Supplementary Information

Highly Efficient and Robust Molecular Water Oxidation Catalysts Based on Ruthenium Complexes

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Experimental details

Preparation of Ru complexes

All chemicals and solvents, if not stated otherwise, were purchased from Sigma−Aldrich without further purification. All of the axial ligands were purchased from Chemtronica. The ligand 2,2′−bipyridine−6,6′−dicarboxylic acid (H_2bda) was purchased from Jinan Henghua Sci. & Tec. Co. Ltd. The ^{1}H NMR spectra were recorded on a 500 MHz NMR of Bruker Avance spectrometer with TMS as internal standard. Mass spectra were performed by a LCQ Advantage Max (Finnigan) instrument. Elemental analyses were performed with a Thermmoquest−Flash EA 1112 apparatus.

Synthesis of [Ru^{II}(bda)(isoquinoline)$_2$] ***(1a)****.* Complex **1a** was prepared by the method reported in literature[1] with modification. A mixture of 2,2′−bipyridine−6,6′−dicarboxylic acid (H_2bda) (100 mg, 0.41 mmol), *cis*−[Ru(dmso)$_4$Cl$_2$] (200 mg, 0.41 mmol) and NEt_3 (0.3 ml) in methanol (20 ml) was degassed with N_2 and refluxed over 4 hours. The suspension solution obtained was filtered, the resulting solid without further purification was dissolve in methanol with 2 equivalent of isoquinoline (107 mg, 0.82 mmol), and the solution reflux overnight under N_2 protection. The solvent was removed,

the rest solid was purified by column chromatography on silica gel using methanol and dichloromethane mixture (1:10, v: v) as eluents, yielding **1a** as a dark red solid (yield = 88%). ^{1}H NMR (500 MHz, CD_3OD (10% $CDCl_3$) with a small amount of (+)−sodium L−ascorbate): δ = 8.61 (s, 2H), 8.51 (d, J = 10.0 Hz, 2H), 8.01 (d, J = 10.0 Hz, 2H), 7. 85 (t, J = 10.0 Hz, 2H), 7.71−7.75 (m, 4H), 7.65 (t, J = 10.0 Hz, 2H), 7.54 (t, J = 10.0 Hz, 4H), 7.45 (t, J = 5.0 Hz, 2H). MS (ESI): m/z$^+$ = 603.01 (M + H$^+$), calcd: 603.06. Calcd. for **1a** ($C_{30}H_{20}N_4O_4Ru{\cdot}0.8CH_3OH$) C,58.98; H, 3.73; N, 8.93. Found: C, 58.72; H, 3.41; N, 8.64.

Similar procedures as described for **1a** were followed to afford the corresponding complexes **1**, **2** and **2a**.

*[Ru^{II}(bda)(6−fluoroisoquinoline)$_2$]**(1)***. Compound **1** was obtained as dark red solid (yield = 82%). ^{1}H NMR [500 MHz, CD_3OD with a small amount of (+)−sodium L−ascorbate]: δ = 8.67 (d, J = 10.0 Hz, 2H), 8.65 (s, 2H), 8.04 (d, J = 10.0 Hz, 2H), 7.92−7.98 (m, 4H), 7.61 (d, J = 10.0 Hz, 2H), 7.57 (d, J = 10.0 Hz, 2H), 7.51 (dd, J = 10.0 Hz, J = 2.0 Hz, 2H), 7.45 (td, J = 10.0 Hz, J = 2.0 Hz, 2H). MS (ESI): m/z$^+$ = 660.87 (M + Na$^+$), calcd: 661.02. Calcd. for **1** ($C_{30}H_{18}F_2N_4O_4Ru{\cdot}0.9CH_3OH{\cdot}0.4CH_2Cl_2$) C,55.69; H, 3.27; N, 8.41. Found: C, 55.42; H, 3.62; N, 8.78.

*[Ru^{II}(bda)(6−bromophthalazine)$_2$]**(2)***. The product was insoluble in MeOH, then it was filtered to give pure product directly. Compound **2** was obtained as dark red solid (yield = 79%). ^{1}H NMR [500 MHz, CD_3OD (10% $CDCl_3$) with a small amount of (+)−sodium L−ascorbate]: δ = 9.68 (s, 2H), 8.52 (s, 2H), 7.97 (d, J = 10.0 Hz, 2H), 7.75 (d, J = 10.0 Hz, 2H), 7.67 (d, J = 10.0 Hz, 2H), 7.61 (d, 2H), 7.49 (t, J = 5.0 Hz, 2H). MS (ESI): m/z+ = 762.88 (M + Na$^+$), calcd: 762.87. Calcd. for **2** ($C_{28}H_{16}Br_2N_6O_4Ru{\cdot}1.0CH_3OH{\cdot}0.3CH_2Cl_2$) C, 42.98; H, 2.54; Cl, 2.60; N, 10.26. Found: C, 42.62; H, 2.69; N, 10.58.

*[Ru^{II}(bda)(phthalazine)$_2$]**(2a)***. Complex **2a** was prepared by the method reported in literature[2] with modification. Compound **2a** was obtained as dark red solid (yield = 87%). ^{1}H NMR [500 MHz, CD_3OD with a small amount of (+)−sodium L−ascorbate]: δ = 9.57 (s, 2H), 8.45 (s, 2H), 7.93 (d, J = 10.0 Hz, 2H), 7.87 (d, J = 10.0 Hz, 2H), 7.55 (t, J = 5.0 Hz, 2H), 7.45−7.51 (m, 6H), 7.38 (t, J = 5.0 Hz, 2H). MS (ESI): m/z+ = 626.88 (M + Na$^+$), calcd: 627.03. Calcd. For **2a**

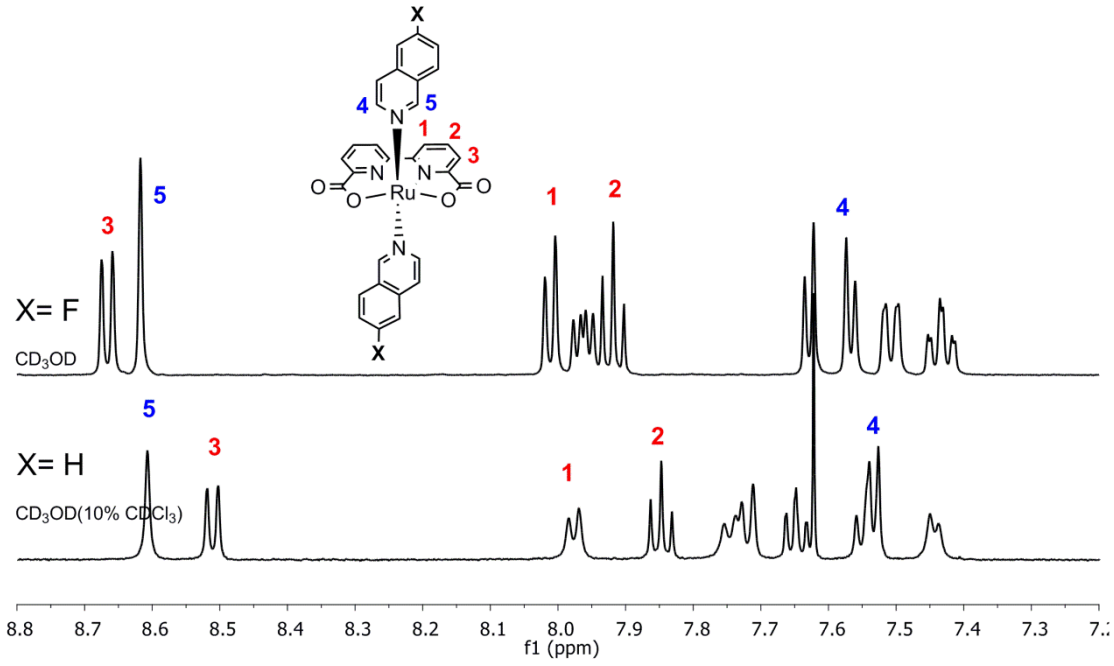
($C_{28}H_{18}N_6O_4Ru{\cdot}1.0CH_3OH{\cdot}0.2CH_2Cl_2$) C, 54.80; H, 3.49; N, 13.22. Found: C, 55.22; H, 3.65; N, 12.88.

Characterizations methods and performance measurements of catalysts

For NMR spectroscopy, the equatorial tetradentate ligand bda^{2-} has strong electron donating ability, that caused these Ru^{II} complexes to be easily oxidized to the paramagnetic Ru^{III} species by molecular oxygen (air) in deuterated solution at ambient temperature, and thus it was difficult to obtain sharp signals in ^1H NMR spectra. This problem has been solved by adding small amount of sodium ascorbate as reductant in the NMR tube and sharp signals in related ^1H NMR spectra were shown. For electrochemical measurements, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out with an Autolab potential station with a GPES electrochemical interface (Eco Chemie), using glassy carbon (basal plane, diameter 3 mm) (GC) as the working electrode, a platinum column as the counter−electrode, and an Ag/AgCl electrode (3 M KCl; 185 mV vs. NHE) as the reference electrode. The cyclic voltammograms were obtained in a 0.1 M CF_3SO_3H aqueous solution (with 20% CF_3CH_2OH). All potentials reported herein are referenced to normal hydrogen electrode (NHE), with $[Ru(bpy)_3]^{2+}$ ($E_{1/2}(Ru)^{III/II}$ = 1.26 V versus NHE) as an internal reference. The oxygen evolution curve was recorded by a pressure transducer (Omega PX138−030A5 V) with a power supply (TTi−PL601) at 8.00 V versus time, the total amount of oxygen was calibrated by GC (GC−2014 Shimadzu, the oxygen in air was detracted). First, the solution of Ce^{IV} (658 mg) in 0.1 M CF_3SO_3H (3.2 mL) was added into the 25 mL two neck round bottom flask, then the aqueous solution (10 % CH_3CN or CF_3CH_2OH) of the catalyst (10 −100 μL, 0.2−2.0 mM) were injected into the above solution under vigorous stirring at ambient temperature (21 ± 1°C). After oxygen generation finished, 500 μL gas phase measurement by Gas chromatography to determine the amount of oxygen produced. In this work, we reported the TOF and TON values as average of three runs with STDEV <10%.

