Supplementary information

Azo-conjugated Half-sandwich Rh/Ru Complexes for Homogeneous Water-oxidation Catalysis

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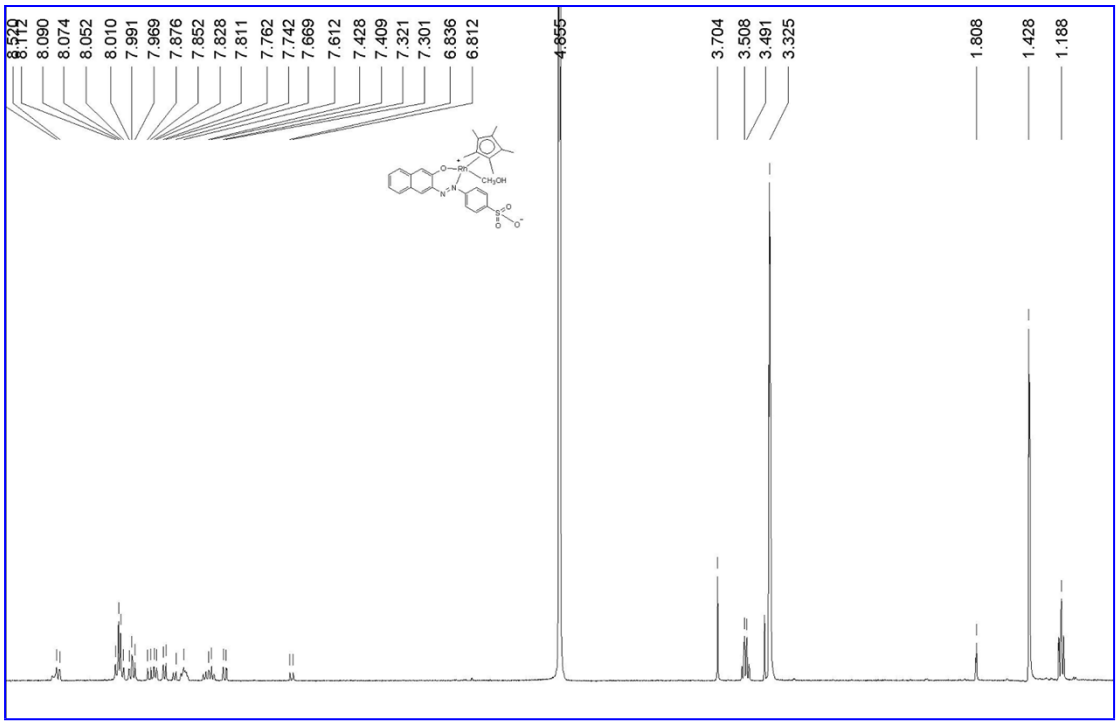

Figure S1. ^{1}H NMR of **1**.

