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Electronic Supplementary Information

Silatranes for Binding Inorganic Complexes to Metal Oxide Surfaces

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Experimental

Materials: The chemicals used in the syntheses and electrochemical measurements include: 2,2'-bipyridine-4,4'-dicarboxylic acid (98%, Alfa Aesar), thionyl chloride (99+%, Alfa Aesar), silver nitrate (99.9+%, Alfa Aesar), phosphoric acid (85%, Macron Fine Chemicals), potassium phosphate (97%, Alfa Aesar), potassium dihydrogen phosphate (99+%, Strem Chemicals), and potassium phosphate dibasic (99.9%, Fisher Chemical). Other solvents and reagents were obtained from commercial sources.

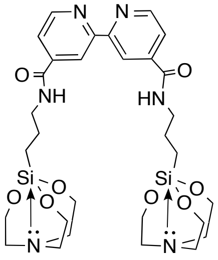
Instruments: UV-visible spectra were collected using a Shimadzu UV-2600 spectrophotometer. Nuclear magnetic resonance measurements were performed using a Varian 400 MHz instrument with values corresponding to ppm versus an internal TMS reference; reported J values are given in Hz. An Agilent Technologies single quadrupole LCMS (LC-1260 Infinity liquid chromatogram/ 6120 single quadrupole mass spectrometer) with an Eclipse Plus C18 column (3.5 µm) was used for mass spectrometry analysis.

A Pine Wavenow potentiostat was used for the electrochemical measurements. During the collection of cyclic voltammograms (CVs), a Ag/AgCl (sat'd NaCl) reference electrode and Pt wire auxiliary electrode were used. Reference electrode conversions from Ag/AgCl (sat'd NaCl) to NHE were calculated by using ferrocyanide as an internal standard, and resulted in a value of 0.236 V Ag/AgCl (sat'd NaCl) vs. NHE for the reference electrode used during the studies.[1]

Syntheses:

2,6–bis(1-methylbenzimidazole-2-yl)pyridine (Mebimpy),[2] Ru(Mebimpy)Cl_3,[2] [((Mebimpy)(Cl)Ru)$_2$$Cl_2$],[2] and 3-aminopropylsilatrane,[3] were synthesized via previously reported methods.

2,2'-bipyridine-4,4'-diamidopropylsilatrane (bpy-Sil):

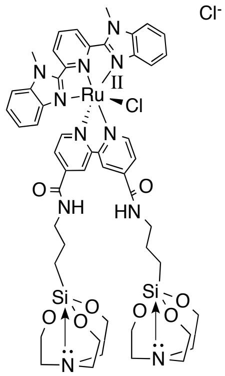


This synthesis was performed following a known procedure.[3] To a dry round bottom flask was added 0.200 g (0.82 mmol) of 2,2'-bipyridine-4,4'-dicarboxylic acid and 4 mL

(54 mmol) thionyl chloride. The suspension was refluxed overnight under nitrogen atmosphere. The solvent was removed under reduced pressure, yielding a yellow solid. The solid was dissolved in 10 mL of warm, dry dichloromethane along with 0.417 g (1.79 mmol) 3-aminopropyl silatrane and 0.560 mL (4.01 mmol) triethylamine. The solution stirred under a nitrogen atmosphere at room temperature for three hours, over which time a pale pink precipitate formed. The reaction was cooled to 0 °C overnight and then filtered to afford a light pink solid (0.548 g, 92 %).

^{1}H NMR: δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.77 – 8.73 (2H, m, CH), 8.67 (2H, s, CH), 7.81 (2H , dd, *J* 5.0, J 1.6, CH), 7.57 – 7.51 (2H, m, NH), 3.77 (12H, t, *J* 5.8, CH_2), 3.49 (4H, q, *J* 6.2, CH_2), 2.79 (12H, t, *J* 5.8, CH_2), 1.79 (4H, p, *J* 7.0, CH_2), 0.57 (4H, t, *J* 7.3, CH_2).

