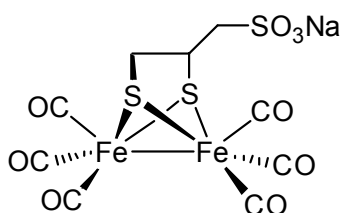


Supporting Information for

Photocatalytic Hydrogen Production from a Simple Water-Soluble [FeFe] Hydrogenase Model System

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Scheme 1 The structure of complex 1

Instrumentation and Methods Infrared spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrophotometer. The UV-Vis absorption spectra were recorded using a Shimadzu 1601 PC spectrophotometer. ¹H-NMR spectra were run on a Bruker-400 spectrometer with tetramethylsilane (¹H) as an internal standard. HR-ESI-MS was performed on a Bruker APEX III 7.0 Tesla FTICR Mass spectrometer combined with Apollo ESI source. Elemental analyses were determined on a FLASH EA1112 elemental analyzer. Electrochemical investigation was studied on a Princeton Applied Research Potentionstat-gravanostat model 283. Voltammograms were obtained using a standard three electrode cell under argon at room temperature with a glassy carbon working electrode and a platinum wire auxiliary electrode. For aqueous system, a

saturated KCl-Ag/AgCl reference electrode was used, and the supporting electrolyte solution was 0.1 M NaCl. All aqueous potentials are reported relative to the Ag/AgCl couple as 0.00 V. For work done in MeCN, a saturated Ag/AgNO₃ reference electrode was used and the supporting electrolyte solution was 0.1 M Et₄NBF₄, and potentials are reported relative to the Fc/Fc⁺ couple as 0.00 V. Between each scan the glassy carbon electrode was removed and polished using a 0.05 μm polycrystalline diamond suspension and rinsed with both acetone and deionized water to remove any adsorbed material. All samples were run at a concentration of 1 mM. The experiment for H₂ production in a Pyrex tube was performed by irradiation with a 500 W high-pressure Hanovia mercury lamp. A glass filter was used to cut off light below 400 nm and thus guarantee the irradiation by visible light. Hydrogen detection was carried out on a Shimadzu GC-14B with methane as an internal standard. The response factor for H₂/CH₄ determined by calibration with known amounts of H₂ and CH₄ was 3.4 under the experimental conditions.

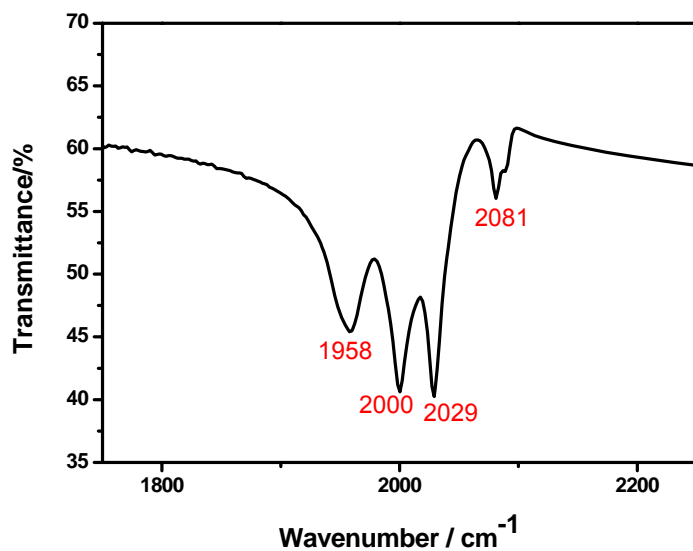
Materials All reactions and operations were carried out under a dry argon atmosphere with standard Schlenk technique. Solvents were dried and distilled prior to use. Fe₃(CO)₁₂, Sodium 2, 3-dimercapto-1-propanesulfonate, [Ru(bpy)₃]Cl₂ and ascorbic acid were purchased from Aldrich and used as received. Complex **1** was synthesized according to the procedures reported in the literature.^[S1]