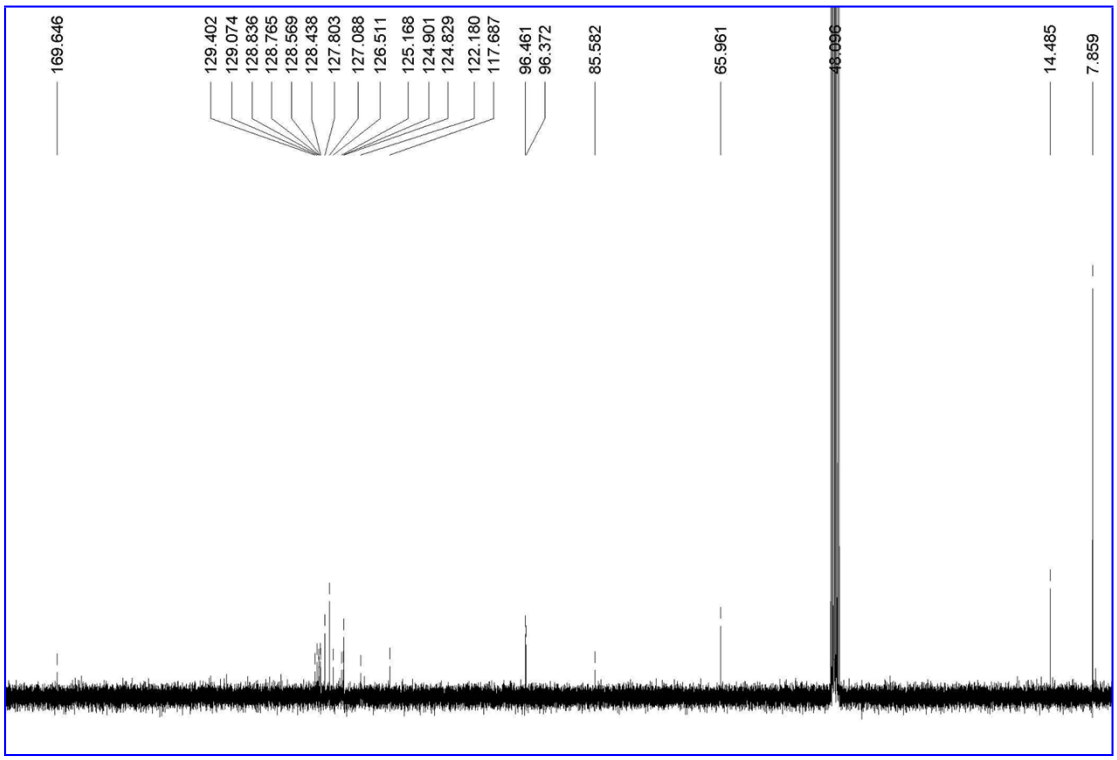

Figure S2. ^{13}C NMR of **1.**

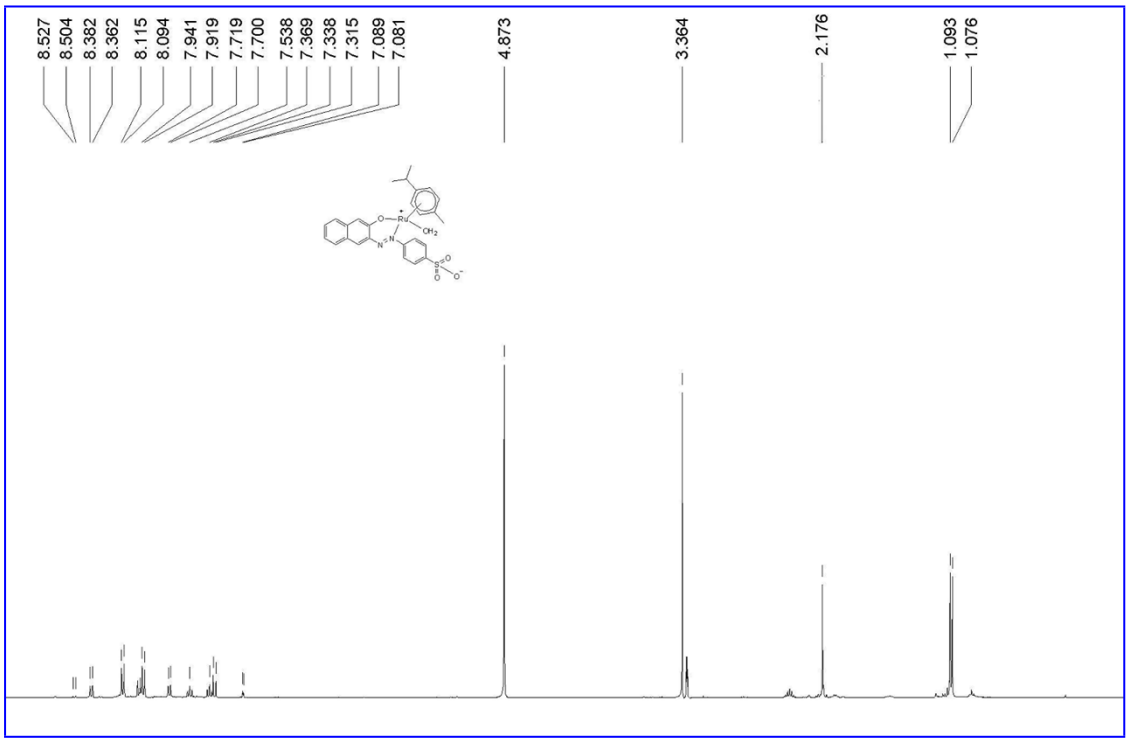

Figure S3. ^{1}H NMR of **2**.