All Density Functional Theory (DFT) calculations were carried out with Jaguar 7.6 program package by Schrödinger LLC. For geometry optimizations, solvation energy, and frequency calculations, Becke's three-parameter hybrid functional and the LYP correlation functional (B3LYP) was used with the LACVP** core potential and basis set,[3] while single point energy corrections were performed

with the M06[4] functional using the LACV3P**++ basis set which, as suggested by Martin,[5] was augmented with two f-polarization functions on Ru. Frequency calculations were performed on the optimized geometries to verify that the geometries correspond to minima or first order saddle points (transition states) on the potential energy surface (PES). The Gibbs free energies were defined as the following equation G = E(M06/LACV3P**++ 2f on Ru) + Gsolv + ZPE + H298 - TS298+1.9 (concentration correction to the free energy of solvation from M(g) to M(aq)). Based on the gas-phase-optimized structures, the effect of solvent was evaluated by single-point calculations using the Poisson Boltzmann reactive field implemented in Jaguar 7.6 (PBF)[6] in water.



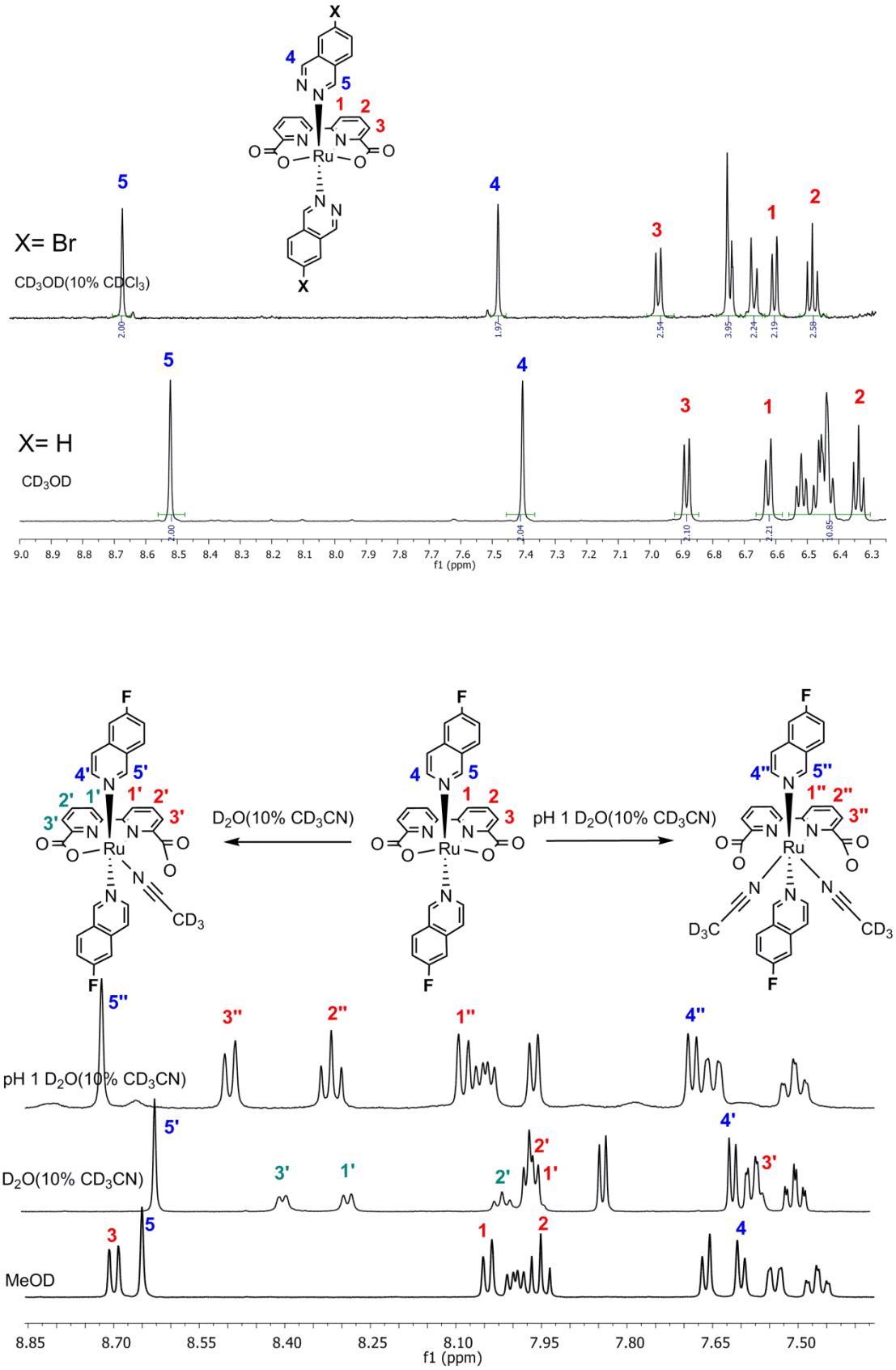
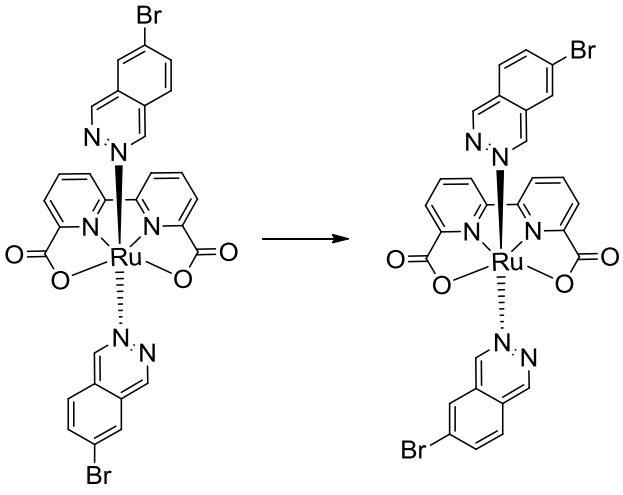


Figure S1. ^{1}H NMR spectra (500 MHz) of all Ru complexes.

The bottom set of NMR spectra in Figure S1 shows complex **1** in varies solutions and the corresponding changes in structures: (lower) methanol−d_4, (middle) D_2O/CD_3CN (v/v = 9/1), and (upper) pH 1 (0.1 M CF_3SO_3D) D_2O/CD_3CN (v/v = 9/1). Complex **1** remains its C_{2v} symmetry in methanol-d4; this C_{2v} symmetry, however, breaks off when D_2O/CD_3CN (v/v = 9/1) is used as solvents, as shown by five broad proton resonance peaks of bda^{2-} with a ratio of 1:1:1:2:1(middle). According to the ^1H NMR spectra, we propose that the resulting product is still a six−coordinate Ru complex (top left) [Ru($\kappa_3^{O,N,N}$−bda)(6−fluoroisoquinoline)$_2$(CD_3CN)] with one carboxylate dissociated from the Ru center. The feature of broad proton resonance peaks of bda^{2-} is likely due to the slow structural change (coordination between carboxylate and Ru^{II} is weak) of the resulting complex. Unexpected, the symmetry of complex **1** did not change when an acidic aqueous solution containing 10% CD_3CN was used as solvent; however the chemical shift of the bda^{2-} protons was significantly changed (upper). It is reasonable to believe that the acetonitrile would still coordinate to the RuII center under acidic conditions as observed in the neutral solution. We thereby propose that complex **1** under acidic conditions could accept two acetonitrile molecules and form complex [Ru(($\kappa_2^{N,N}$ −bda)(6−fluoroisoquinoline)$_2$(CD_3CN)$_2$].



