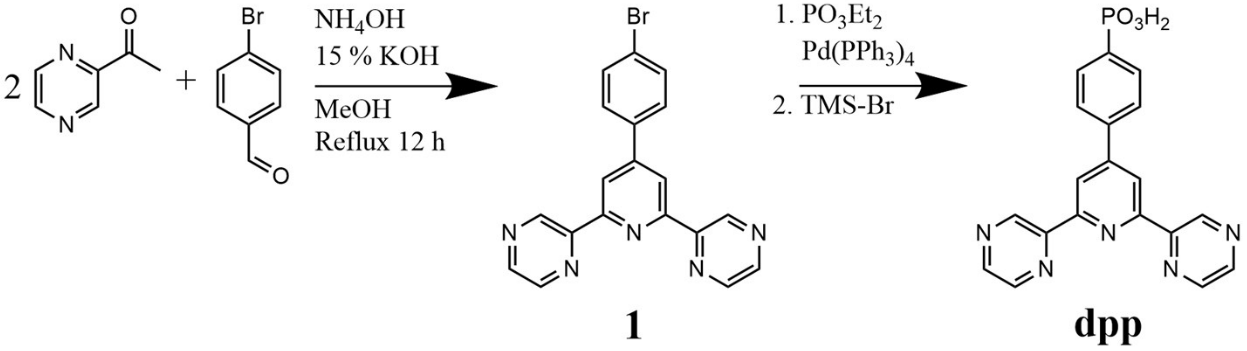
Experimental Section.

Scheme S1. Synthetic scheme for 4′-phosphonyl-(4-phenyl)-2,6-di(2-pyrazinyl)pyridine (pdpp) based on references 1 and 2.



4′-bromo-(4-phenyl)-2,6-di(2-pyrazinyl)pyridine (1) was synthesized according to Reference 1.[1] 2-Acetylpyridine (5.000 g, 0.041 mol), 4-bromobenzaldehyde (3.700 g, 0.020 mol) concentrated NH_4OH (13.3 ml), and 15 % KOH (116 mL) were heated to reflux for 12 h. The resultant precipitate (4.27 g) was filtered and sequentially washed with copious amounts of methanol, water, and diethyl ether. Yield of the pure product was 4.27 g (54.7 %). ^{1}H-NMR (400 MHz, $CDCl_3$) 9.89 (s, 2H), 8.71 (s, 2H), 8.69 (s, 4H), 7.77 (m, 2H), 7.69 (m, 2H).

4′-diethylphosphonate-(4-phenyl)-2,6-di(2-pyrazinyl)pyridine (2) was synthesized using a modified preparation from Reference 2.[2] (1) (500 mg, 1.28 mmol), diethylphosphite (0.25 mL, 1.92 mmol), and Et_3N (0.27 mL, 1.92 mmol) were added together to anhydrous toluene. 10 % mol $Pd(PPh_3)_4$ was added as a C-P coupling catalyst. The reaction mixture was heated to 95 ° C for 24 h. 248 mg of (2) was obtained pure after recrystallization from toluene (43 % yield). ^{1}H-NMR (400 MHz, $CDCl_3$) 9.87 (s, 2H), 8.74 (s, 2H), 8.67 (s, 4H), 7.96 (m, 4H), 4.17 (m, 4H), 1.36 (m, 6H). ^{31}P-NMR (400 MHz, $CDCl_3$) 17.95 (s).

4′-(phosphonic acid)-(4-phenyl)-2,6-di(2-pyrazinyl)pyridine (dpp) was synthesized using a modified preparation from Reference 2. (2) was hydrolyzed by first dissolving 100.0 mg (0.22 mmol) in an anhydrous, oxygen free 1:1 acetonitrile:toluene solution. 3.6 equivalents (0.11 mL, 0.80 mmol) of TMS-Br were added, and the solution was stirred at room temperature for 22 h. The solvent was subsequently removed under reduced pressure at room temperature. The off-white powder was recrystallized from methanol. ^{1}H-NMR (400 MHz, DMSO-d_6) 9.88 (s, 2H), 8.83 (d, 4H), 8.72 (s, 2H), 8.05 (s, 2H), 7.88 (m, 2H). ^{31}P-NMR (400 MHz, DMSO-d_6) 11.83 (s).