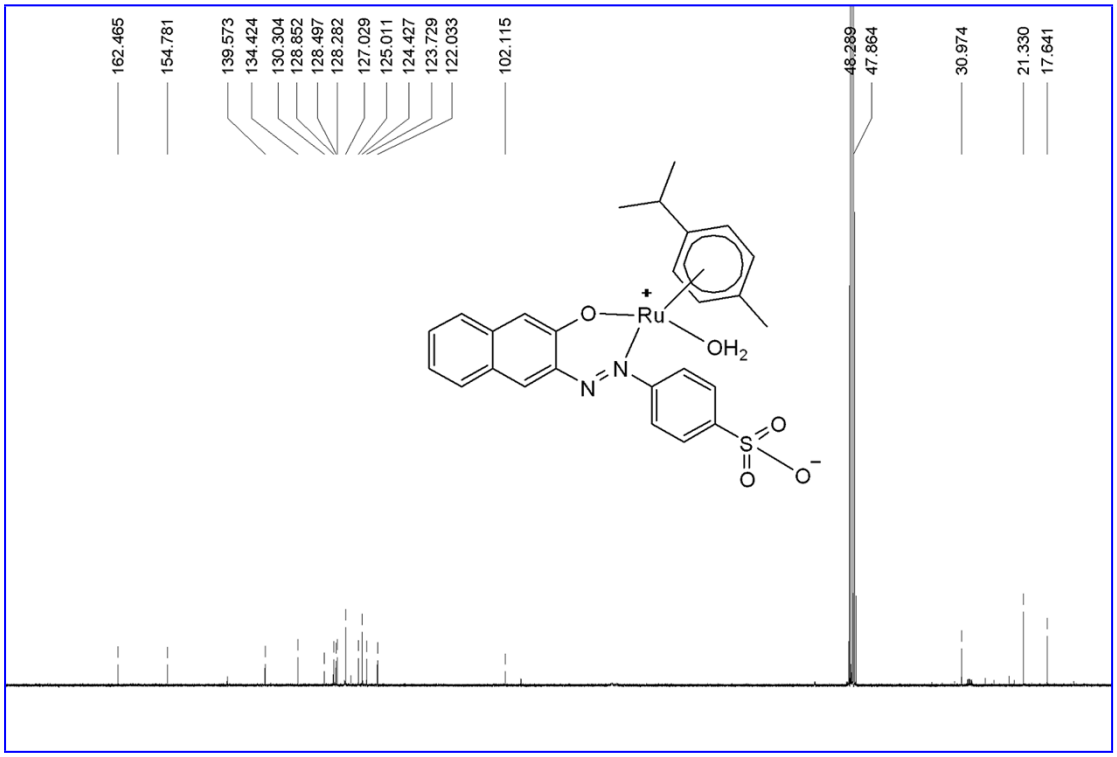

Figure S4. ^{13}C NMR of **2**.