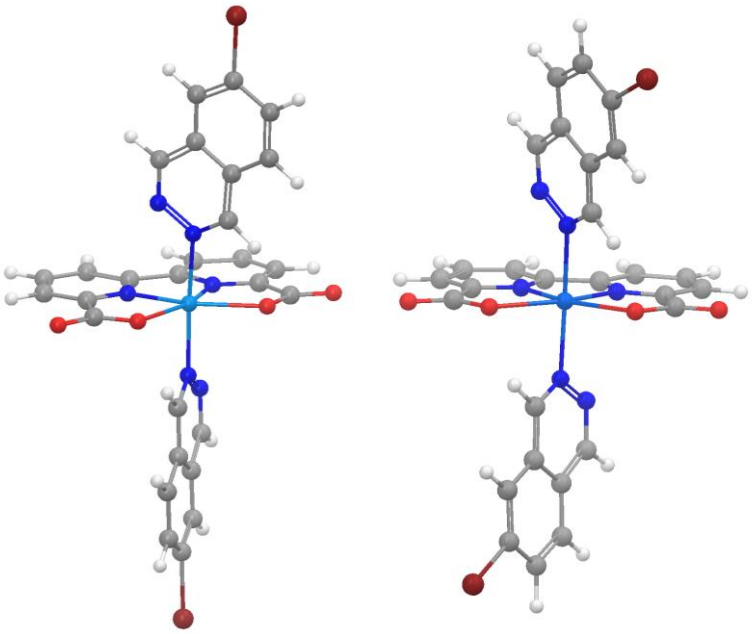
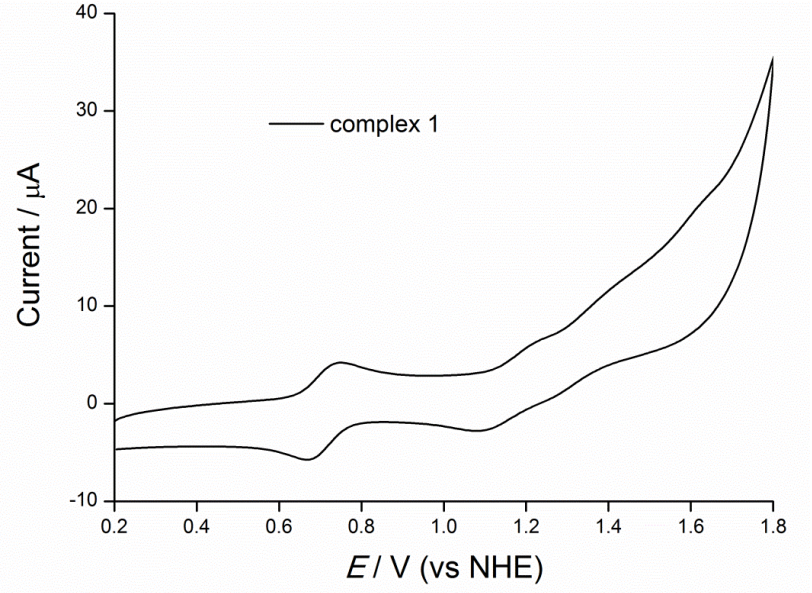
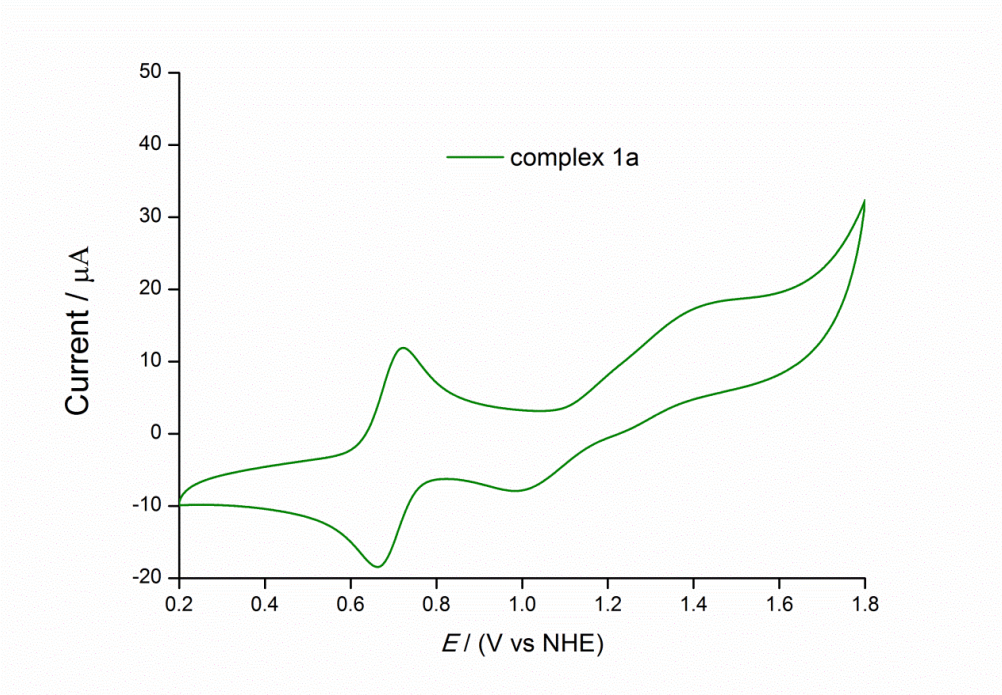
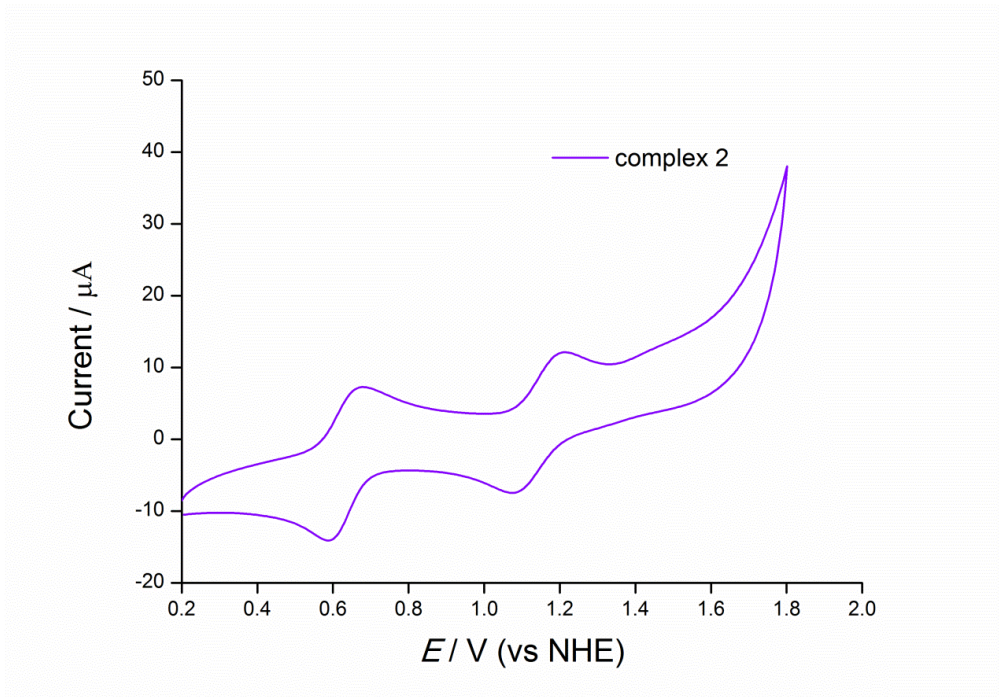


Figure S2. Profile of the calculated relative G for the isomer of complex **2**.




complex 1a
Current / μA
E / (V vs NHE)
50
40
30
20
10
0
-10
-20
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8


complex 2
Current / μA
E / V (vs NHE)
50
40
30
20
10
0
-10
-20
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0

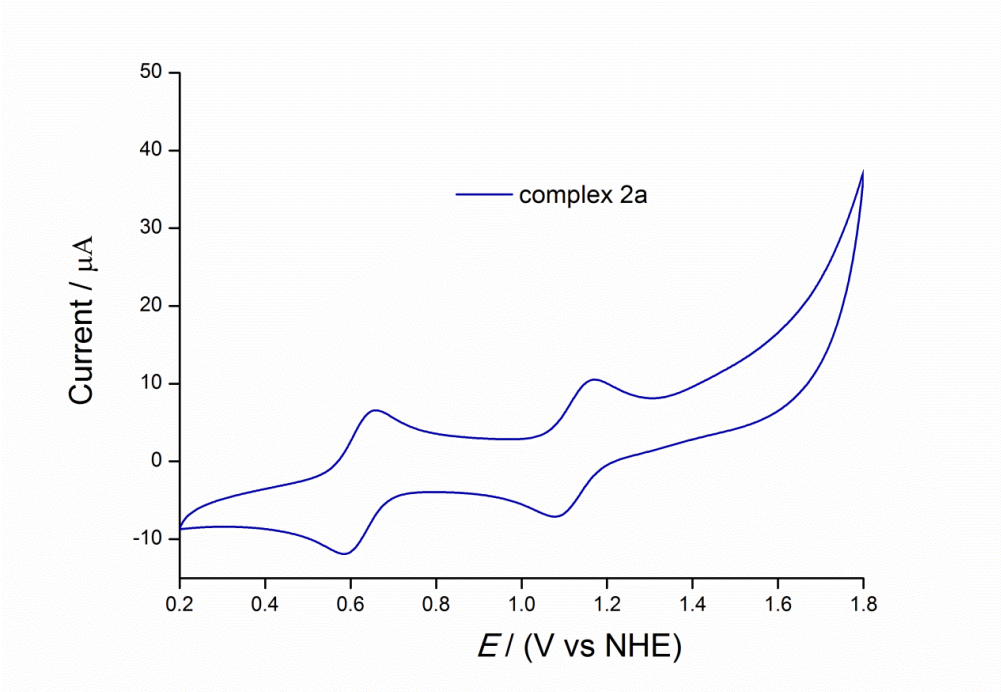


Figure S3. CVs of complexes **1**, **1a**, **2** and **2a**. Conditions: 0.1 M CF_3SO_3H aqueous solution (20% of CF_3CH_2OH); working electrode, Glass carbon; scan rate, 0.1 V/s; blank has been subtracted.