[(Ru(Mebimpy)(bpy-Sil)Cl)]Cl:



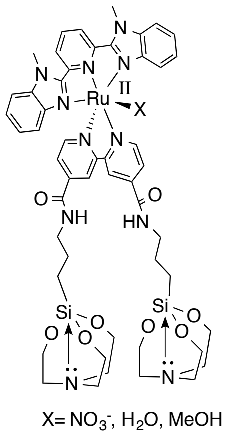
This synthesis was performed via adaptations to a known procedure.[2] To a dry round bottom flask was added 0.153 g (0.149 mmol) [((Mebimpy)(Cl)Ru)$_2$Cl$_2$], 0.202 g (0.299 mmol) bpy-Sil, and 40 mL DMF, which was degassed under nitrogen for ten minutes. The solution was refluxed for four hours under nitrogen, cooled to room temperature, and the solvent evaporated by distillation under reduced pressure. The red solid was recrystallized using MeOH / diethyl (0.068 g, 20%).

^{1}H NMR: δ_H (400 MHz, Methanol-d_4, Me_4Si) 10.80 (1H, d, *J* 5.9, CH), 9.27 – 9.22 (1H, m, CH), 8.81 – 8.71 (3H, m, CH), 8.43 (1H, dd, *J* 5.9, J 1.8, CH), 8.29 (1H, t, *J* 8.2, CH), 7.69 (2H, dd, *J* 7.2, J 4.8, CH), 7.39 (2H, t, *J* 7.8, CH), 7.33 (1H, dd, *J* 6.0, J 1.8, CH), 7.06 (2H, t, *J* 7.7, CH), 6.19 (2H, d, *J* 8.3, CH), 4.51 (6H, s, CH_3), 3.78 (6H, t, *J* 5.8, CH_2), 3.65 (6H, t, *J* 5.9, CH_2), 3.54 (2H, t, *J* 7.1, CH_2), 3.20 (2H, t, *J* 7.0, CH_2), 2.91 (6H, t, *J* 5.9, CH_2), 2.81 (6H, t, *J* 6.0, CH_2), 1.89 – 1.80 (2H, m, CH_2), 1.60 – 1.51 (2H, m, CH_2), 0.54 – 0.47 (2H, m, CH_2), 0.27 – 0.21 (2H, m, CH_2).

Mass Spectrometry Results:

Formula: $C_{51}H_{61}ClN_{11}O_8RuSi_2^+$; Calculated (*m/z*): 1148; Experimental (*m/z*): 1148.

[Ru^{II}(Mebimpy)(bpy-Sil)X], X= CH_3OH, H_2O, NO_3^-; coordination description of X when dissolved in methanol: ([Ru-OH_2]$(NO_3)_2$, [Ru-($HOCH_3$)]$(NO_3)_2$, or [Ru-(NO_3)](NO_3); Ru^{II} in all cases



1

This synthesis was performed via adaption to a known procedure.[2] In a dry round bottom flask was dissolved 0.040 g (0.03 mmol) of [Ru(Mebimpy)(bpy-Sil)Cl]Cl in 10 mL methanol. To the red solution was added 0.012 g $AgNO_3$ (0.06 mmol). The mixture was stirred at room temperature overnight under a nitrogen atmosphere. The resulting AgCl was filtered off and the filtrate solvent was removed by evaporation under a nitrogen atmosphere, yielding a dark red solid (0.031 g, 74%). Characterizations by NMR and mass spectrometry revealed the labile ligand X is easily interchanged with a solvent species.

^{1}H NMR: δ_H (400 MHz, Methanol-d_4, Me_4Si) 10.35 (1H, d, *J* 5.9), 10.20 (1H, d, *J* 5.9), 10.15 (1H, d, *J* 5.8), 9.30 (2H, s,), 9.25 (1H, d, *J* 1.8), 8.88 – 8.74 (9H, m), 8.57 (1H, dd, *J* 5.9, 1.8), 8.52 (1H, td, *J* 5.7, 1.8), 8.46 – 8.32 (3H, m), 7.76 (3H, t, *J* 8.4), 7.69 (2H, dd, *J* 7.2, J 5.7), 7.59 (2H, dd, *J* 14.4, 6.1), 7.48 – 7.32 (9H, m), 7.19 – 7.06 (6H, m), 6.27 – 6.20 (6H, m), 4.57 (6H, s), 4.55 (6H, s), 4.52 (6H, s), 3.78 (18H, t, *J* 5.9), 3.65 (18H, t, *J* 5.8), 3.57 – 3.51 (6H, m), 3.20 (6H, dd, *J* 7.7, J 5.7), 2.93 – 2.89 (18H, m), 2.82 (18H, dd, *J* 6.6, J 5.3), 1.90 – 1.80 (6H, m), 1.55 (6H, dq, *J* 13.1, 7.5), 0.54 – 0.47 (6H, m), 0.23 (6H, ddd, *J* 11.4, J 5.2, J 2.8).