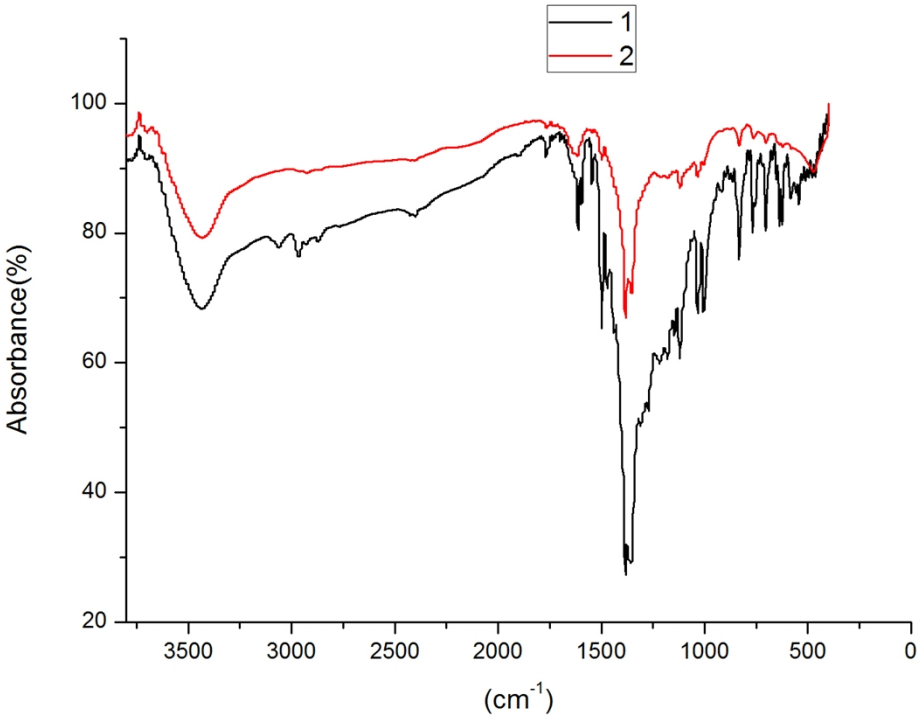

Figure S5. IR spectra of complexes **1** and **2**.

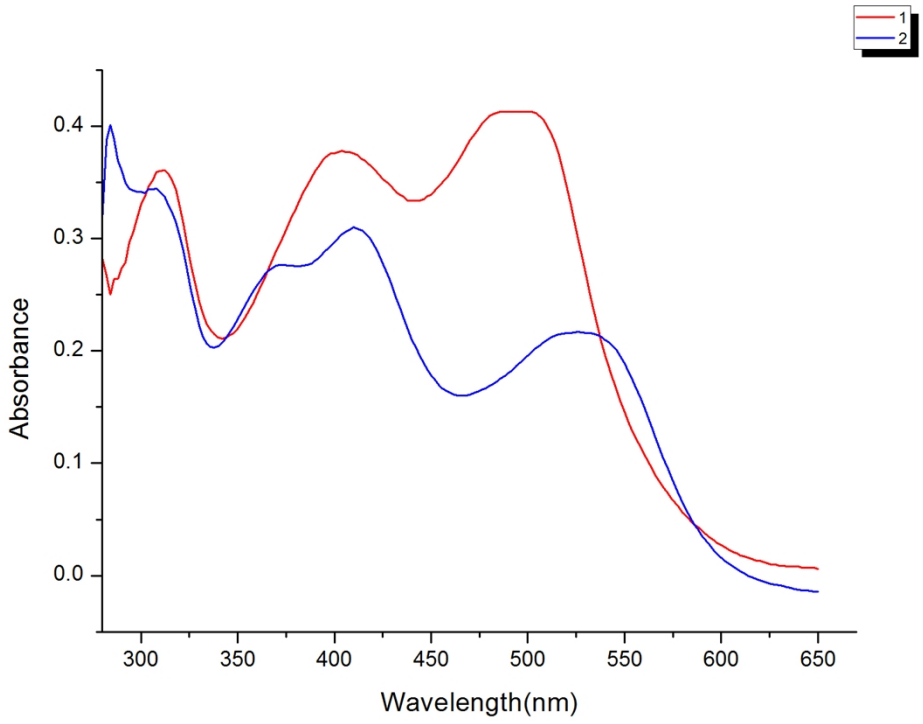

Figure S6. Uv-vis spectra of Complexex **1** and **2** in methanol.