Nano ITO electrodes were prepared using a previously described procedure.[3] Briefly, a 15 wt. % suspension of ITO nanoparticles ITO (18 nm particle size, purchased from US-Nano) with 5 wt. % hydroxypropylcellulose (80,000 MW) was sonicated using a sonicating horn until homogenized (5-10 min, with 1 min breaks in-between sonicating to prevent overheating). The resultant suspension was doctor-bladed onto FTO-glass (15 MΩ, Hartford Glass), dried, and subsequently annealed in air for 1 h at 500 °C. The resultant pale yellow electrodes (Figure S4) were cut such that the active *nano*ITO area was approximately 1 cm^2.

Caution: 243Am is a radioactive material, and should only be used in facilities designated for such use. A radiologically designated fumehood with a high-efficiency particulate-absorbing (HEPA) filtered exhaust was used for all Am work. Stock solutions of 243Am were on hand from previous work at Idaho National Laboratory. These solutions consisted of 0.1 M nitric acid with 1.5 mM Am(III) (quantified by gamma spectroscopy), and were diluted with additional 0.1 M nitric acid to yield a nominally 0.8-1.0 mM solution of Am(III).

Electrochemical experiments were performed using a CH Instruments 601E potentiostat, or a Princeton Applied Research VersaStat 3. A saturated calomel electrode (SCE) was used as the reference electrode for all aqueous studies, and a graphite rod, or platinum wire were used as the counter electrode. A custom built 2-compartment cell comprised of a 1 cm path length borosilicate cuvette connected to a length of square borosilicate glass through a fine glass frit was used for all americium based electrochemical, spectroscopic, and spectroelectrochemical studies.

In nonaqueous solutions, a Ag/AgCl quasi-reference electrode was used and potentials referenced to an internal standard of either *nano*ITO-RuP^{2+} or ferrocene; a graphite rod was used as the counter electrode. Spectroelectrochemistry was performed using an Agilent HP8454 UV-vis spectrometer using a modified spectrophotometric cell.

Scanning Electron Microscope images were collected on a Hitachi S-4700 SEM. Energy Dispersive Spectra were collected using the same Hitachi S-4700 SEM, which is equipped with an INCA PentaFET-x3 EDS from Oxford Instruments.