[Fe₂(CO)₆(SCH₂)(SCH)CH₂SO₃Na] (1) Sodium 2,3-dimercapto-1-propanesulfonate (50 mg, 0.2 mmol) was added to the solution of Fe₃(CO)₁₂ (110 mg, 0.2 mmol) in methanol (20 ml), and the mixture was refluxed at 65°C for 30 min under Ar atmosphere. After the color changed from deep green to reddish-brown, the solvent was removed on a rotary evaporator, and the crude product was purified by column chromatography on silica gel with CH₂Cl₂/methanol (3:1, v/v) as eluent. The orange product was obtained in a yield of 52%. ¹H NMR (400 MHz, D₂O) δ 3.36 (dd, *J* = 14.0, 4.5 Hz, 1H), 3.20 (dd, *J* = 7.7, 4.6 Hz, 1H), 2.93 (dt, *J* = 13.5, 8.4 Hz, 2H), 2.29 (dd, *J* = 13.4, 5.1 Hz, 1H). TOF-ESI-MS: *m/z* Calcd for C₉H₅Fe₂NaO₉S₃: 487.98; Found: 464.8(M-Na⁺). Anal. Calcd for C₉H₅Fe₂NaO₉S₃: C 22.15, H 1.03; Found: C

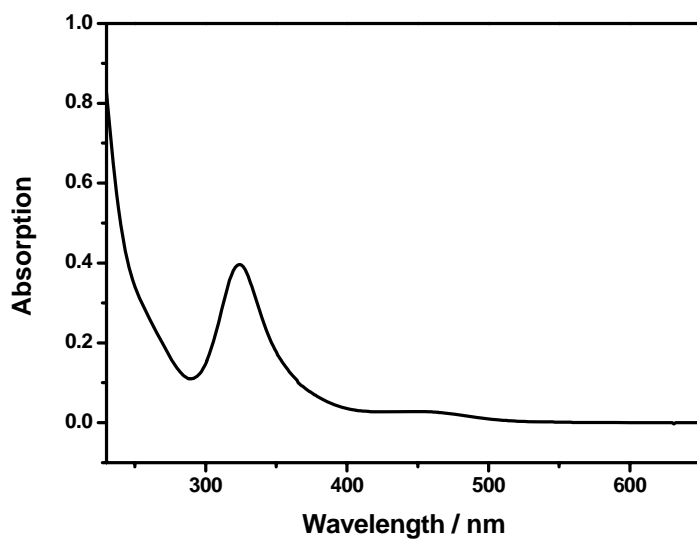
22.65, H 1.88; IR: $\nu(\text{CO})$ 2081, 2029, 2000, 1985 cm^{-1} .

Reference:

[S1]. E. J. Lyon, I. P. Georgakaki, J. H. Reibenspies, M. P. Soriaga, and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 2001, **123**, 3268.



(a)



(b)

Figure S1 (a) IR spectrum, and (b) UV-Vis absorption spectrum of complex **1**.

