Supporting Information

Insight into Water Oxidation by Mononuclear Polypyridyl Ru Catalysts

Derek J. Wasylenko,[1] *Chelladurai Ganesamoorthy,*[1] *Bryan D. Koivisto,*[1] *Matthew A. Henderson,*[2] *and Curtis P. Berlinguette*[1]*

[1]Department of Chemistry and Institute for Sustainable Energy, Environment & Economy,
University of Calgary, 2500 University Drive N.W., Calgary, Canada T2N-1N4.

[2]Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada V38-3V6

E-mail: cberling@ucalgary.ca

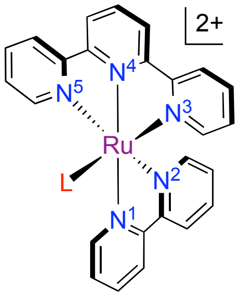
Table S1. Compilation of Reaction Conditions Used for Water Oxidation Studies for Various Molecular Catalysts in the Literature.

Reference	**Conditions**	**Oxidant**	**Physical probe**[a]
1	1M $HClO_4$ / 1M CF_3SO_3H	Ce^{IV}	electrode/GC
2	0.5M H_2SO_4	Ce^{IV}	electrode/GC
	1.0M H_2SO_4	Co^{III}	
3	pH > ~8, 2% H_2O/MeCN, 20% sulfolane, 0.1M Bu_4NClO_4, $5x10^{-6}$ M Bu_4NOH	$E_{app} > 2.3$ V vs NHE	electrode
4	pH = 8.6/4.5	OCl^-/HSO_5^-	electrode/GC
5	pH = 4 (ITO); 10% H_2O/CF_3CH_2OH/ether	$E_{app} > 1.4$ V vs NHE	GC
6	0.1M CF_3SO_3H	Ce^{IV}	GC
7	0.1M CF_3SO_3H/MeCN	Ce^{IV}	optical/GC
8	0.7M CF_3SO_3H	Ce^{IV}	pressure/GC
9	1M CF_3SO_3H/MeCN	Ce^{IV}	optical/GC
10	1M HNO_3	Ce^{IV}	electrode
11	pH 0.8, CF_3SO_3H/MeCN	Ce^{IV}	electrode
12	pH 0.95	Ce^{IV}	electrode
13	pH 1.0, CF_3SO_3H	Ce^{IV}	electrode
14	pH 0.43, H_2O/MeCN	Ce^{IV}	electrode

[a] Electrode = Clark-type electrochemical probe for selective dioxygen detection; GC = gas-chromatographic techniques used for dioxygen quantification; optical = optical dioxygen probe used to measure dioxygen levels; pressure = pressure transducer.

Table S2. Bond Lengths (Å) for **1b−10b** Determined by Geometry-Optimized DFT Calculations. Numbering Scheme is Provided Below.

	Compound	Ru-N^1	Ru-N^2	Ru-N^3	Ru-N^4	Ru-N^5
1b	$[Ru(tpy)(bpy)(OH_2)]^{2+}$	2.101	2.056	2.112	2.006	2.112
2b	$[Ru(tpyOMe)(bpy)(OH_2)]^{2+}$	2.098	2.054	2.113	2.010	2.113
3b	$[Ru(tpy)(bpyOMe)(OH_2)]^{2+}$	2.109	2.061	2.109	2.000	2.109
4b	$[Ru(tpyOMe)(bpyOMe)(OH_2)]^{2+}$	2.108	2.060	2.109	2.005	2.110
5b	$[Ru(tpyCl)(bpy)(OH_2)]^{2+}$	2.101	2.056	2.113	2.004	2.113
6b	$[Ru(tpy)(bpyCl)(OH_2)]^{2+}$	2.101	2.057	2.114	2.006	2.114
7b	$[Ru(tpyCl)(bpyCl)(OH_2)]^{2+}$	2.106	2.057	2.115	2.006	2.115
8b	$[Ru(tpyCOOH)(bpy)(OH_2)]^{2+}$	2.103	2.056	2.113	1.998	2.113
9b	$[Ru(tpy)(bpyCOOH)(OH_2)]^{2+}$	2.093	2.050	2.114	2.009	2.114
10b	$[Ru(tpyCOOH)(bpyCOOH)(OH_2)]^{2+}$	2.096	2.051	2.003	2.003	2.116



L = OH_2, OH^-, O^{2-}

Table S3. Bond Lengths (Å) for **1b** and Likely Higher-Valent Ru Catalytic Intermediates Determined by DFT. Numbering Scheme for N Atoms is Provided Above.