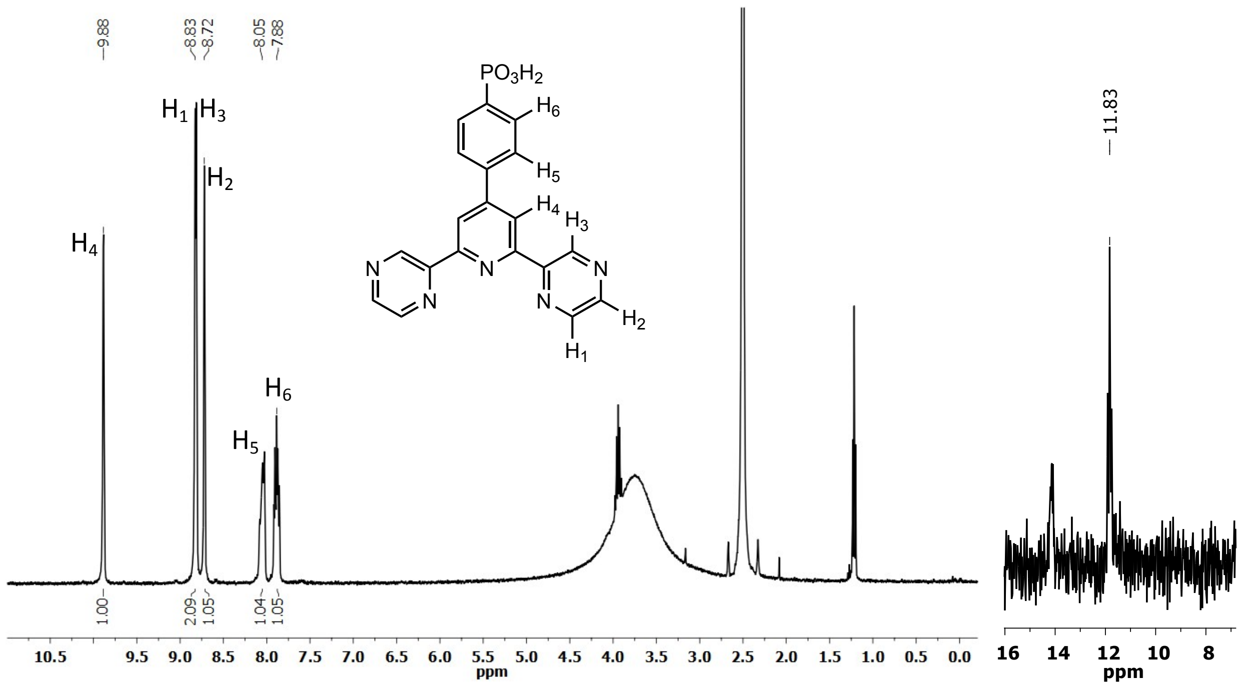


Figure S1. ^{1}H-NMR (Left), and ^{31}P-NMR (Right) spectra of **pdpp** in DMSO-d_6.

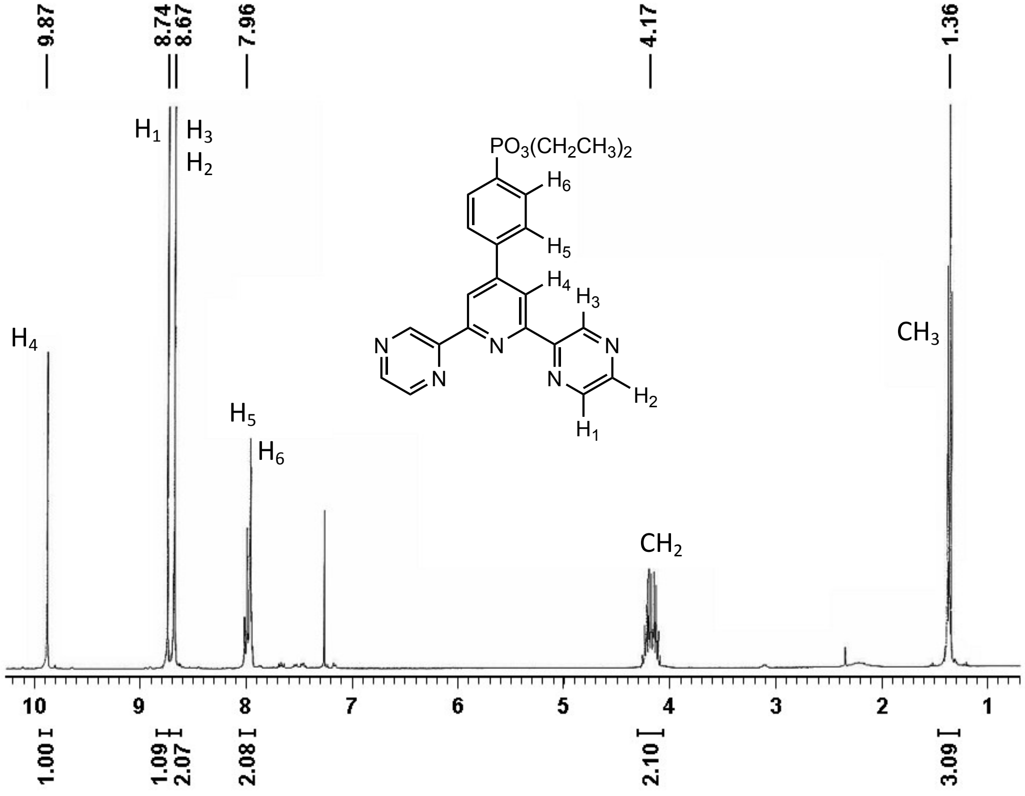


Figure S2. ^{1}H-NMR spectrum of PO_3Et_2-dpp in $CDCl_3$.