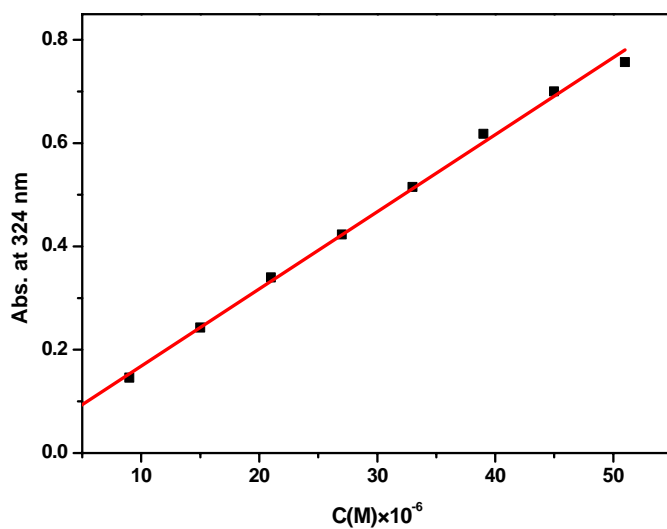


Figure S2 The standard solubility curve of complex **1** in water

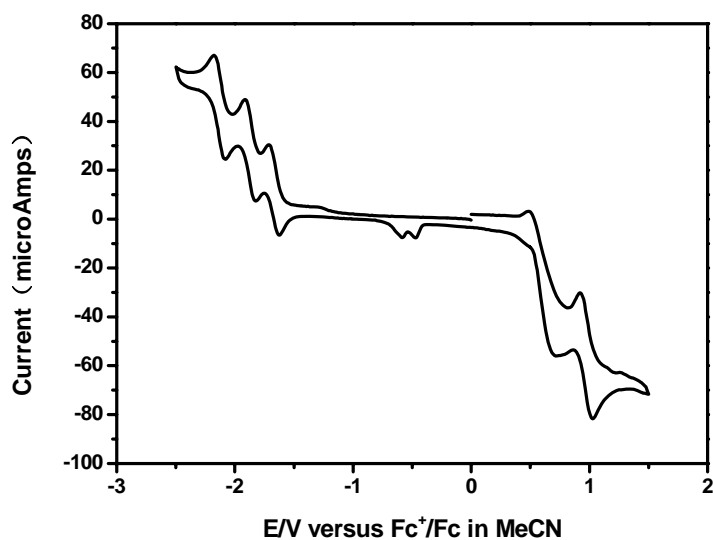
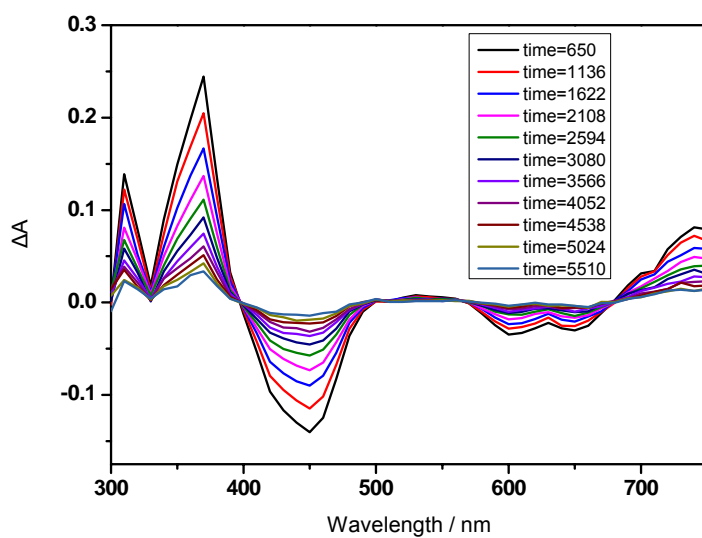
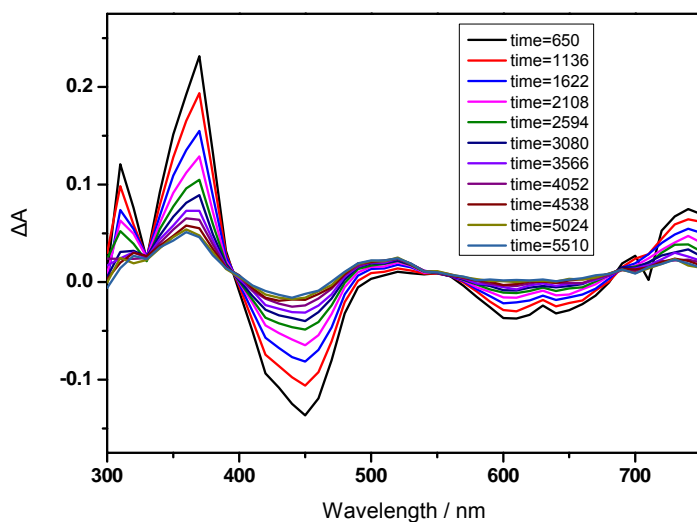


Figure S3 Cyclic voltammogram of $\text{Ru}(\text{bpy})_3^{2+}$ with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ in CH_3CN , at a scan rate of 100 mV/s. The concentration of sample is 1 mM.



(a)



(b)

Figure S4 Transient absorption spectra obtained following laser flash photolysis of a deoxygenated $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (9:1) solution containing (a) $\text{Ru}(\text{bpy})_3^{2+}$ (0.03 mM), (b) $\text{Ru}(\text{bpy})_3^{2+}$ (0.03 mM) and H_2A (0.1 M).

