Electronic Supplementary Material (ESI) for Faraday Discussions.

Ruthenium Catalysts for Water Oxidation Involving Tetradentate Polypyridine-type Ligands

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Supporting Information Page

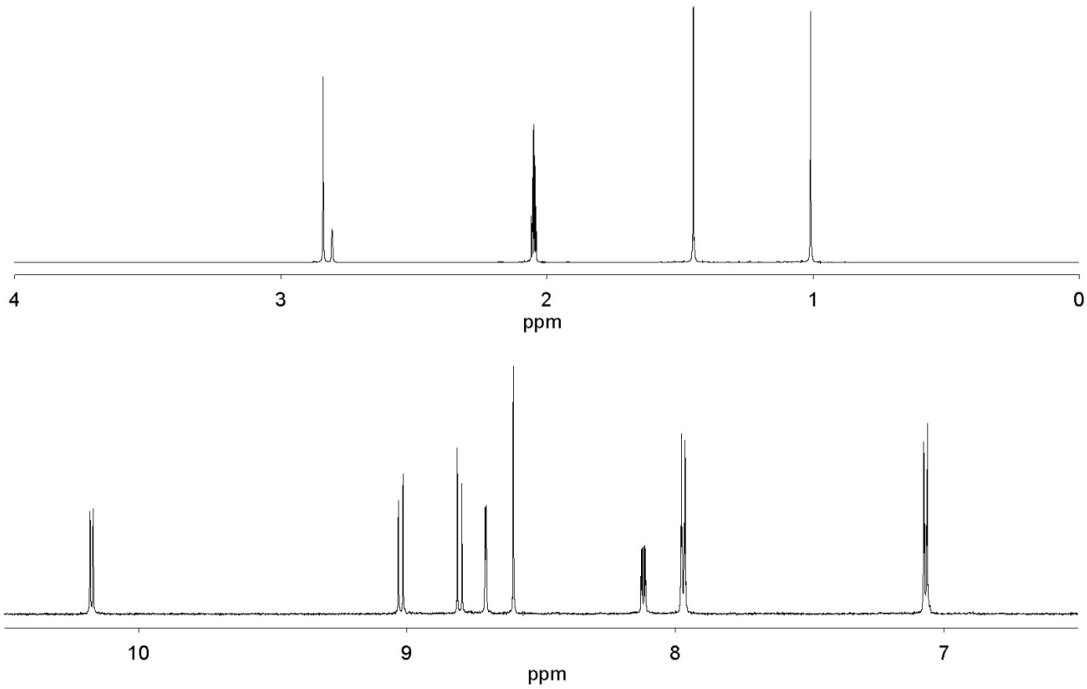

Figure S1. ^{1}H NMR of **4b**$(PF_6)_2$ in acetone-d_6.

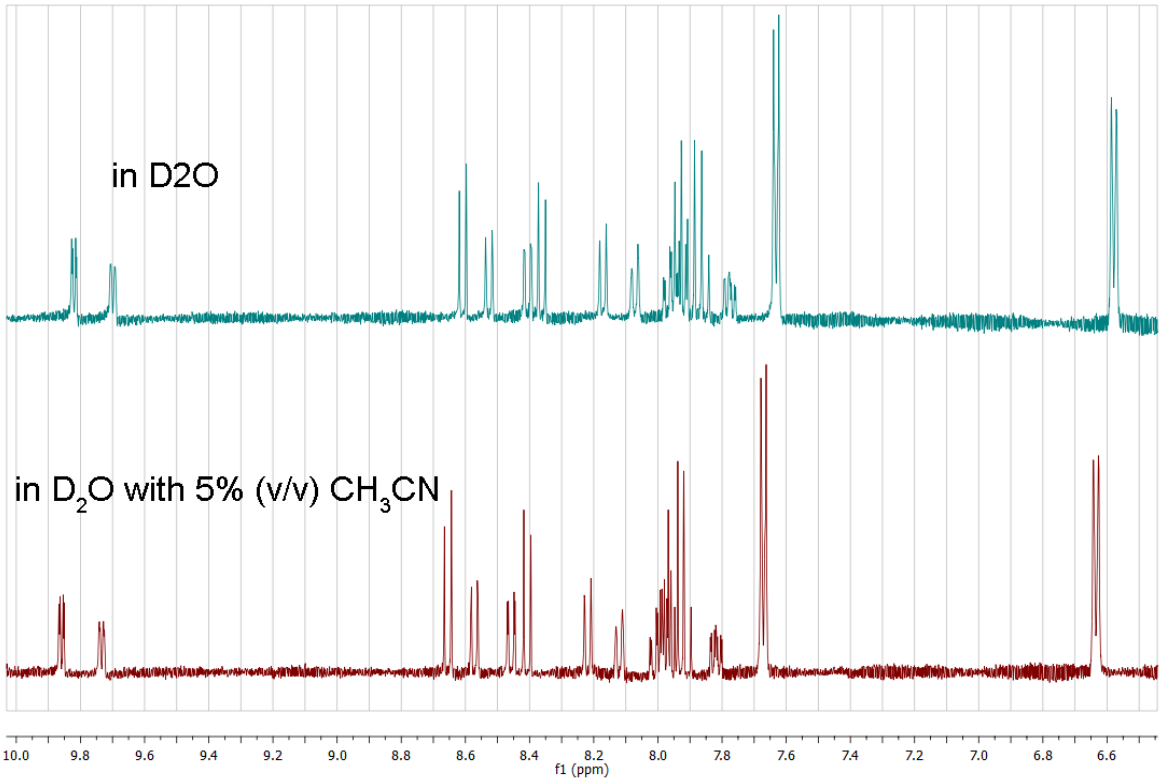

Figure S2. ^{1}H NMR of **6**$(Cl)_2$ in D_2O with or without acetonitrile (5%, v/v).