Mass Spectrometry Results:

Formula: $C_{51}H_{61}N_{12}O_{11}RuSi_2^+$; Calculated (*m/z*): 1175; Experimental (*m/z*) 1175.

Formula: $C_{51}H_{63}N_{11}O_9RuSi_2^+$; Calculated (*m/z*): 1131; Experimental (*m/z*): 1131.

Formula: $C_{52}H_{65}N_{11}O_9RuSi_2^{2+}$; Calculated (*m/z*): 572; Experimental (*m/z*): 572.

Figures S1 – S5 and Table S1

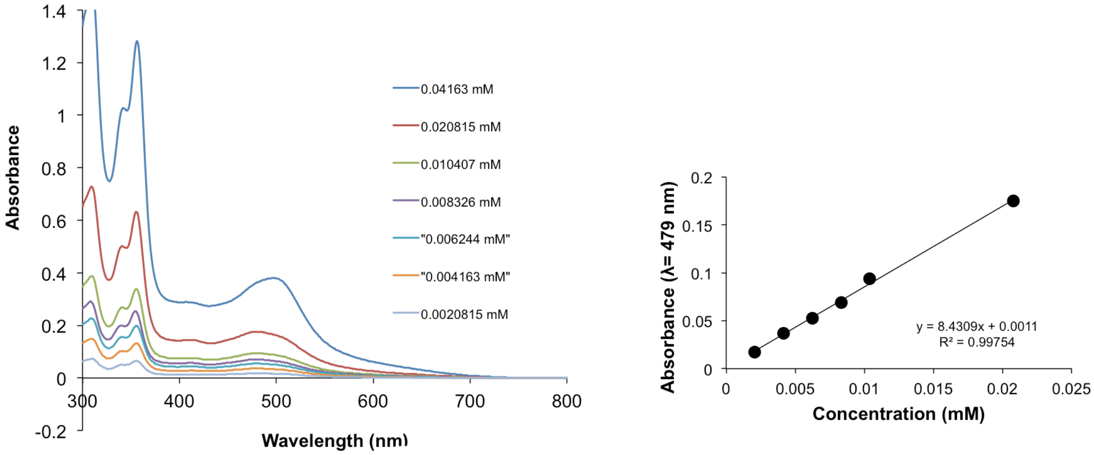
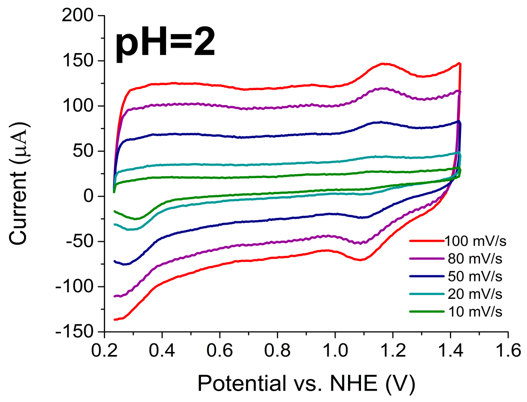