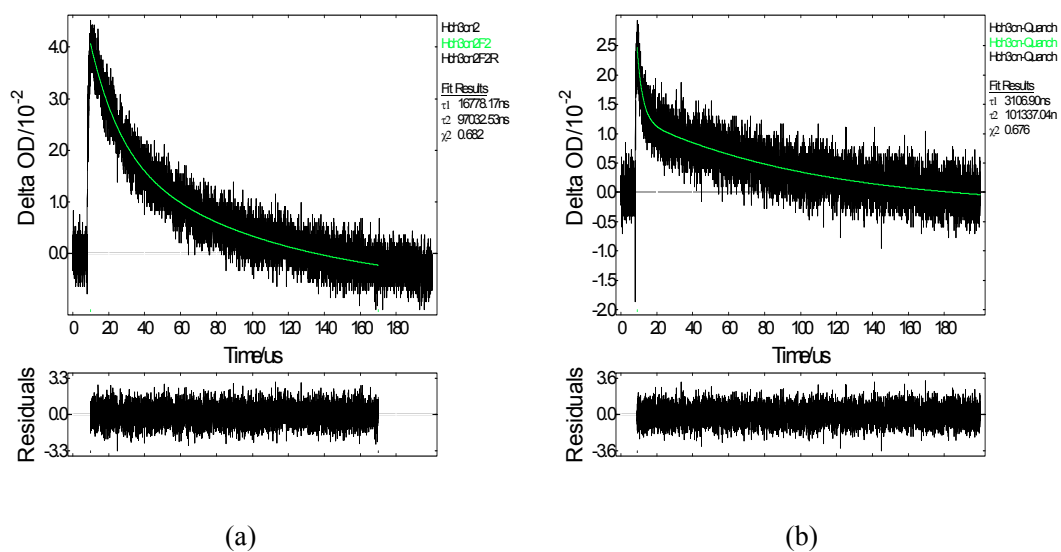
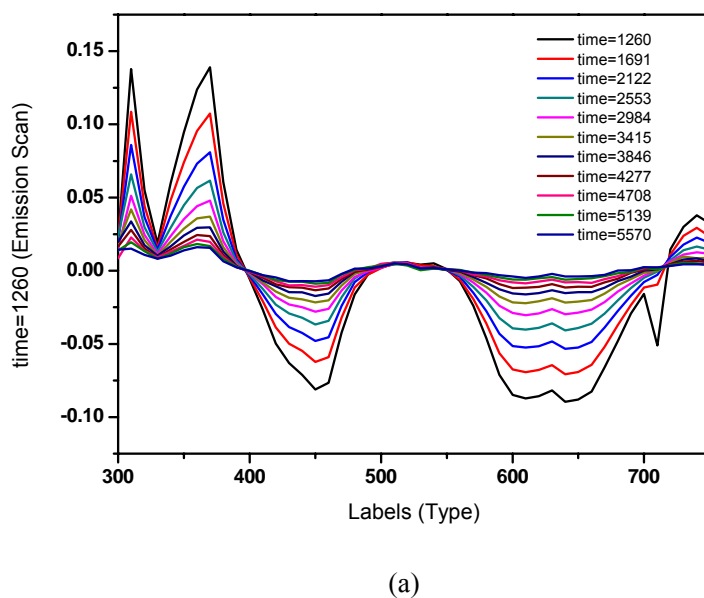
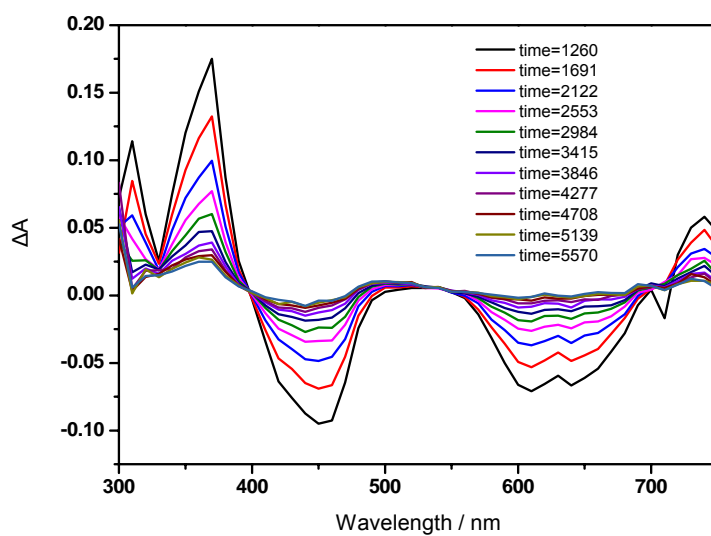