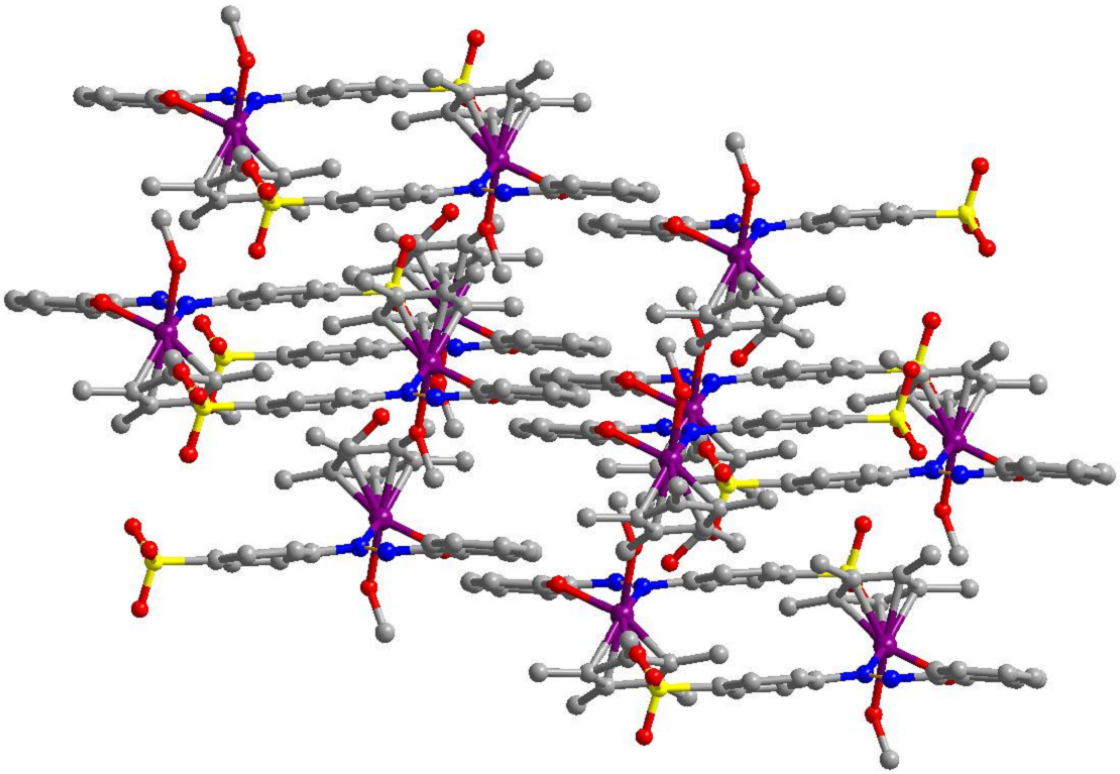

Figure S7. Packing-mode of **1**. Rh, Dark red; S, Yellow; O, Red; N, Blue; C,Gray. All H atoms were omitted for clarity.