Figure S1. UV-visible spectra as a function of concentration and Beer's Law plot for absorbance values at λ = 479 nm.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100
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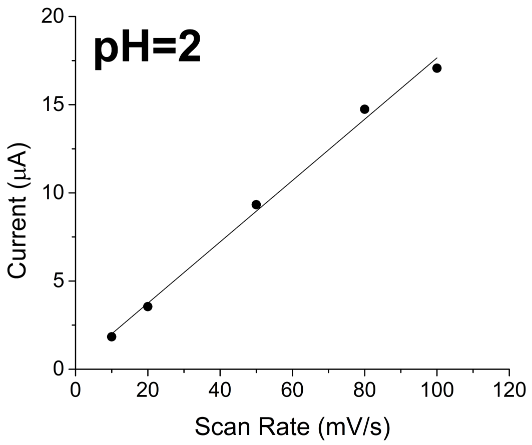
-100
-150
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
Potential vs. NHE (V)
100 mV/s
80 mV/s
50 mV/s
20 mV/s
10 mV/s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15
10
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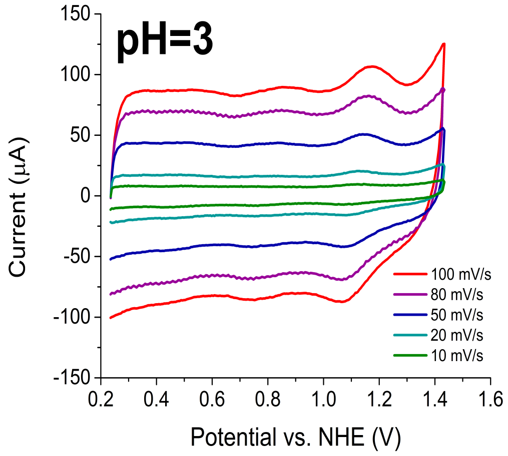
0
0
20
40
60
80
100
120
Scan Rate (mV/s)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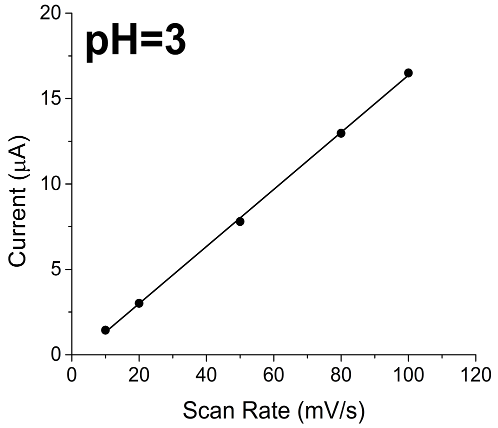
100
50
0
-50
-100
-150
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
Potential vs. NHE (V)
100 mV/s
80 mV/s
50 mV/s
20 mV/s
10 mV/s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10
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0
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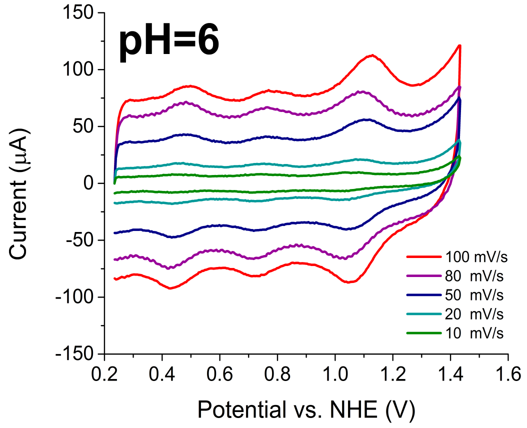
20
40
60
80
100
120
Scan Rate (mV/s)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Current (μA)
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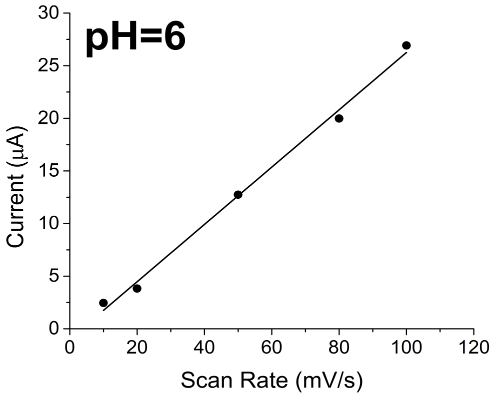
100
50
0
-50
-100
-150
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
Potential vs. NHE (V)
100 mV/s
80 mV/s
50 mV/s
20 mV/s
10 mV/s


pH=6
Current (μA)
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25
20
15
10
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0
0
20
40
60
80
100
120
Scan Rate (mV/s)