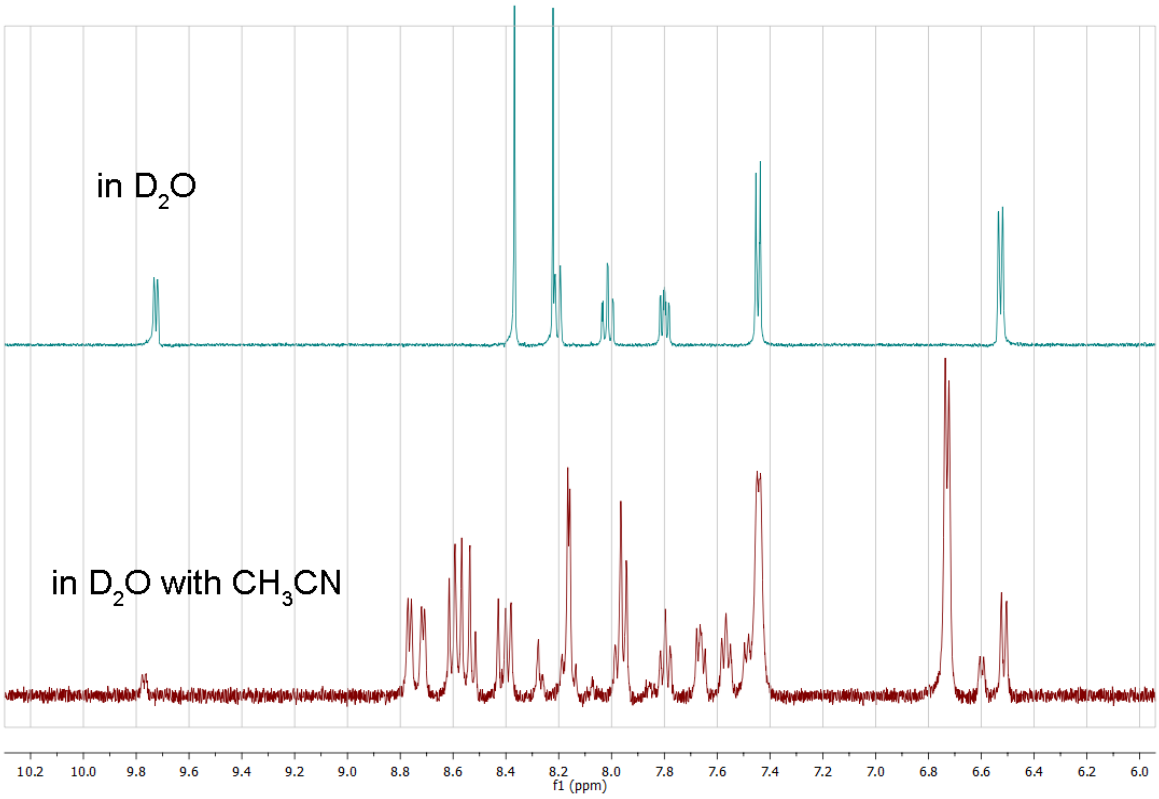

Figure S3. ^{1}H NMR of **3**$(Cl)_2$ in D_2O with or without acetonitrile (5%, v/v).

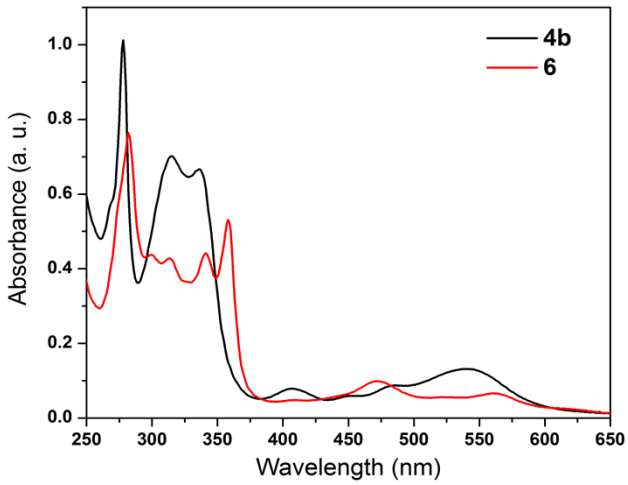

Figure S4. Electronic absorption spectra of complexes **4b**$(Cl)_2$ and **6**$(Cl)_2$ (2×10^{-5} M) in water at room temperature.