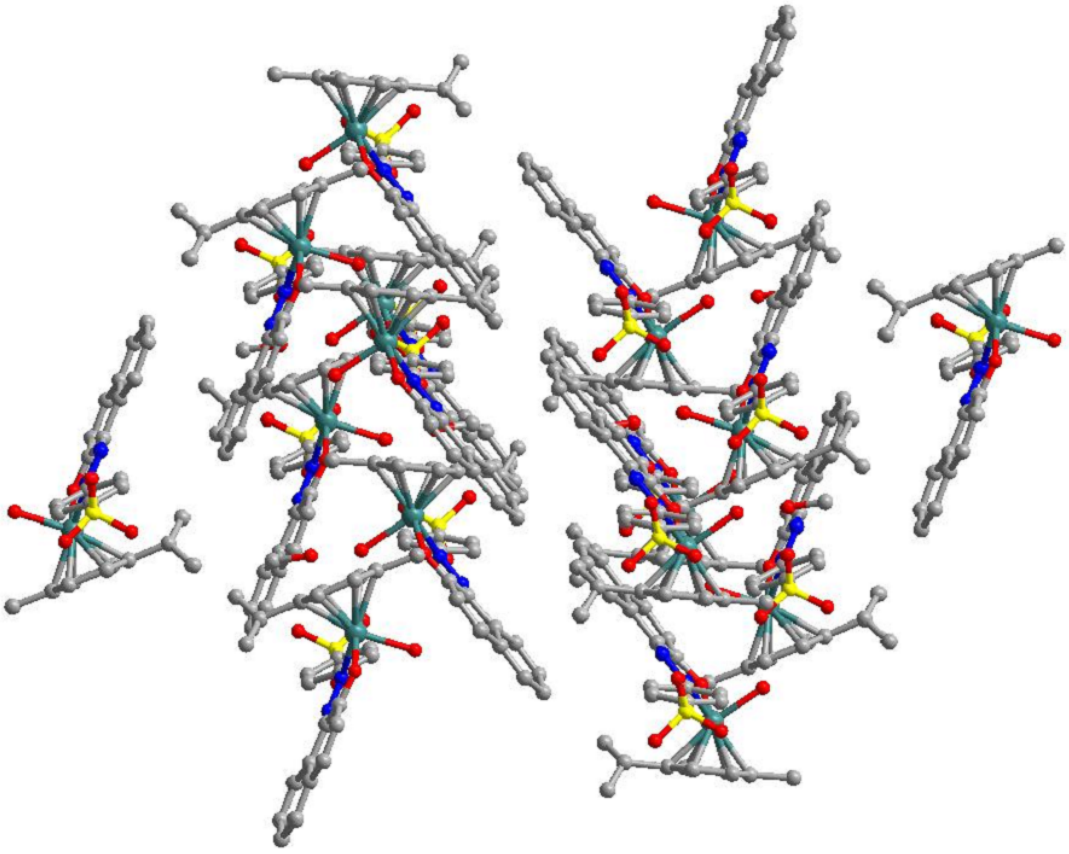

Figure S8. Packing-mode of **2**. Rh, Light green; S, Yellow; O, Red; N, Blue; C,Gray. All H atoms were omitted for clarity.

Table 1. Crystal data and structure refinement for **1**.

Identification code	**1**
Empirical formula	C28 H32 N2 O6 Rh S
Formula weight	627.53
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.4832(12) A alpha = 72.944(2) deg. b = 11.8088(16) A beta = 81.433(2) deg. c = 15.522(2) A gamma = 69.411(2) deg.
Volume	1389.8(3) A^3
Z, Calculated density	2, 1.500 Mg/m^3
Absorption coefficient	0.734 mm^-1
F(000)	646
Crystal size	0.31 x 0.25 x 0.20 mm
Theta range for data collection	2.63 to 27.49 deg.
Limiting indices	-10<=h<=10, -13<=k<=15, -18<=l<=20
Reflections collected / unique	8716 / 6141 [R(int) = 0.0144]
Completeness to theta = 27.49	96.3 %
Max. and min. transmission	0.8671 and 0.8045
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6141 / 359 / 351
Goodness-of-fit on F^2	0.968
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.1213
R indices (all data)	R1 = 0.0465, wR2 = 0.1298
Largest diff. peak and hole	0.659 and -0.583 e.A^-3

Table 2. Crystal data and structure refinement for **2**.

Identification code	**2**
Empirical formula	C27 H30 N2 O6 Ru S
Formula weight	611.66
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 8.1613(19) A alpha = 90 deg.
	b = 23.432(5) A beta = 100.121(3) deg.
	c = 14.284(3) A gamma = 90 deg.
Volume	2689.1(11) A^3
Z, Calculated density	4, 1.511 Mg/m^3
Absorption coefficient	0.704 mm^-1
F(000)	1256
Crystal size	0.25 x 0.21 x 0.10 mm
Theta range for data collection	2.68 to 27.48 deg.
Limiting indices	-10<=h<=9, -30<=k<=29, -14<=l<=18
Reflections collected / unique	16485 / 6104 [R(int) = 0.0485]
Completeness to theta = 27.48	98.9 %
Max. and min. transmission	0.9329 and 0.8436
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6104 / 357 / 340
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0556, wR2 = 0.1579
R indices (all data)	R1 = 0.0807, wR2 = 0.1747
Largest diff. peak and hole	1.401 and -0.717 e.A^-3