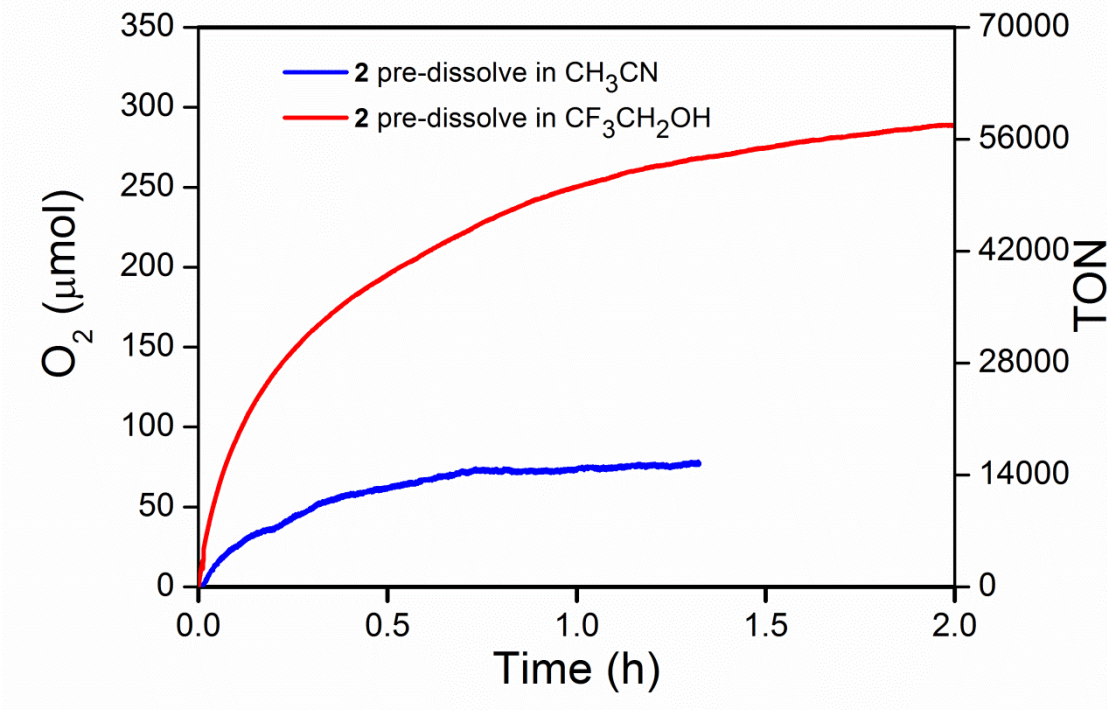


Figure S4. Oxygen evolution curves catalyzed by **2** recorded in the gas phase with pressure sensor and calibrated by GC. Conditions: an aqueous solution of CF_3SO_3H (Initial pH 1.0, 3.225 mL) containing 0.365 M Ce^{IV} and 1.550 $\times 10^{-6}$ M catalyst.

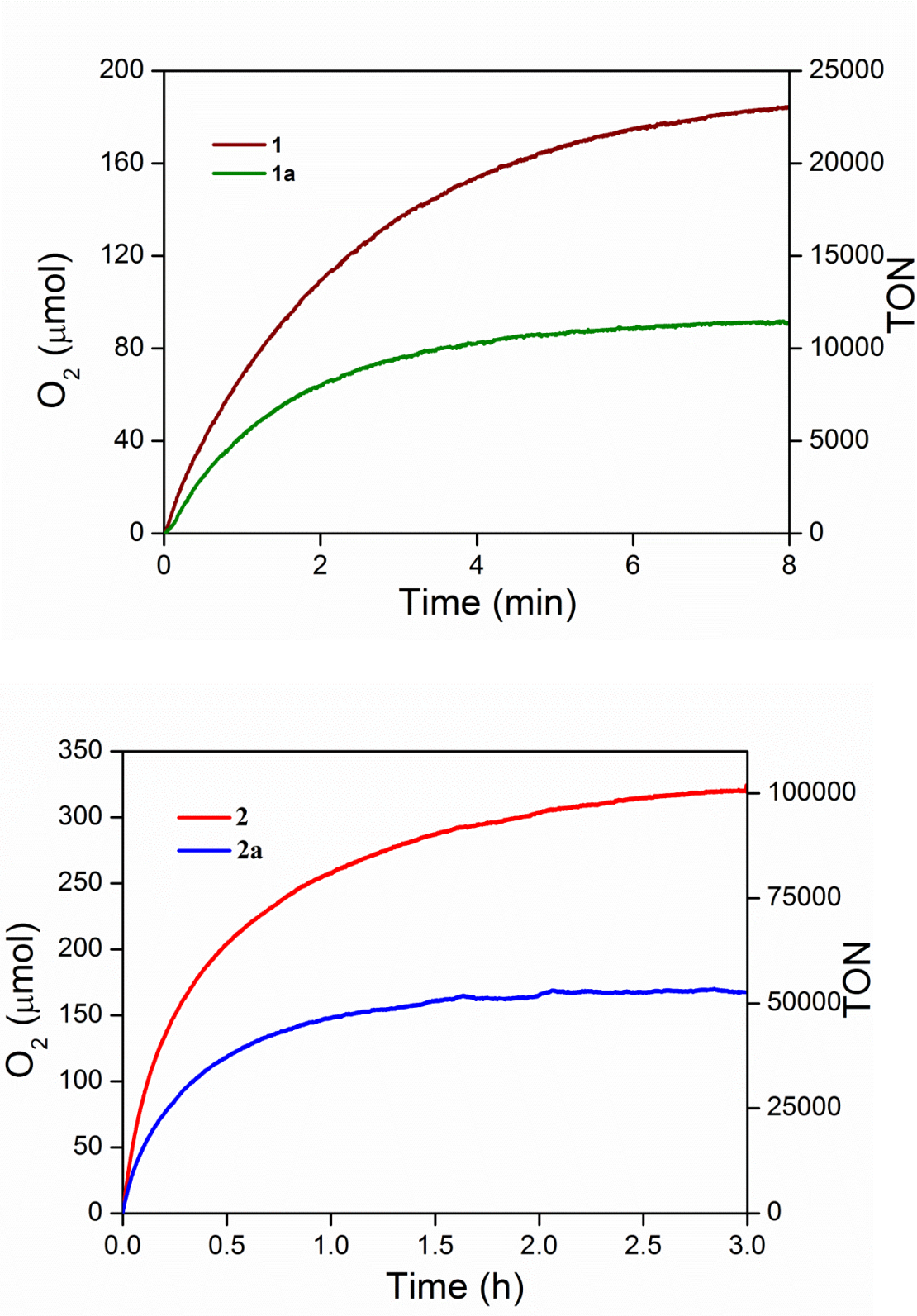
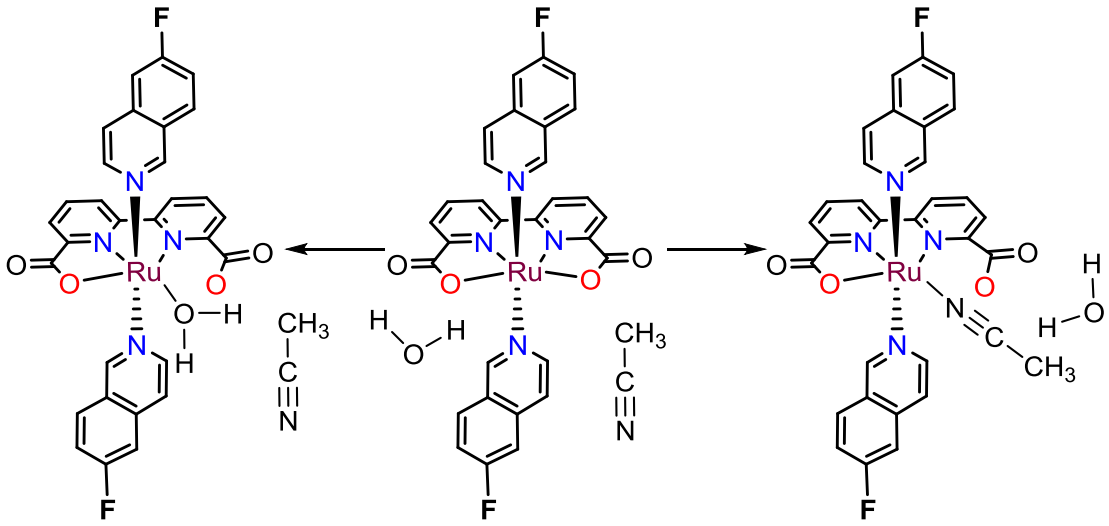
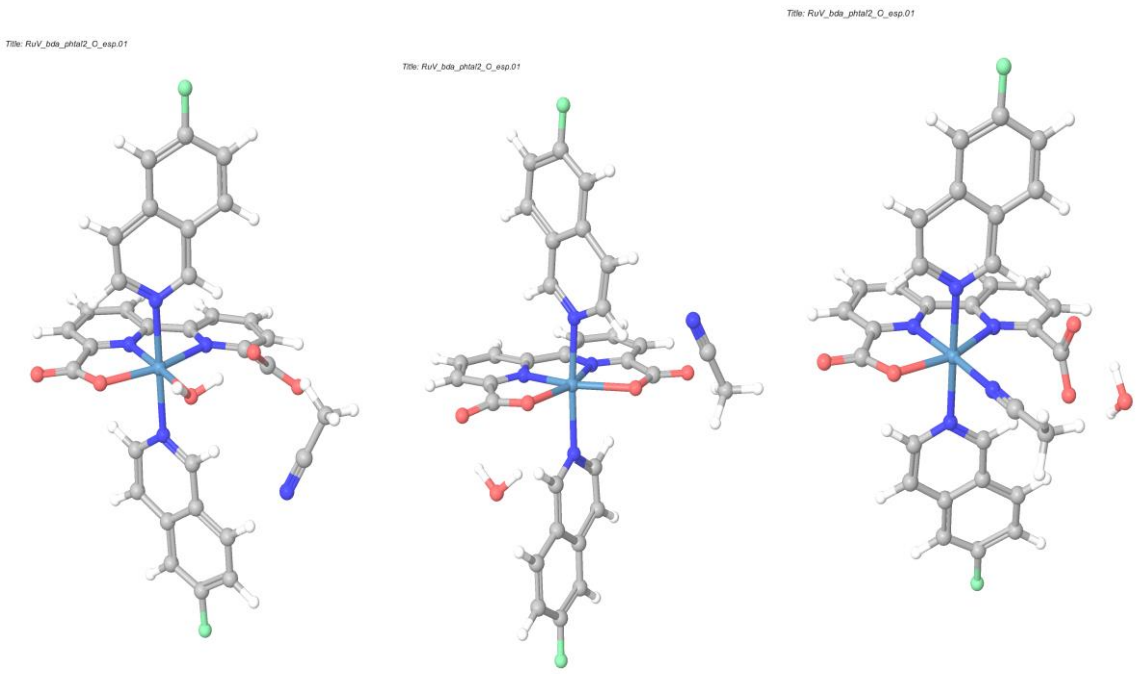


Figure S5. CF_3CH_2OH (~2% in water) was used as co-solvent for catalytic oxygen generation of all the catalysts as the function of time at 20 °C: [Ce^{IV}] = 0.365 M; [**1**] = [**1a**] = 2.469×10^{-6} M; [**2**] = [**2a**] = 0.933×10^{-6} M.