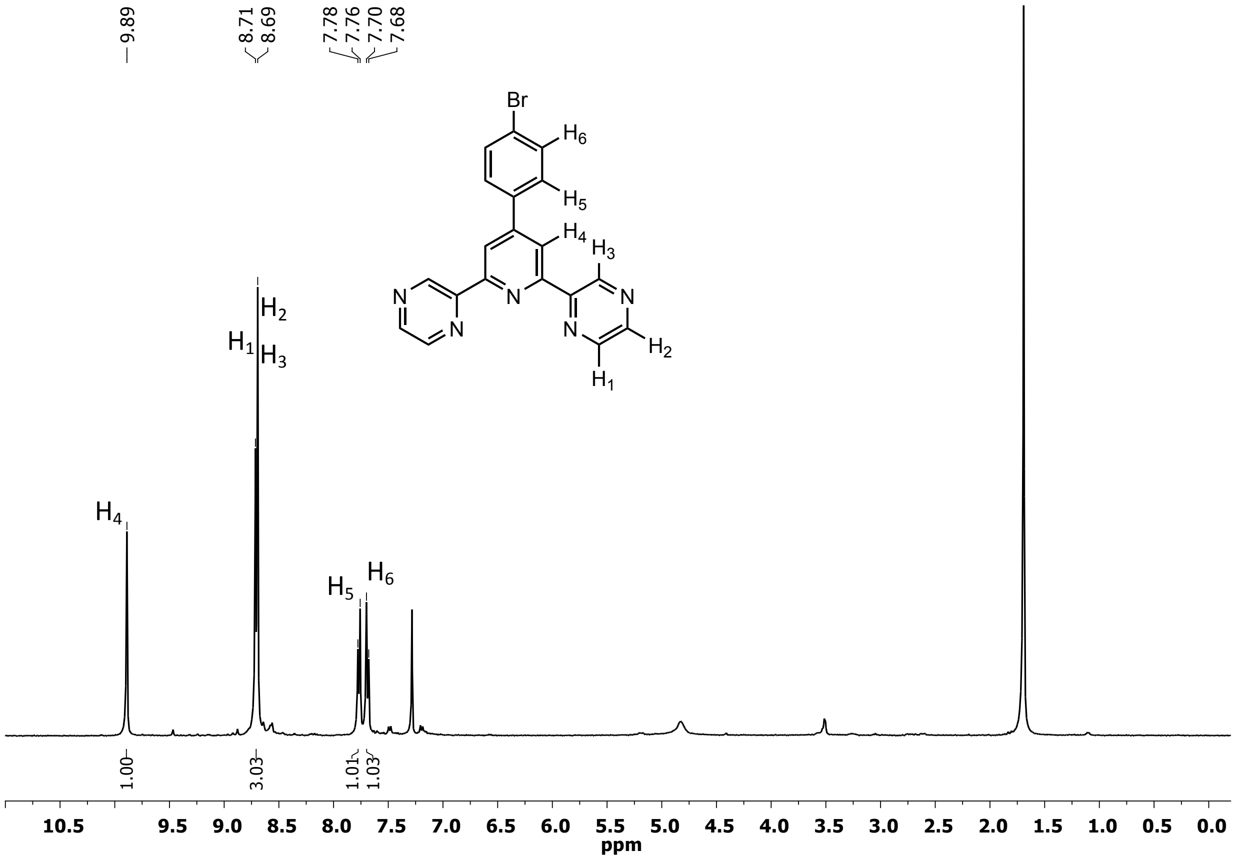


Figure S3. ^1H-NMR spectrum of **1** in $CDCl_3$.

The *nano*ITO films were fabricated atop FTO as reported in the literature. A 15 wt. % suspension of ITO nanoparticles ITO (18 nm particle size, purchased from US-Nano) with 5 wt. % hydroxypropylcellulose (80,000 MW) was sonicated using a sonicating horn until homogenized (5-10 min, with 1 min breaks in-between sonicating to prevent overheating). The resultant suspension was doctor-bladed onto FTO-glass (15 MΩ, Hartford Glass), dried, and subsequently annealed in air for 1 h at 500 °C to affort the *nano*ITO electrodes. The pale yellow electrodes were then cut such that the area of *nano*ITO was 1 cm^2.

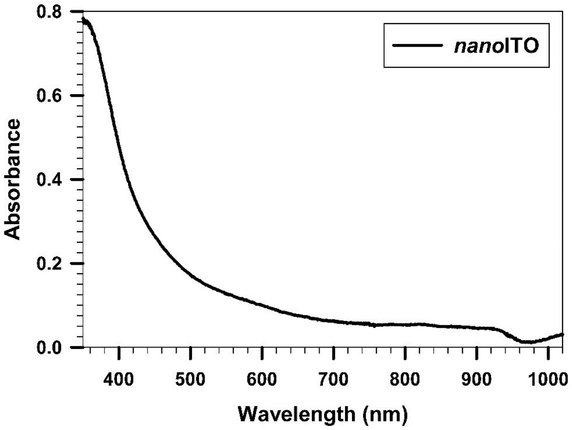


Figure S4. UV-visible spectrum of a *nano*ITO electrode in 0.1 M HNO_3.