	Compound	Ru-N^1	Ru-N^2	Ru-N^3	Ru-N^4	Ru-N^5
Ru^{II}	$[Ru(tpy)(bpy)(OH_2)]^{2+}$	2.101	2.056	2.112	2.006	2.112
Ru^{III}	$[Ru(tpy)(bpy)(OH)]^{2+}$	2.101	2.125	2.115	2.012	2.115
Ru^{IV}	$[Ru(tpy)(bpy)(O)]^{2+}$	2.112	2.203	2.104	2.008	2.104

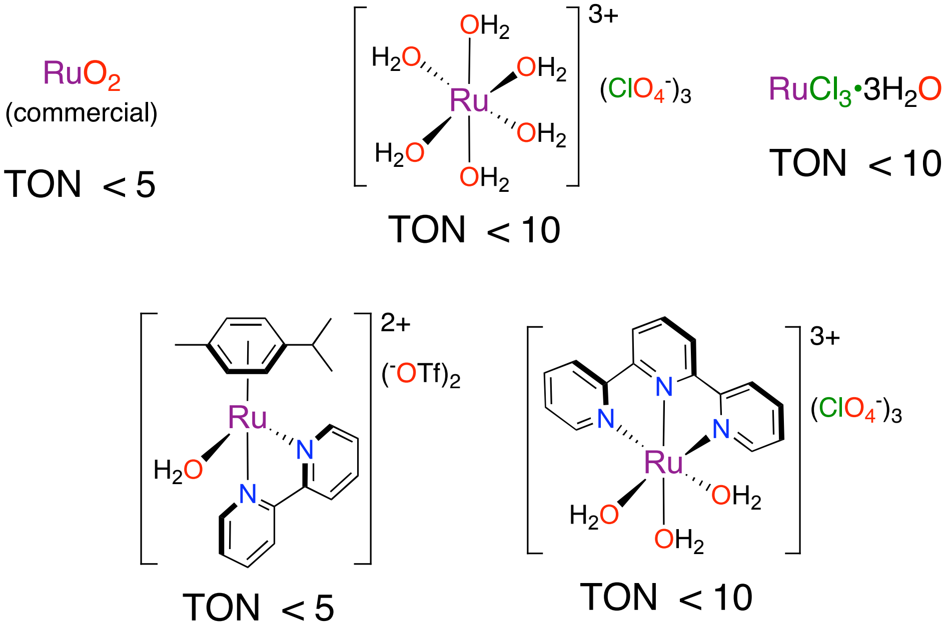


Figure S1. A series of Ru-based materials and complexes[15] analyzed under reaction conditions relevant to water oxidation. For each compound minimal activity was observed under our conditions; 1M $HClO_4$, [Ru complex] = 6.7×10^{-5} M, Ce:Ru = 5000:1.