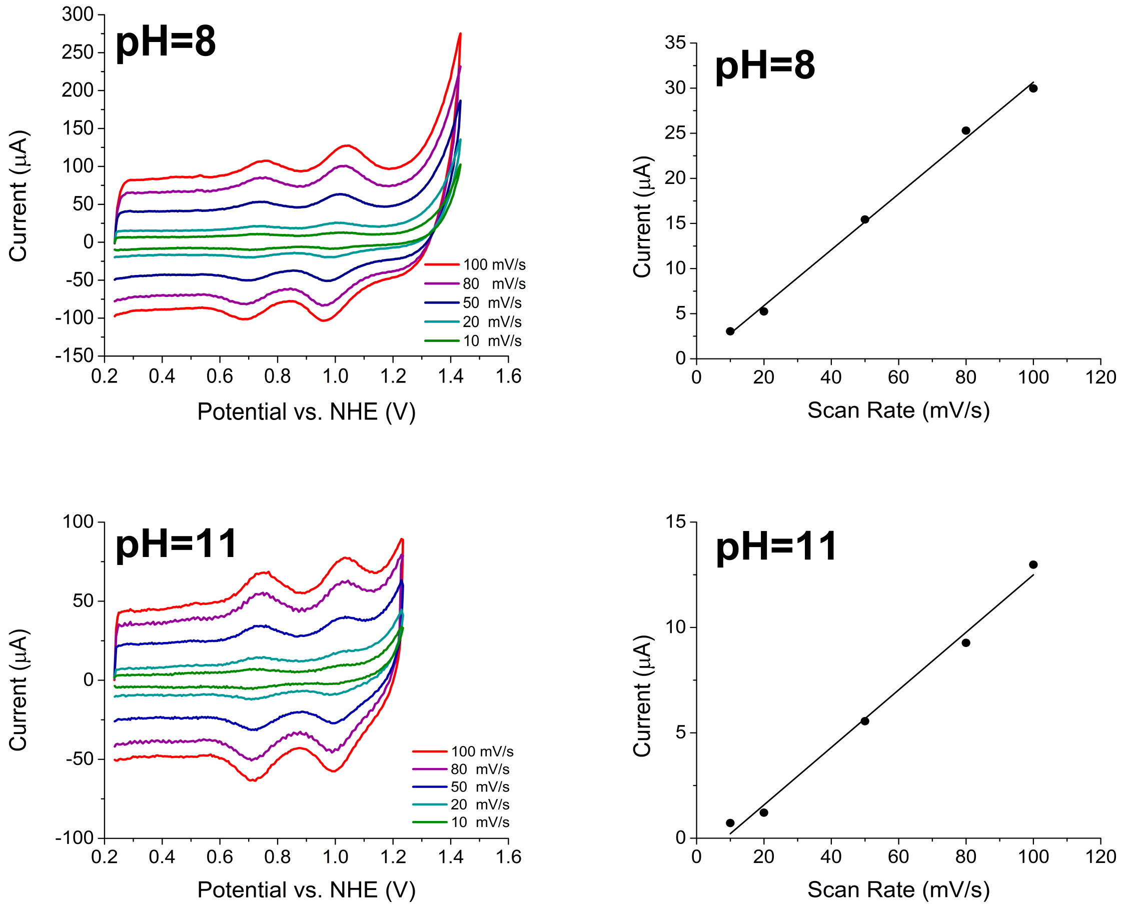

Figure S2. Cyclic voltammograms of *nano*ITO-**1** with scan rates of 100 mV/s (red), 80 mV/s (purple), 50 mV/s (blue), 20 mV/s (teal), and 10 mV/s (green) mV/s and their corresponding scan rate vs. peak Faradaic current at pH 2, 3, 6, 8, and 11.