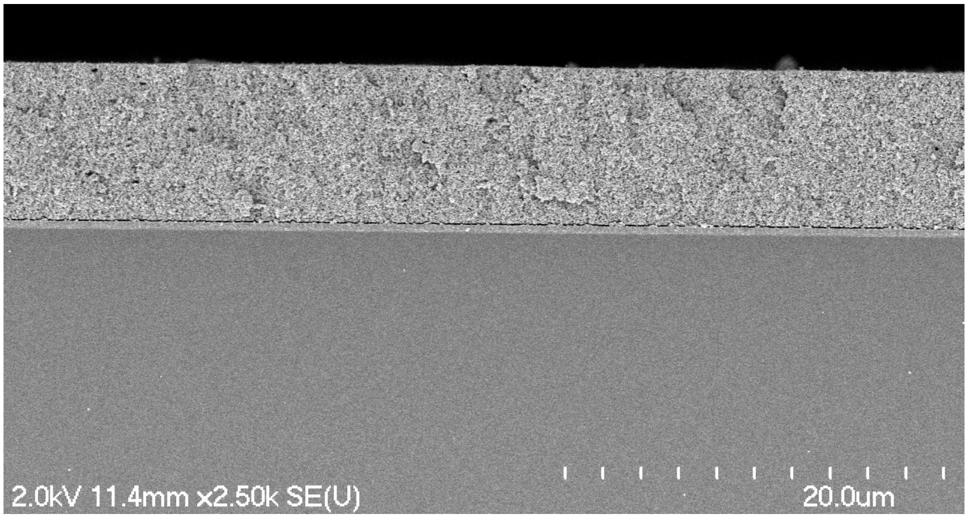


Figure S5. Cross-sectional SEM image of a *nano*ITO electrode.

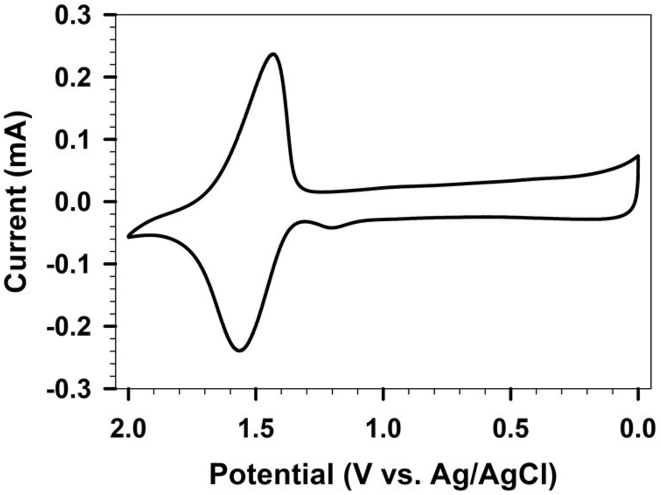


Figure S6. Cyclic voltammogram of *nano*ITO|Fe(dpp)$_2^{2+}$ in acetonitrile with 0.1 M TBAPF$_6$. Scan rate is 20 mV/s.

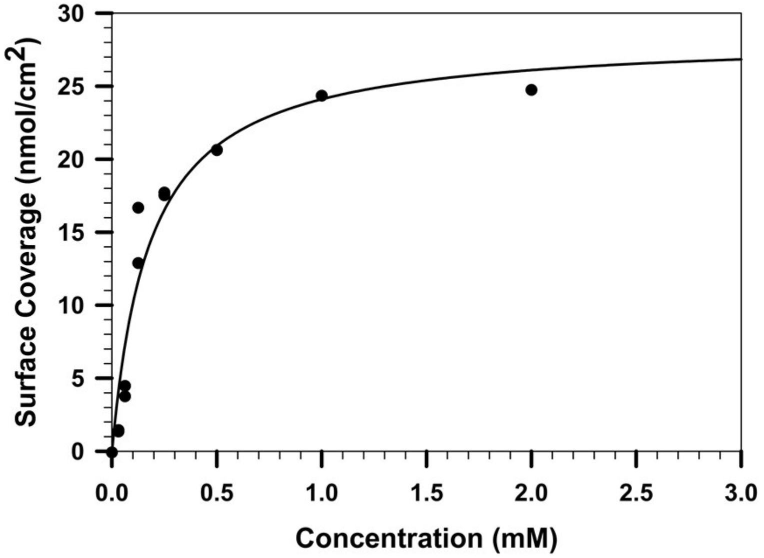


Figure S7. Langmuir binding isotherm for dpp to *nano*ITO. The line fitting the isotherm was $\Gamma = \Gamma_{max}[dpp]/(K_d+[dpp])$, where Γ is the surface coverage in mol/cm^2, and K_d is the dissociation constant. $\Gamma_{max} = 29$ nmol/cm^2, and $K_d = 0.0002$ M^{-1}.