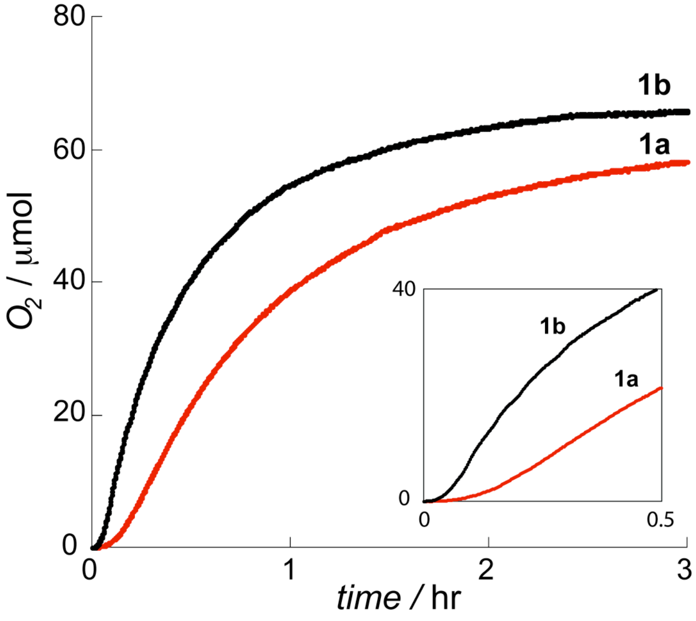


Figure S2. Comparison of dioxygen evolution in water oxidation where **1a** and **1b** are used as catalysts ([Ru catalyst] = 6.7×10^{-5} M).