ΔG = +1.7 kcal mol^{-1} ΔG = 0 kcal mol^{-1} ΔG = -5.3 kcal mol^{-1}



1 **2** **3**

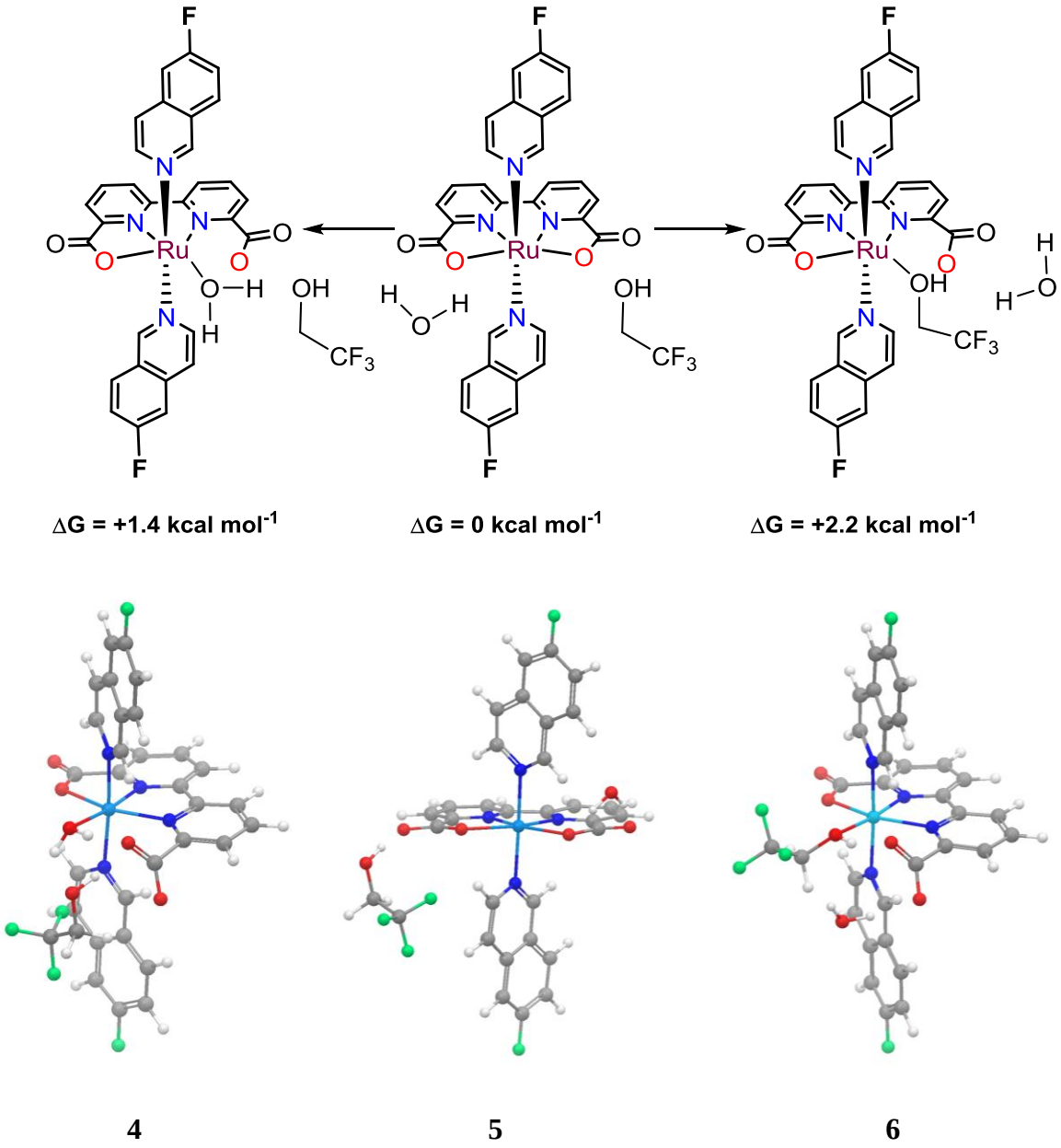
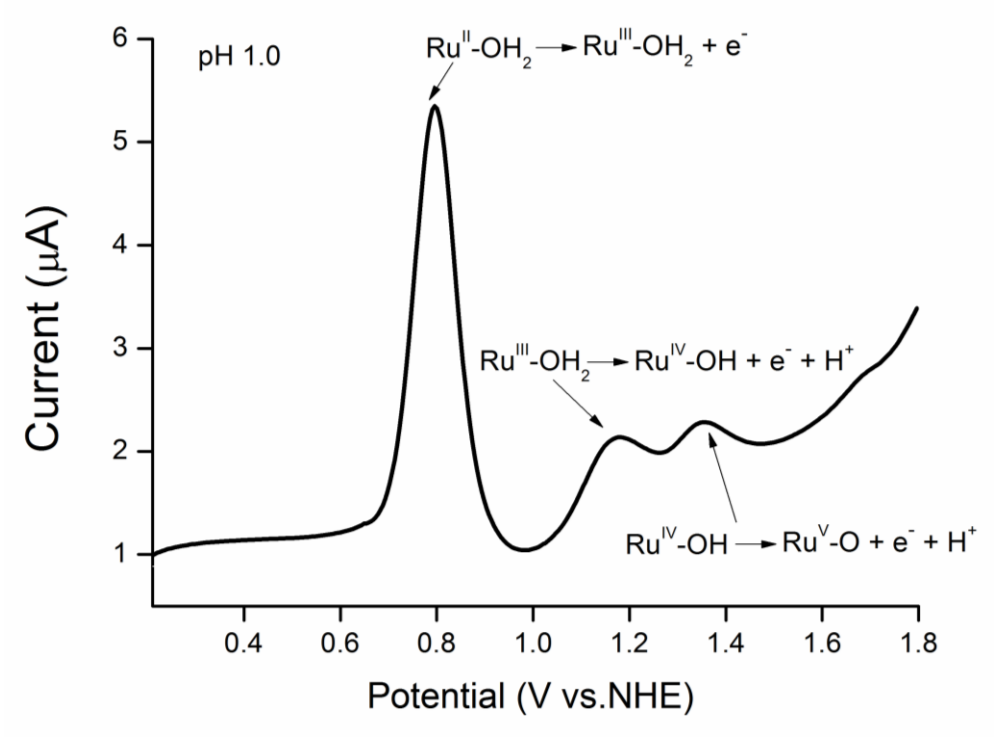


Figure S6. The calculated free energy difference of the solvent coordinated species of complex **1**. Optimized geometries of. a) **para**; b) **Para-isomer**; c) **1**; d) **2**; e) **3**; f) **4**; g) **5**; h) **6**; (Red = O; Blue = N; Light blue = Ru; Grey = C; White = H; light green = F).

	Gsolv(lacvp**) a.u.	E(M06/lacv3p **++(+f)) a.u.	ZPE(lacvp* *) kcal/mol	Htot (298) kcal/mol	Stot(298) cal/K/mol
para	-0.05771	-1825.53	248.478	21.024	211.842
Para-isomer	-0.05716	-1825.53	248.515	20.983	211.073
1	-0.0484461	-2176.061557	312.722	25.521	245.32
2	-0.0469025	-2176.064779	312.372	25.88	247.616
3	-0.0473647	-2176.076842	313.304	25.422	240.522
4	-0.0438797	-2496.109759	321.185	26.302	248.015
5	-0.0469994	-2496.103807	320.438	27.237	259.27
6	-0.0429456	-2496.108116	320.669	26.511	249.425