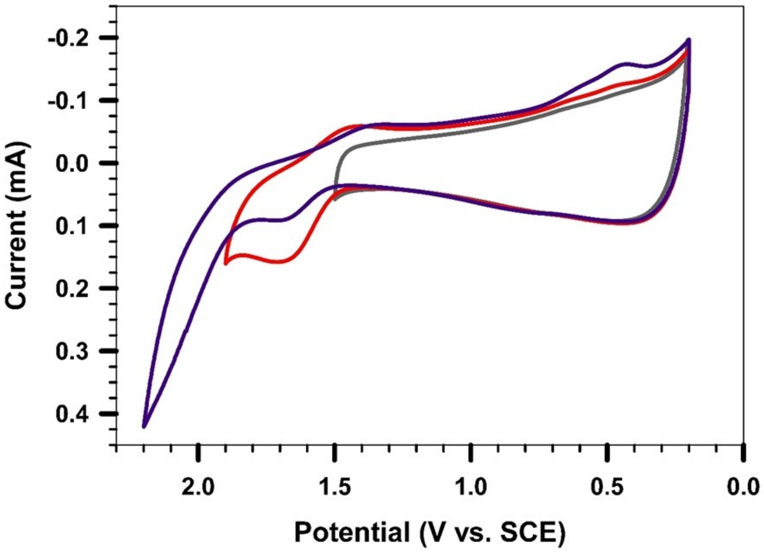


Figure S8. Cyclic voltammograms of a 0.81 mM solution of Am(III) in 0.1 M HNO_3 with a *nano*ITO|dpp working electrode with sequentially higher anodic scan limits (grey: +1.5 V, red: +1.9 V, purple: +2.2 V). Scan rate is 50 mV/s.

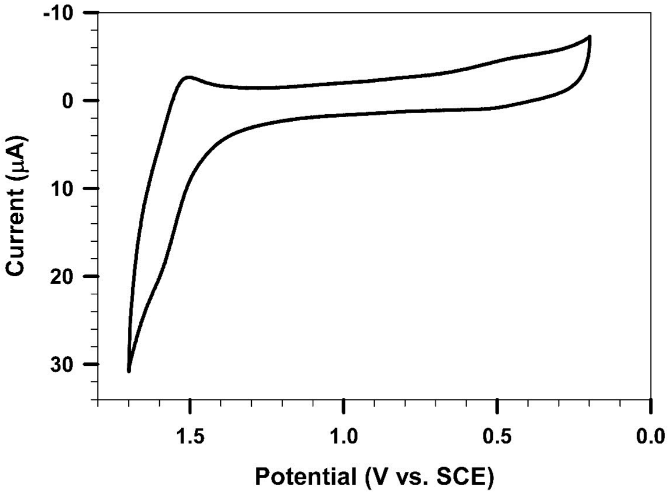


Figure S9. Cyclic voltammogram of the 0.85 mM Am solution after bulk electrolysis for 10.5 h at 1.8-2.1 V vs SCE. The working electrode is a 3 mm diameter glassy carbon disc.

References

1. Dares, C.; Manivannan, T.; Potvin, P. G.; Lever, A. B. P. Hydroxyphenyl- and Octoxyphenyl-Substituted Dipyrazinylpyridine Complexes of Ruthenium(II), Iron(II) and Nickel(II). *Inorganica Chim. Acta* **2011**, *374*, 606.
2. Norris, M. R.; Concepcion, J. J.; Glasson, C. R.; Fang, Z.; Lapides, A. M.; Ashford, D. L.; Templeton, J. L.; Meyer, T. J. Synthesis of Phosphonic Acid Derivatized Bipyridine Ligands and Their Ruthenium Complexes. *Inorg. Chem.* **2013**, *52*, 12492-12501.
3. Dares, C. J.; Lapides, A. M.; Mincher, B. J.; Meyer, T. J., Electrochemical oxidation of ^{243}Am(III) in nitric acid by a terpyridyl-derivatized electrode. *Science* **2015,** *350* (6261), 652-655.