Table S1. Electrochemical data of *nano*ITO-**1** from CVs pH 2-11 including midpoint potentials of observable redox features and relevant anodic and cathodic peak separations. The peak separations were determined by linear extrapolation from scan rate dependence.

pH	**$Ru^{IV}(OO)^{2+}/Ru^{III}OOH^{2+}$ and $Ru^{III}(OOH)^{2+}/Ru^{II}(HOOH)^{2+}$ (V vs. NHE)**	**$Ru^{II/III}$ (V vs. NHE)**	**$Ru^{III/IV}$ (V vs. NHE)**	**$Ru^{II/III}$ peak separation (mV)**	**$Ru^{III/IV}$ peak separation (mV)**
2	---	0.91	1.12	20.0	4.0
3	---	0.83	1.12	16.0	28.0
6	0.46	0.82	1.07	10.0	35.0
7	0.45	0.77	1.16	9.0	14.0
8	---	0.79	1.01	9.0	4.0
11	---	0.77	1.00	6.0	9.0

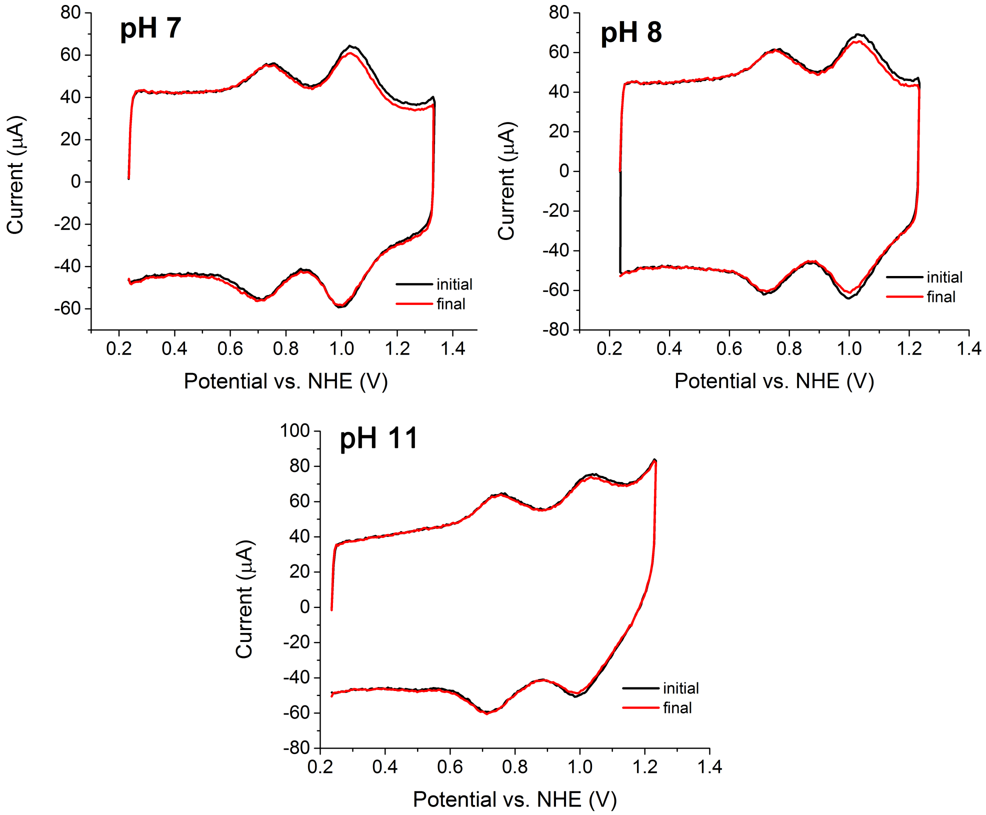

Figure S3. Stability tests from pH = 7 - 11: cyclic voltammograms (100 mV/s) were collected 54 times sequentially at each pH. Cyclic voltammograms comparing an initial and a final scan are shown in each panel.