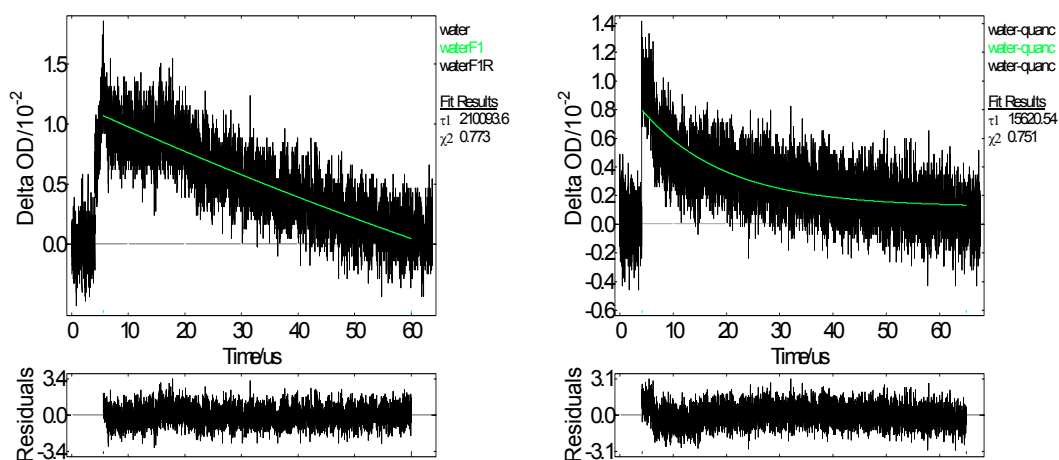
Figure S5 Kinetic traces at 520 nm obtained following laser flash photolysis of a deoxygenated mixture of CH₃CN/H₂O (9:1) containing (a) Ru(bpy)₃²⁺ (0.03 mM) and H₂A (0.1 M), (b) the same mixture but with 0.2 mM complex **1**.





(b)

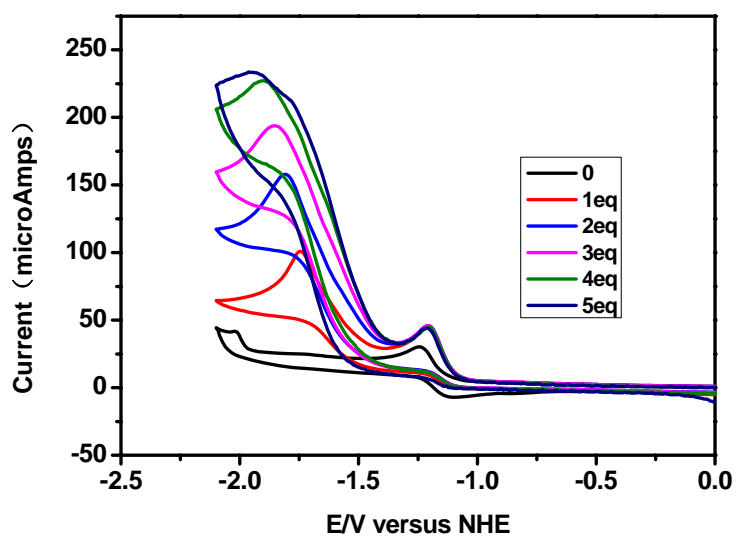
Figure S6 Transient absorption spectra obtained following laser flash photolysis of a deoxygenated water containing (a) $\text{Ru}(\text{bpy})_3^{2+}$ (0.03 mM), (b) $\text{Ru}(\text{bpy})_3^{2+}$ (0.03 mM), H_2A (0.1 M).