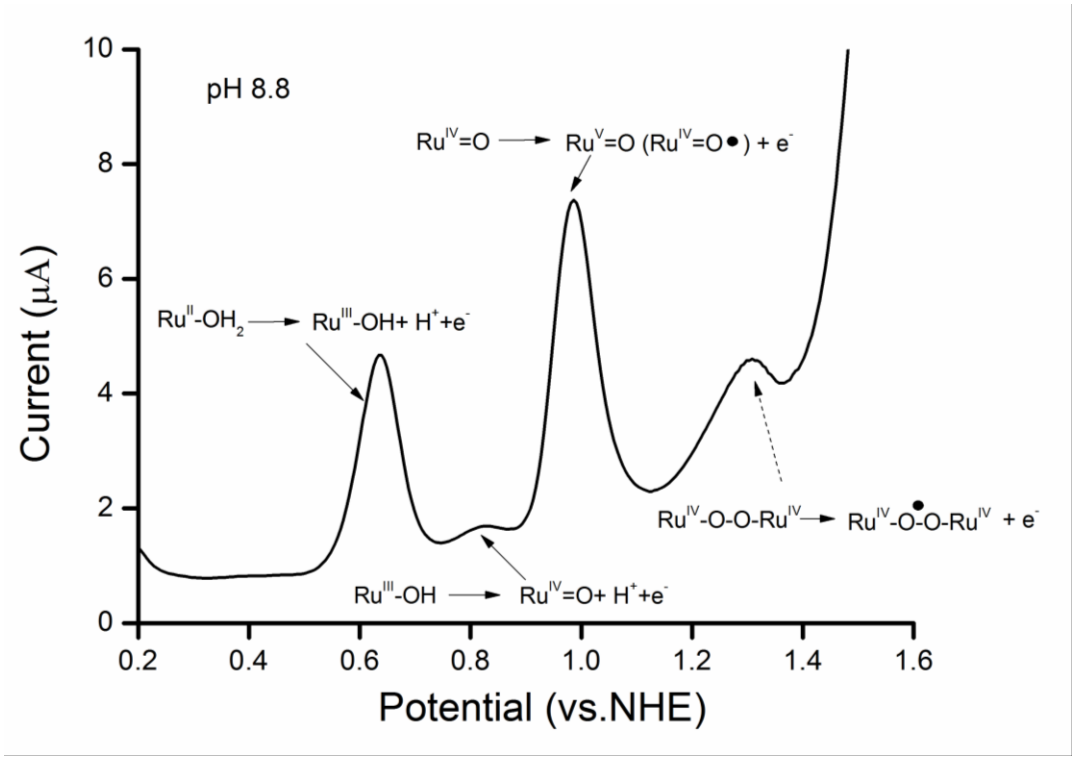


Figure S7. The DPV of complex **1** under pH 1.0 and pH 8.8 buffer solutions respectively. For the later one, the fourth peak was tentatively assign it to the oxidation of $[Ru^{IV}–O–O–Ru^{IV}]^{2+}$ to $[Ru^{IV}–O–O–Ru^{IV}]^{3+\bullet}$.

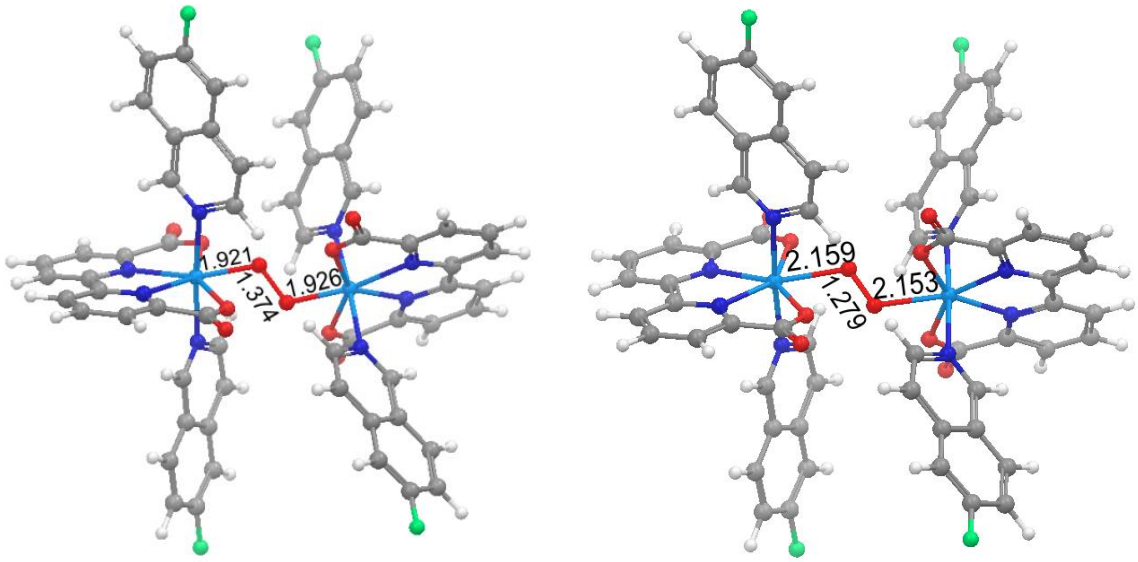


Figure S8. The calculated oxidation of $[Ru^{IV}–O–O–Ru^{IV}]^{2+}$/$[Ru^{IV}–O–O–Ru^{IV}]^{3+\bullet}$.

Spin density of $[Ru^{IV}–O–O–Ru^{IV}]^{3+\bullet}$.

Atom	Ru	O	O	Ru
Density	-0.03853	0.51883	0.52032	-0.03876

	Gsolv(lacvp**) a.u.	E(M06/lacv3p**++(+f)) a.u.	ZPE(lacvp**) kcal/mol	Htot (298) kcal/mol	Stot(298) cal/K/mol
$[Ru\text{-}OO\text{-}Ru]^{2+}$	-0.2024041	-4083.682473	541.03	42.95	370.266
$[Ru\text{-}OO\text{-}Ru]^{3+}$	-0.3825039	-4083.28584	541.773	43.356	373.137

Cartesian coordinates of $[Ru\text{-}OO\text{-}Ru]^{2+}$

atom	x	y	z
C1	-0.8943408066	2.1772247854	0.0731180752
C2	-1.6301990321	3.1669910958	-0.7870271717
C3	-2.9757440874	3.0615461020	-1.1228368952
C4	-3.5040554236	3.9667403328	-2.0421774733
C5	-2.6659753760	4.9216939546	-2.6189559230
C6	-1.3250714252	4.9727691540	-2.2302105194
C7	-0.3082182946	5.8836606712	-2.7538223719
C8	-0.4828381796	6.8132667197	-3.7822295765
C9	0.5933712253	7.6175019210	-4.1601277934
C10	1.8042741065	7.4997711307	-3.4800746665
C11	1.9006950320	6.5627328549	-2.4567888583
C12	3.0935555278	6.4098083917	-1.5580326121
C13	0.1420586909	6.6172497828	1.0756155519
C14	-0.2460642611	5.2176081604	3.4094315948
C15	0.2334879052	4.6209510153	2.2735251837
C16	1.3902239976	2.2179568923	-2.8711312328
C17	4.1195858242	2.2616642330	-3.1816703575
C18	3.4719081526	3.0707907203	-2.2861513693
N19	-0.8408737529	4.1184646721	-1.3006320781
N20	0.8831485403	5.7569635684	-2.1279949647
N21	0.4163513411	5.3177075861	1.1042099212
N22	2.1107711380	3.0510671952	-2.1269041983