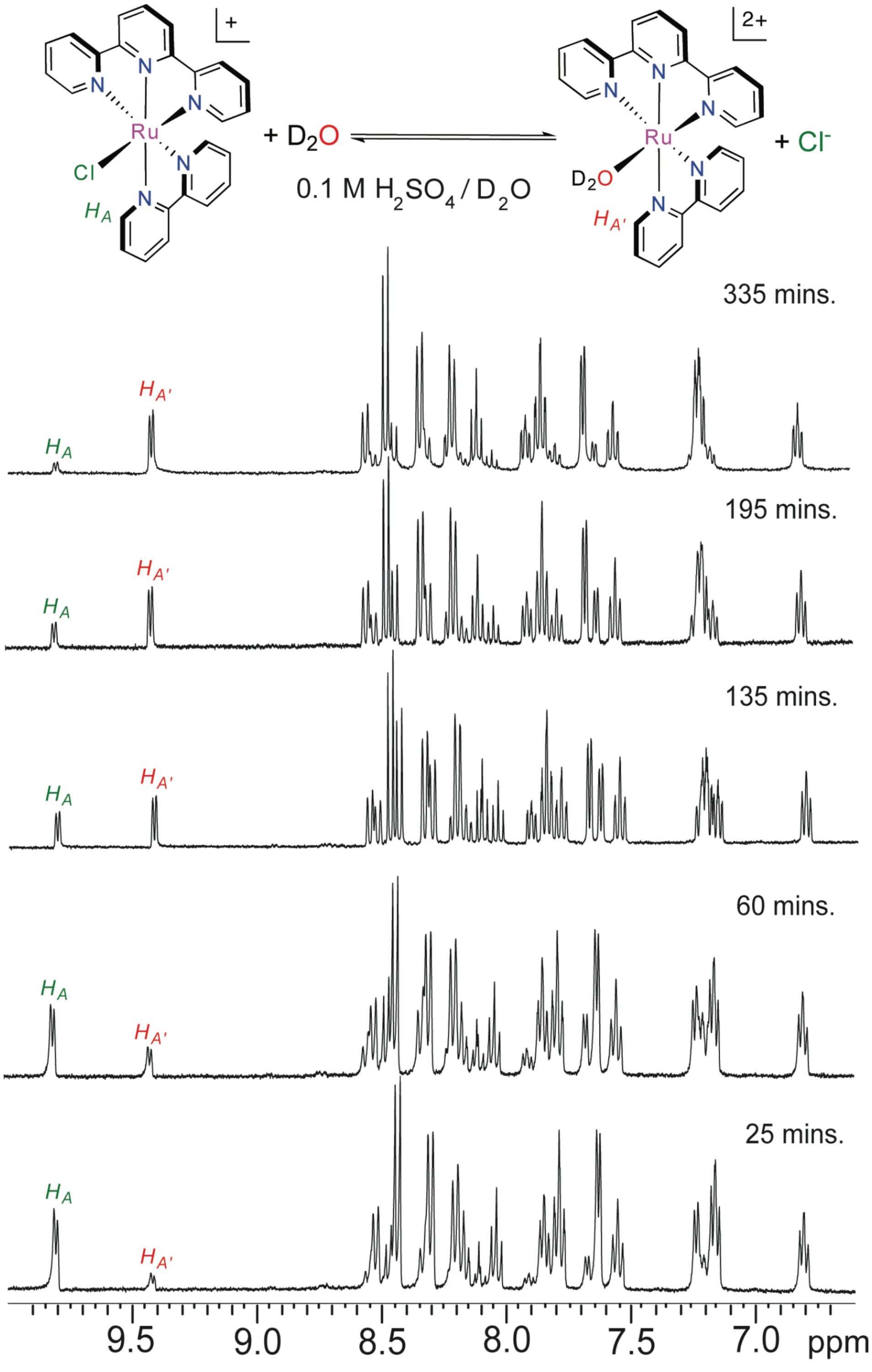


Figure S3. ^{1}H-NMR spectra highlighting the conversion of **1a** to **1b** in aqueous acidic media as a function of time.

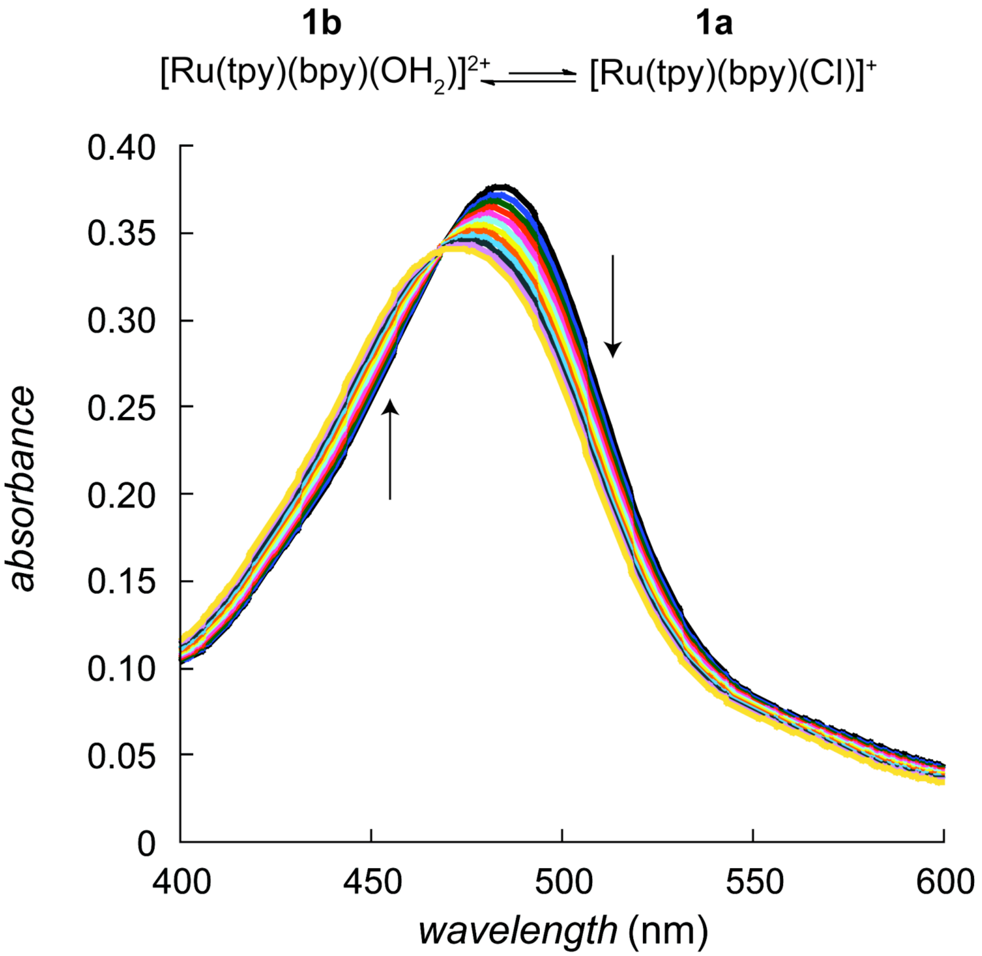


Figure S4. UV-Vis spectra highlighting the conversion of **1a** to **1b** in 1M $HClO_4$ as a function of time (taken at 15 min intervals). MLCT bands are indicated with arrows.