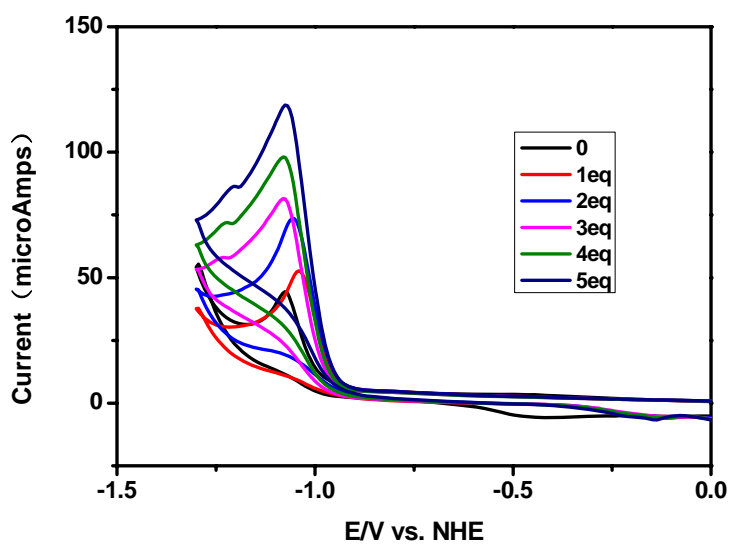
(a)

(b)

Figure S7. Kinetic traces at 520 nm obtained following laser flash photolysis of a deoxygenated water containing (a) $\text{Ru}(\text{bpy})_3^{2+}$ (0.03 mM) and H_2A (0.1 M), (b) the same mixture but with 0.2 mM complex **1**.

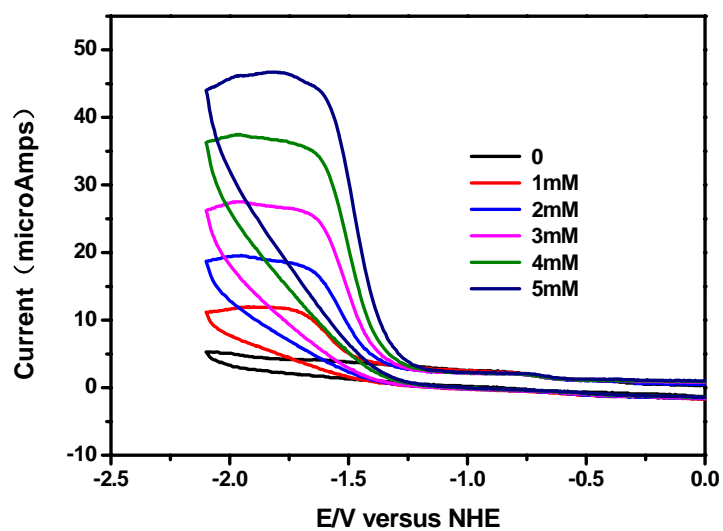


(a)

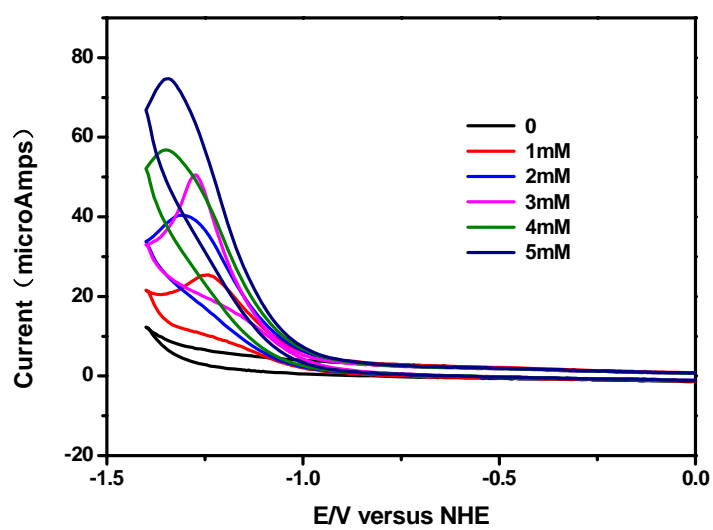


(b)

Figure S8 Cyclic voltammogram of complex **1** upon addition of HOAc (a) with 0.1 M *n*-Bu₄NPF₆ in CH₃CN, (b) with 0.1 M NaCl in water at a scan rate of 100 mV/s. The concentration of sample is 1 mM.



(a)



(b)

Figure S9 Cyclic voltammogram of HOAc in the absence of complex **1** (a) with 0.1 M *n*-Bu₄NPF₆ in CH₃CN, (b) with 0.1 M NaCl in water at a scan rate of 100 mV/s.