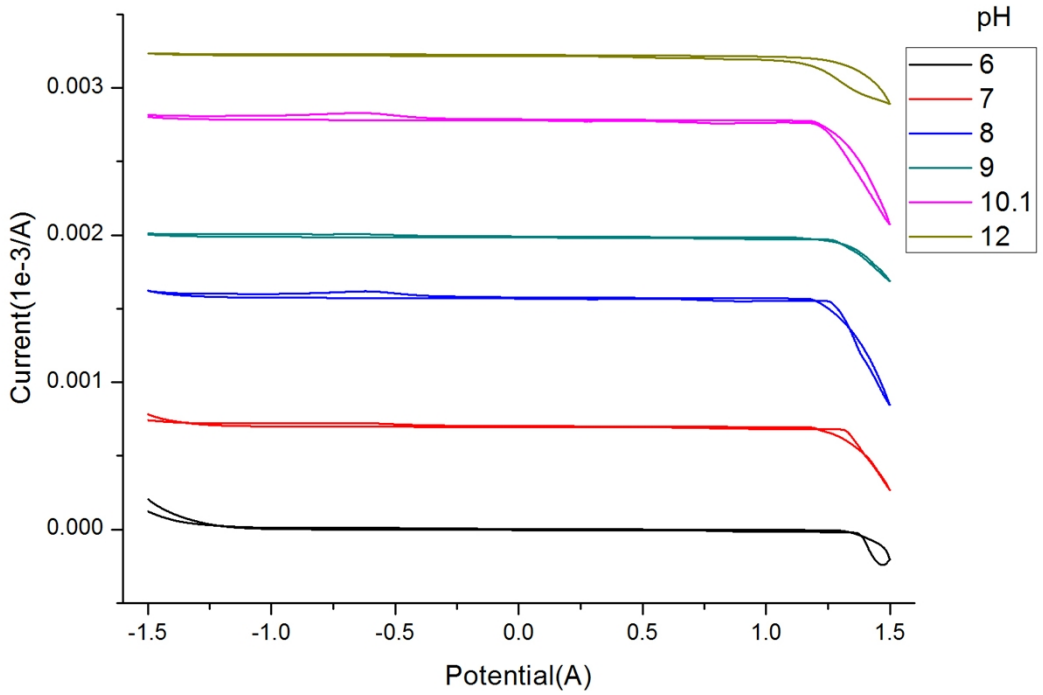

Figure S9. pH-dependent cyclic voltammograms of complex **2** in aqueous solution (Concentration: 0.04mM, scan rate: 50 mV/s).

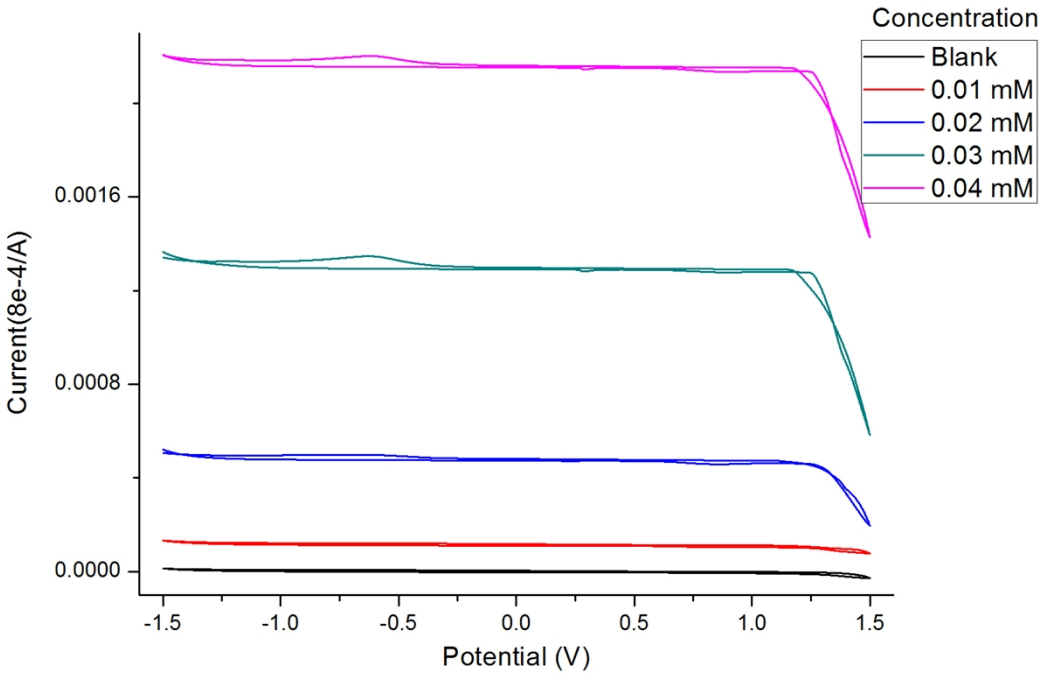

Figure S10. Concentration-dependent cyclic voltammograms of complex **2** in aqueous solution (pH = 8.0, scan rate: 50 mV/s).