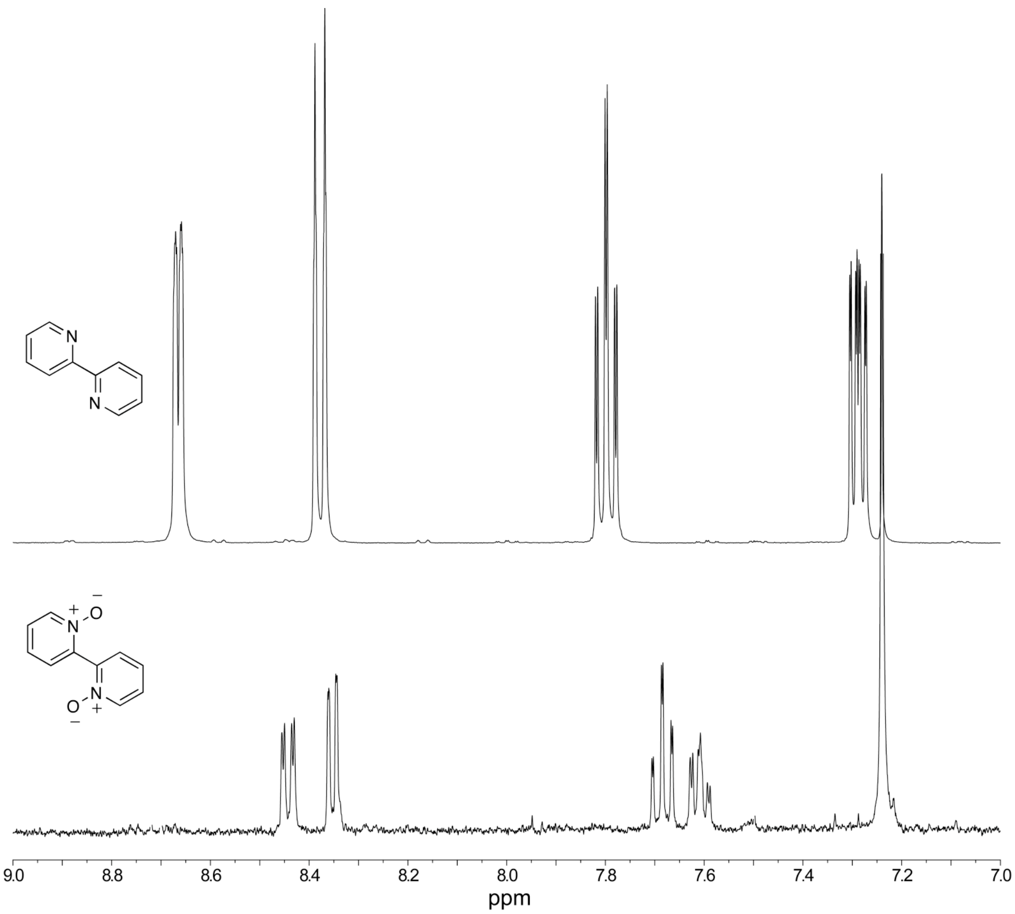


Figure S5. ^{1}H-NMR of bpy and 2,2'-bipyridine-*N,N'*-dioxide (bpydo) in $CDCl_3$ following a large scale water oxidation. The identity of bpydo was also confirmed by ESI-MS. % recovery of bpydo is 52% after 50 mg of **1b** was subjected to 1000 eq of $(NH_4)_2Ce(NO_3)_6$ in 1M $HClO_4$ for 24 h.