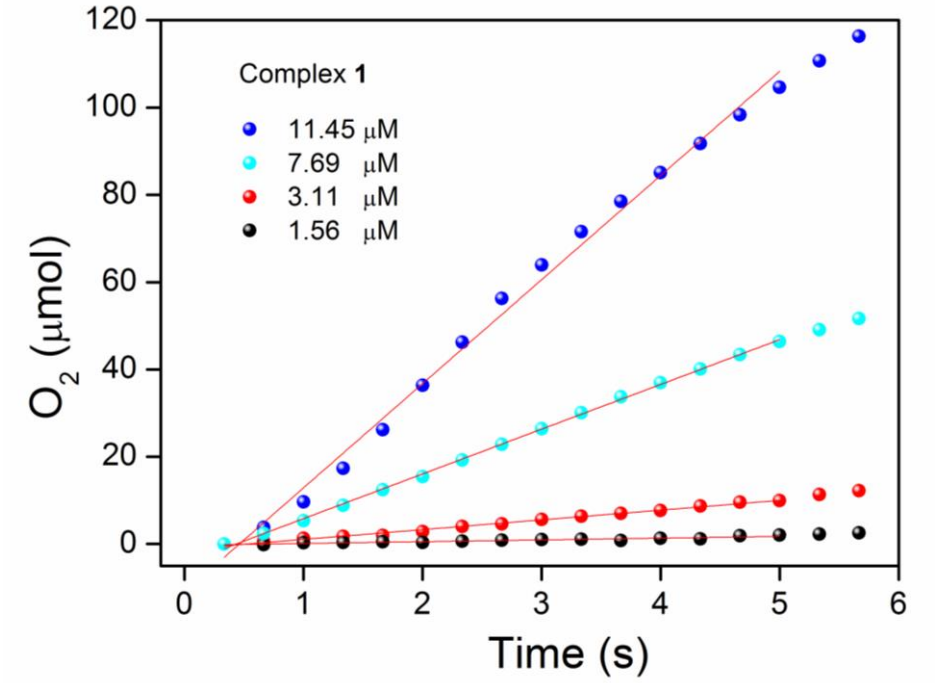
O23	-1.4436187531	1.2182853283	0.5865617305
O24	0.3857775779	2.4417420390	0.1208478570
O25	2.8464386563	5.5846084853	-0.5764971126
O26	4.1285733621	7.0311477538	-1.7298489132
Ru27	1.2267265036	4.2331771822	-0.5631655169
H28	-3.5586126566	2.2680539798	-0.6675703047
H29	-4.5506830272	3.9189813258	-2.3258670871
H30	-3.0457967038	5.6151081512	-3.3604617618
H31	-1.4411809577	6.9041168943	-4.2803334929
H32	0.4793588613	8.3372412113	-4.9646963366
H33	2.6719482161	8.1132146808	-3.6987361067
H34	0.3229726766	7.1411280838	0.1428616782
H35	-0.3600313878	4.6151139839	4.3051916228
H36	0.5221353478	3.5802245485	2.2600946530
H37	0.3191646594	2.2076858313	-2.7066464669
H38	5.2036160575	2.2878330960	-3.2287534476
H39	4.0076538139	3.7520569841	-1.6427355865
O40	2.4580433080	3.6263071000	0.7805094841
C43	-0.5667479504	6.5992261163	3.4110504292
C44	-0.3537433981	7.3223014876	2.1929234086
C45	-0.6402419148	8.7152912527	2.1421443124
C46	-1.1224602326	9.3617627238	3.2523549056
C47	-1.3292155840	8.6245380362	4.4418945564
C48	-1.0660596326	7.2807740002	4.5451672199
H49	-0.4723157209	9.2645918097	1.2198939083
H50	-1.3506759238	10.4221419261	3.2489081132
F51	-1.8004039343	9.2846877345	5.5024135045
H52	-1.2412247262	6.7606964342	5.4802342523
C53	1.9554016782	1.3573727904	-3.8347462620
C54	3.3785279854	1.3701232244	-3.9993837215
C55	3.9756919045	0.5051607809	-4.9459866852
C56	3.1647716196	-0.3215376837	-5.6843099503
C57	1.7567260814	-0.3510016236	-5.5429403366
C58	1.1623419886	0.4798201059	-4.6263881794
H59	5.0500253633	0.4899176206	-5.0920247234
F60	3.7108845068	-1.1454644478	-6.5820397561
H61	1.1837500302	-1.0316558920	-6.1630362290
H62	0.0834707458	0.4699921325	-4.4988839870
C61	6.5383252443	1.6221669708	0.0015784051
C62	7.1895846364	1.3112229008	1.3198108421
C63	8.5442187781	1.0381347072	1.4787405218
C64	8.9981468066	0.6428341173	2.7355555983
C65	8.0819865678	0.5095087983	3.7793135591
C66	6.7380136209	0.8118879042	3.5511176844
C67	5.6498304719	0.7119924009	4.5233795175
C68	5.7456176804	0.2211315169	5.8275555659
C69	4.6106546317	0.2106590101	6.6386557426
C70	3.4159967104	0.7301810475	6.1432919831
C71	3.3952433814	1.2117903876	4.8390307856
C72	2.2300340517	1.9334834283	4.2246246690
C73	5.0329281616	4.4083823705	3.4436549293
C74	5.8438774771	5.8426555294	1.2454570171
C75	5.3764690005	4.5587843452	1.1514437959
C76	4.1826156393	-1.2017966750	1.4841559549
C77	1.4579008270	-1.4321828675	1.2207403938
C78	2.0648161185	-0.2267069616	1.4575800251
N79	6.3213134647	1.2333540286	2.3360127214
N80	4.4715007449	1.1679455968	4.0437291265
N81	4.9773462871	3.8364057277	2.2459375981
N82	3.4258231976	-0.1154826518	1.6011442888
O83	7.1755709669	1.7562647313	-1.0295908745
O84	5.2371766390	1.6750822896	0.1145347152
O85	2.5296619370	2.4013181348	3.0421649545
O86	1.1785364695	2.1069971100	4.8174163388
Ru87	4.2343006988	1.8342699828	1.9616783960
H88	9.1925128788	1.1292000594	0.6137896838
H89	10.0479309471	0.4221476351	2.9016940777
H90	8.4069792687	0.1773998651	4.7589871565
H91	6.6936970578	-0.1479654869	6.2022284739
H92	4.6679600961	-0.1786555297	7.6503506823
H93	2.5054021571	0.7929782051	6.7294668419
H94	4.6839915525	3.8243308440	4.2878518655
H95	6.1032781531	6.3786247613	0.3384906269
H96	5.2846436496	4.0559095858	0.2010294035
H97	5.2555972505	-1.0704652592	1.5809043357
H98	0.3780088059	-1.4609569147	1.1142438037
H99	1.5005613483	0.6939694815	1.5144462996

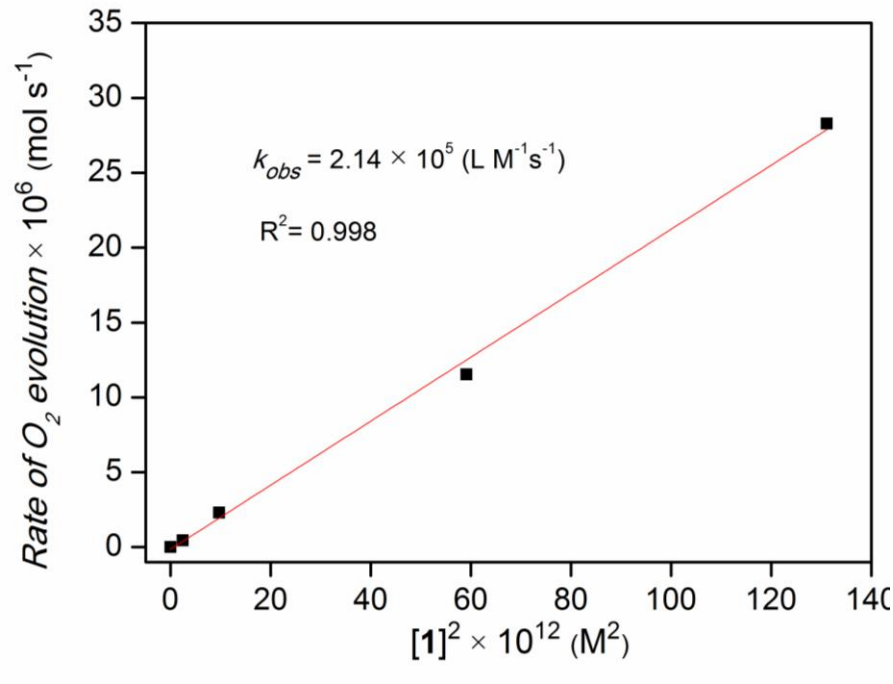
O100	2.9640393262	2.3598047495	0.6120454808
C101	5.9412092884	6.4726784788	2.5120985447
C102	5.5126659047	5.7188616598	3.6512285936
C103	5.5810063849	6.3028125238	4.9470239203
C104	6.0586605673	7.5793951229	5.1050264758
C105	6.4765231815	8.3033946365	3.9637077905
C106	6.4279419071	7.7886740395	2.6916098504
H107	5.2529142828	5.7314391073	5.8104152606
H108	6.1265361338	8.0536080464	6.0782812127
F109	6.9348436206	9.5429405066	4.1546711357
H110	6.7596508431	8.3839153742	1.8484084426
C111	3.6529445609	-2.4856944605	1.2391065379
C112	2.2316663367	-2.6161298001	1.1078195730
C113	1.6702151174	-3.8919511037	0.8678367132
C114	2.5125117505	-4.9719029958	0.7659595502
C115	3.9181537380	-4.8684552276	0.8888320790
C116	4.4788794130	-3.6381152972	1.1220891064
H117	0.5986513060	-4.0250709808	0.7657057614
F118	2.0014541295	-6.1839087886	0.5394587542
H119	4.5182206731	-5.7670503935	0.7942414768
H120	5.5561279927	-3.5377556654	1.2169154463

Cartesian coordinates of $[Ru\text{-}OO\text{-}Ru]^{3+}$

atom	x	y	z
C1	-0.7334781196	2.0480697776	0.0224063432
C2	-1.5645360191	2.8799516619	-0.9056328521
C3	-2.8750451934	2.6027424641	-1.2741083444
C4	-3.4848085859	3.4227829789	-2.2255974398
C5	-2.7637073988	4.4783592747	-2.7863477381
C6	-1.4525667616	4.7098523931	-2.3632370023
C7	-0.5478487949	5.7589942493	-2.8276523632
C8	-0.7840793825	6.6880131470	-3.8433303499
C9	0.2026037306	7.6283486897	-4.1489237113
C10	1.3923151035	7.6388959265	-3.4188430854
C11	1.5597113084	6.6931189095	-2.4143489510
C12	2.7407395948	6.6078851287	-1.4945633233
C13	-0.3302832481	6.5541428808	0.8869692715
C14	-0.3487507666	5.2653267180	3.3138875721
C15	0.1435305672	4.6740751034	2.1813089113
C16	1.5009127008	2.2932201876	-2.9977503012
C17	4.2049792720	2.6916783503	-3.2749521402
C18	3.4504372994	3.4073541222	-2.3849180235
N19	-0.8874231078	3.9157589030	-1.4239984648
N20	0.6229249172	5.7729069479	-2.1470774041
N21	0.1495998980	5.3134645131	0.9642158578
N22	2.0973261720	3.2134838715	-2.2411547781
O23	-1.1359654719	1.0583318598	0.5951495560
O24	0.5084123924	2.4972310425	0.0839509349
O25	2.5563815669	5.6764192462	-0.5687028786
O26	3.7154886590	7.3192854707	-1.5704071095
Ru27	1.0607774601	4.2983080173	-0.6881008794
H28	-3.3745584115	1.7537695541	-0.8183458985
H29	-4.5077061252	3.2371640789	-2.5381804294
H30	-3.2145590640	5.1142666463	-3.5392233418
H31	-1.7212066894	6.6735130072	-4.3884745997
H32	0.0373985818	8.3506307725	-4.9423537590
H33	2.1875144466	8.3566803345	-3.5939586312
H34	-0.2948803412	7.0424920823	-0.0812524820
H35	-0.3148492960	4.7112941813	4.2466711851
H36	0.5654377294	3.6804419217	2.2083384837
H37	0.4360677537	2.1444053408	-2.8533546628
H38	5.2750130795	2.8647903817	-3.3264103919
H39	3.8929855253	4.1523264678	-1.7393659069
O40	2.5591671451	3.7168085091	0.7535966121
C43	-0.8798870152	6.5800262137	3.2641756609
C44	-0.8626298945	7.2453662084	1.9926423146
C45	-1.3705784738	8.5707898955	1.8856389743
C46	-1.8751266368	9.2049138417	2.9922710849
C47	-1.8833596910	8.5258587792	4.2347327305
C48	-1.4041355233	7.2466947245	4.3928650905
H49	-1.3548295502	9.0791779451	0.9257598364
H50	-2.2693890136	10.2145085905	2.9482380947
F51	-2.3793630042	9.1712401833	5.2855823460
H52	-1.4342768377	6.7707854430	5.3670288496
C53	2.1848257251	1.5143556623	-3.9528410312
C54	3.5974394688	1.7130754185	-4.1032531494
C55	4.3165375365	0.9428705221	-5.0427485585