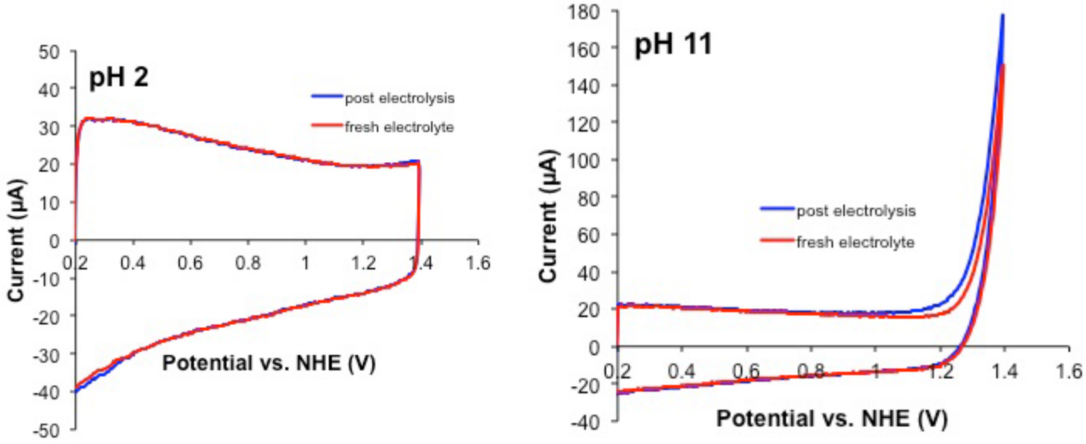

Figure S4. Cyclic voltammograms of *nano*ITO blank electrodes in phosphate electrolytes at pH 2 and pH 11, 100 mV/s. Data are shown for phosphate electrolyte post electrolysis using *nano*ITO-**1** and in fresh phosphate electrolyte.

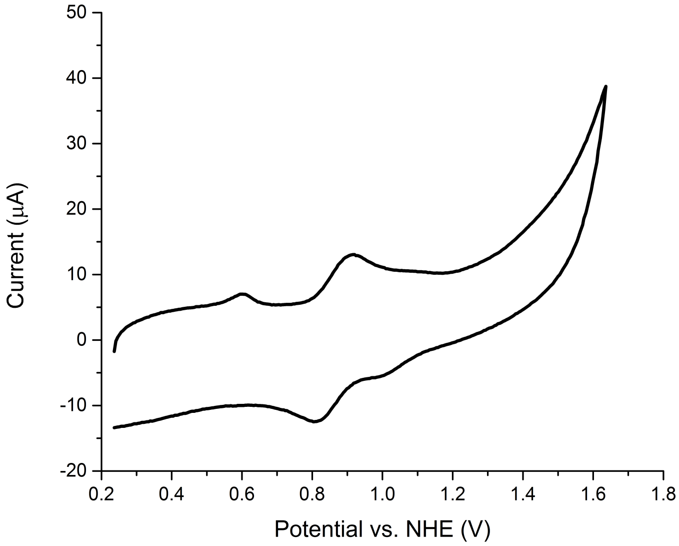

Figure S5. Cyclic voltammogram of **1** in 0.1 M phosphate buffer at pH 3, 200 mV/s. The $E_{1/2}$ for the $Ru^{II/III}$ redox couple is 0.86 V vs. NHE (peak separation 0.11 V) and 1.04 V for $Ru^{III/IV}$ (peak separation 0.09 V). The feature at 0.59 V is the previously reported $Ru^{IV}(OO)^{2+}/Ru^{III}(OOH)^{2+}$ or $Ru^{III}(OOH)^{2+}/Ru^{II}(HOOH)$ couple.[4]

References:

1. J. E. O'Reilly, *Biochimica et Biophysica Acta (BBA) - Bioenergetics*, 1973, **292**, 509-515.
2. J. J. Concepcion, M. K. Tsai, J. T. Muckerman and T. J. Meyer, *J Am Chem Soc*, 2010, **132**, 1545-1557.
3. B. J. Brennan, A. E. Keirstead, P. A. Liddell, S. A. Vail, T. A. Moore, A. L. Moore and D. Gust, *Nanotechnology*, 2009, **20**, 505203.
4. Z. Chen, J. J. Concepcion, J. F. Hull, P. G. Hoertz and T. J. Meyer, *Dalton Trans*, 2010, **39**, 6950-6952.