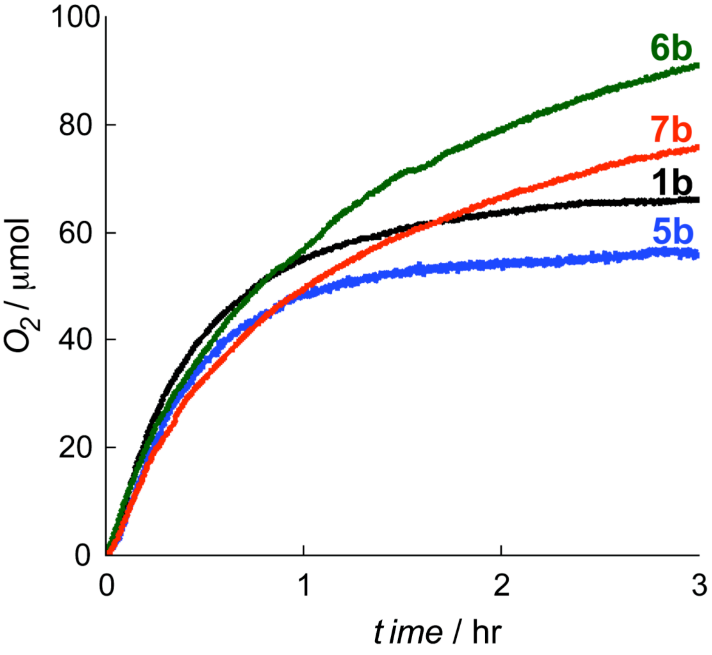


Figure S6. O_2 evolution data for the –Cl series **5b–7b**. The parent compound is provided as a benchmark ([Ru catalyst] = 6.7 x 10^{-5} M).

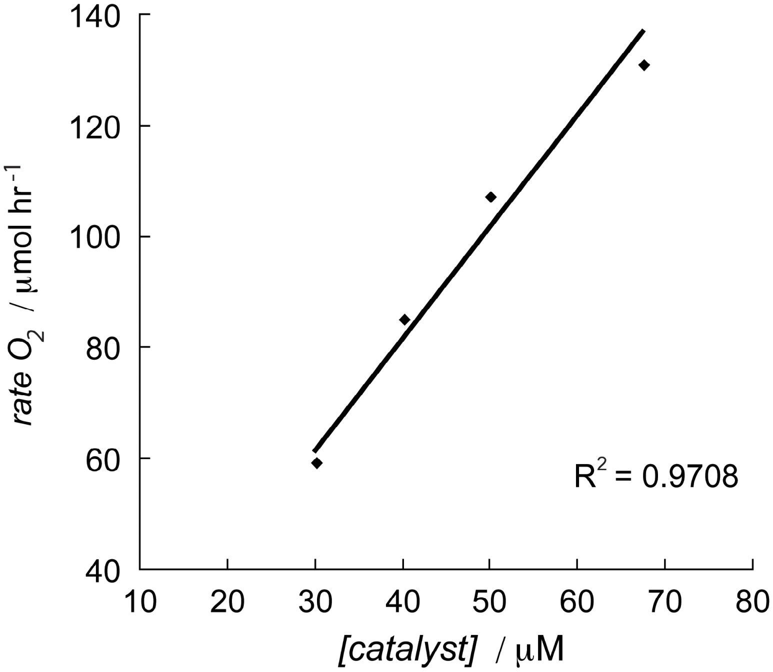
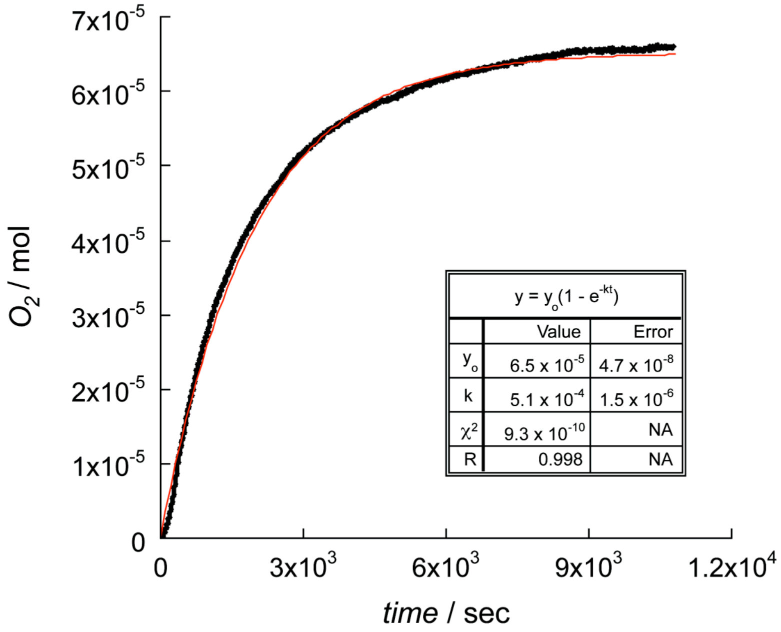