C56	3.6295558450	0.0186061193	-5.7940036287
C57	2.2360645335	-0.1963353228	-5.6665249783
C58	1.5238185185	0.5425698555	-4.7558476897
H59	5.3851400111	1.0705617836	-5.1786180879
F60	4.2872813787	-0.7187745367	-6.6837023918
H61	1.7653055581	-0.9436541958	-6.2964558841
H62	0.4542941878	0.3874690241	-4.6451097568
C61	6.4786859156	1.4597846784	0.0154028978
C62	7.1604971470	1.0111618223	1.2734095329
C63	8.4769272885	0.5753002139	1.3608497312
C64	8.9417426776	0.1140993774	2.5935908680
C65	8.0771827555	0.0929754433	3.6899418040
C66	6.7690206920	0.5567821317	3.5383655597
C67	5.7263991970	0.6206455560	4.5616318898
C68	5.7998735037	0.1511415561	5.8744257600
C69	4.7016120927	0.3115265525	6.7211092004
C70	3.5609202064	0.9640920934	6.2502220067
C71	3.5532460928	1.4139092884	4.9359483844
C72	2.4555588074	2.2117831935	4.2996567476
C73	5.5511743546	4.2765849092	3.5836900480
C74	6.2022071559	5.7537724189	1.3628927795
C75	5.6421434234	4.5073548928	1.2692034171
C76	4.0665780459	-1.1998472437	1.5941301840
C77	1.3209502113	-1.1966712833	1.4980271867
C78	2.0425552329	-0.0521714706	1.7114290061
N79	6.3455222609	1.0162946650	2.3377527932
N80	4.5989483286	1.2237829466	4.1176461468
N81	5.3181911087	3.7615487106	2.3766905205
N82	3.4158242119	-0.0505527457	1.7716878953
O83	7.0302857671	1.5707895035	-1.0556470297
O84	5.1879849330	1.6719509840	0.2264085666
O85	2.7841969865	2.5810518953	3.0729758421
O86	1.4262396330	2.5232425022	4.8574847673
Ru87	4.4049399697	1.8275251407	2.1021292304
H88	9.0931483272	0.5988743486	0.4676648096
H89	9.9639147905	-0.2353104407	2.7015631397
H90	8.4166441353	-0.2748010995	4.6520506404
H91	6.7026363418	-0.3342452769	6.2287370121
H92	4.7443479205	-0.0573175534	7.7412241513
H93	2.6861197508	1.1442019452	6.8667983125
H94	5.2701416982	3.6775597369	4.4429915373
H95	6.4233477260	6.3065657992	0.4553173985
H96	5.4248704372	4.0526051646	0.3130585766
H97	5.1507322479	-1.1683349885	1.6211965398
H98	0.2392022747	-1.1268664517	1.4485172103
H99	1.5532583871	0.9041306462	1.8203906301
O100	3.0307416122	2.5374511111	0.6043102266
C101	6.4801460176	6.3220505286	2.6340413093
C102	6.1340869178	5.5427815362	3.7875125613
C103	6.3878891604	6.0618537357	5.0888562490
C104	6.9627063860	7.2987056135	5.2382693774
C105	7.2943081577	8.0475675963	4.0826306537
C106	7.0685518741	7.5941621972	2.8035039603
H107	6.1251050964	5.4740899576	5.9632749609
H108	7.1726631027	7.7244130345	6.2135897826
F109	7.8479586479	9.2424910907	4.2615449102
H110	7.3434577434	8.2087533614	1.9529981530
C111	3.4149591300	-2.4295065197	1.3734768875
C112	1.9815999221	-2.4412955337	1.3313726301
C113	1.3008467487	-3.6607953838	1.1212546656
C114	2.0431732763	-4.8073481204	0.9589686474
C115	3.4585813371	-4.8213533991	0.9918930290
C116	4.1346621920	-3.6454364749	1.1962735235
H117	0.2176657278	-3.7051988187	1.0888496041
F118	1.4212280890	-5.9652292746	0.7594241091
H119	3.9736705615	-5.7661162163	0.8538131785
H120	5.2206821085	-3.6388742182	1.2228254183


Complex 1
11.45 μM
7.69 μM
3.11 μM
1.56 μM
O2 (μmol)
Time (s)


kobs = 2.14 × 10^5 (L M^-1 s^-1)
R^2 = 0.998
Rate of O2 evolution × 10^6 (mol s^-1)
[1]^2 × 10^12 (M^2)

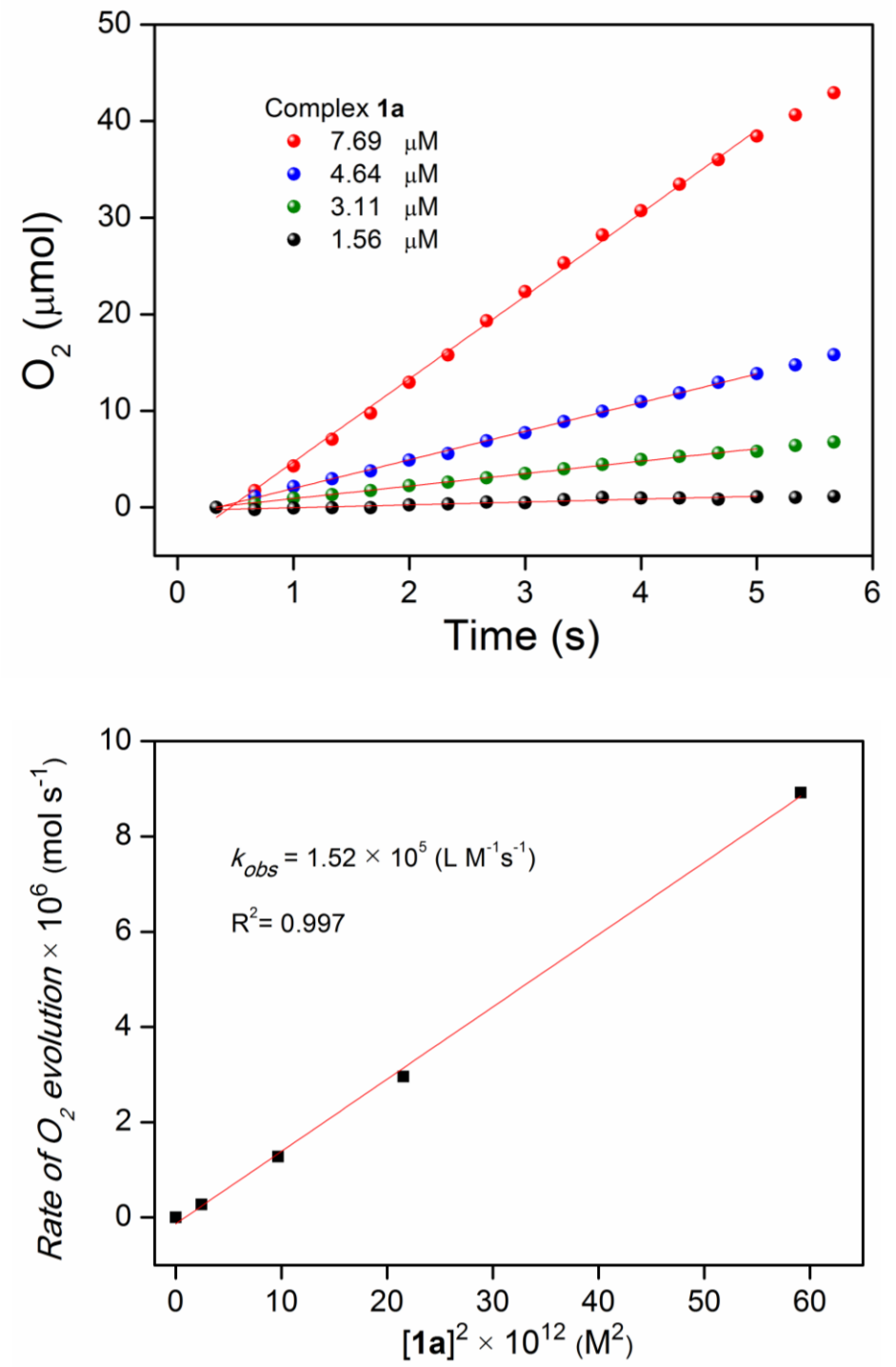


Figure S9. Plots of k_{obs} (the initial rates were calculated by linear fitting the data from 0 to 5 s) versus $[cat]^2$. Second-order plots of initial rate data were obtained for both **1** and **1a**: the rate constants were determined by the linear relationship between O_2 (mol s^{-1}) generation rate and square of the catalyst concentration (M^2);[7] the unit derivation is: mol s^{-1}/ M^2 = L M^{-1} s^{-1}. Therefore 2.54×10^5 (L M^{-1} s^{-1}) and 1.52×10^5 (L M^{-1} s^{-1}) were calculated for **1** and **1a** respectively.

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