Figure S7. Rate of dioxygen evolution as a function of catalyst concentration using **1b** in aqueous 1M $HClO_4$.



$y = y_o(1 - e^{-kt})$

	Value	Error
y_o	6.5×10^{-5}	4.7×10^{-8}
k	5.1×10^{-4}	1.5×10^{-6}
χ^2	9.3×10^{-10}	NA
R	0.998	NA

Figure S8. First-order exponential fit to the dioxygen evolution versus time plot for **1b**.

References

(1) Binstead, R. A.; Chronister, C. W.; Ni, J. F.; Hartshorn, C. M.; Meyer, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 8464-8473.

(2) Rotzinger, F. P.; Munavalli, S.; Comte, P.; Hurst, J. K.; Gratzel, M.; Pern, F. J.; Frank, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 6619-6626.

(3) Naruta, Y.; Sasayama, M.; Sasaki, T. *Angew. Chem.-Int. Ed.* **1994**, *33*, 1839-1841.

(4) Limburg, J.; Vrettos, J. S.; Chen, H. Y.; de Paula, J. C.; Crabtree, R. H.; Brudvig, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 423-430.

(5) Wada, T.; Tsuge, K.; Tanaka, K. *Inorg. Chem.* **2001**, *40*, 329-337.

(6) Sens, C.; Romero, I.; Rodriguez, M.; Llobet, A.; Parella, T.; Benet-Buchholz, J. *J. Am. Chem. Soc.* **2004**, *126*, 7798-7799.

(7) Deng, Z. P.; Tseng, H. W.; Zong, R. F.; Wang, D.; Thummel, R. *Inorg. Chem.* **2008**, *47*, 1835-1848.

(8) McDaniel, N. D.; Coughlin, F. J.; Tinker, L. L.; Bernhard, S. *J. Am. Chem. Soc.* **2008**, *130*, 210-217.

(9) Tseng, H. W.; Zong, R.; Muckerman, J. T.; Thummel, R. *Inorg. Chem.* **2008**, *47*, 11763-11773.

(10) Concepcion, J. J.; Jurss, J. W.; Templeton, J. L.; Meyer, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 16462-16463.

(11) Xu, Y. H.; Akermark, T.; Gyollai, V.; Zou, D. P.; Eriksson, L.; Duan, L. L.; Zhang, R.; Akermark, B.; Sun, L. C. *Inorg. Chem.* **2009**, *48*, 2717-2719.

(12) Hull, J. F.; Balcells, D.; Blakemore, J. D.; Incarvito, C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 8730-8732.

(13) Duan, L. L.; Fischer, A.; Xu, Y. H.; Sun, L. C. *J. Am. Chem. Soc.* **2009**, *131*, 10397-10399.

(14) Masaoka, S.; Sakai, K. *Chem. Lett.* **2009**, *38*, 182-183.

(15) Dykeman, R. R.; Luska, K. L.; Thibault, M. E.; Jones, M. D.; Schlaf, M.; Khanfar, M.; Taylor, N. J.; Britten, J. F.; Harrington, L. *J. Mol. Catal. A: Chem.* **2007**, *277*, 233-251.