Table S1. Electronic absorption data for Ru^{II} complexes at room temperature.

Complexes	Absorbance λ_{max}, nm (log ε)
3$(PF_6)_2$[a]	259(4.71), 281(4.87), 313(4.78), 445(3.61), 479(3.67), 514(3.71), 580(3.81)
4a$(PF_6)_2$[b]	332(4.47), 423(3.73), 460(sh, 3.67), 488(3.83), 547(3.88), 592(sh, 3.58)
4b$(Cl)_2$[c]	278(4.69), 314(4.54), 336(4.52), 407(3.59), 484(sh, 3.63), 540(3.80)
5$(PF_6)_2$[b]	345(4.60), 405(3.47), 446(3.52), 471(3.76), 536(3.78)
6$(Cl)_2$[c]	282(4.58), 300(4.34), 313(4.33), 340(4.34), 358(4.43), 472(3.69), 564(3.51)

[a] Cited from ref 5a, measured in CH_2Cl_2. [b] Cited from ref 5b, measured in acetone; sh = shoulder. [c] This work, 2×10^{-5} M in water.

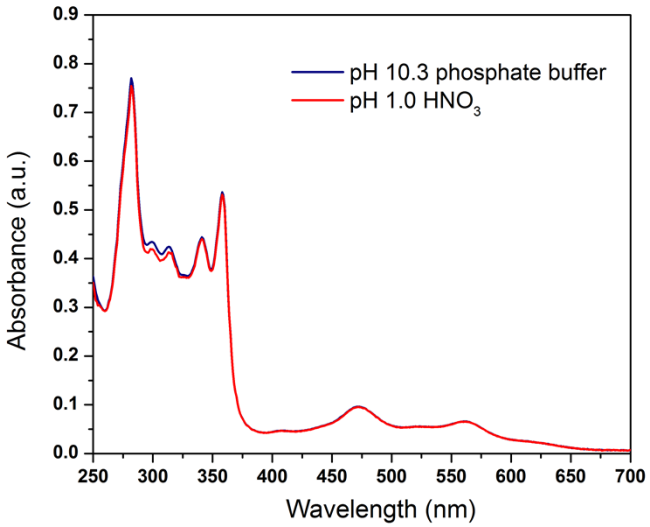

Figure S5. Electronic absorption spectra of complexes **6**$(Cl)_2$ (2 x 10^{-5} M) in HNO_3 (pH = 1) and phosphate buffer (pH = 10.3).

Table S2. Summary of the crystal data for **6**$(Cl)_2$.

formula	$C_{37.35}H_{42.46}Cl_2N_6O_{3.88}Ru$
weight	809.48
space group	P -1
a/Å	10.4996(4)
b/Å	13.3012(5)
c/Å	3.4802(6)
α/deg	80.434(2)
β/deg	82.981(2)
γ/deg	86.221(2)
V/Å^3	1840.52
Z	2
D_c/g cm^{-3}	1.461
T/K	123
F(000)	835
wavelength(MoKR)/Å	1.54178
refl. collected	8829
Goodness-of-fit on F^2	1.096
$R_1{}^a$ [$I > 2\sigma(I)$] (all)	0.0395
$wR_2{}^b$ [$I > 2\sigma(I)$] (all)	0.1039

^{a} $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; ^{b} $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

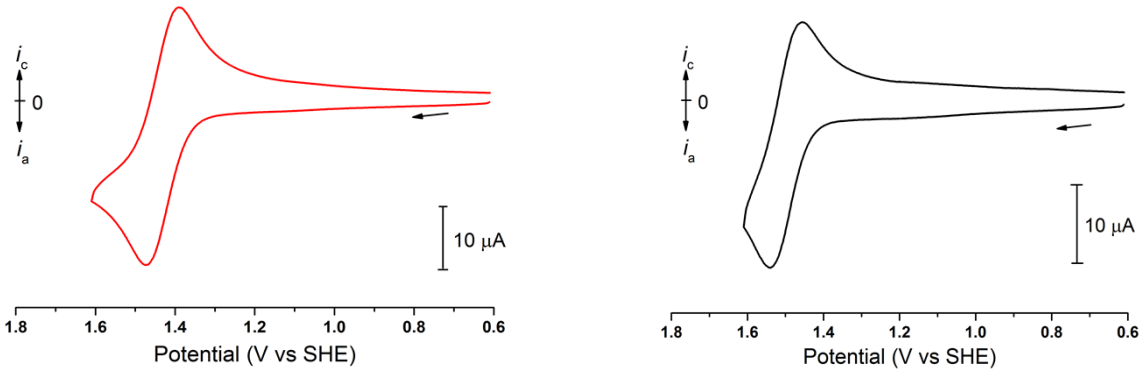

Figure S6. CV of **6**$(ClO_4)_2$ (1 mM, left) and **4b**$(PF_6)_2$ (1mM, right) in acetonitrile containing 0.1 M ^{n}Bu$_4$N(PF_6); glass carbon working electrode, scan rate = 100 mA/s.

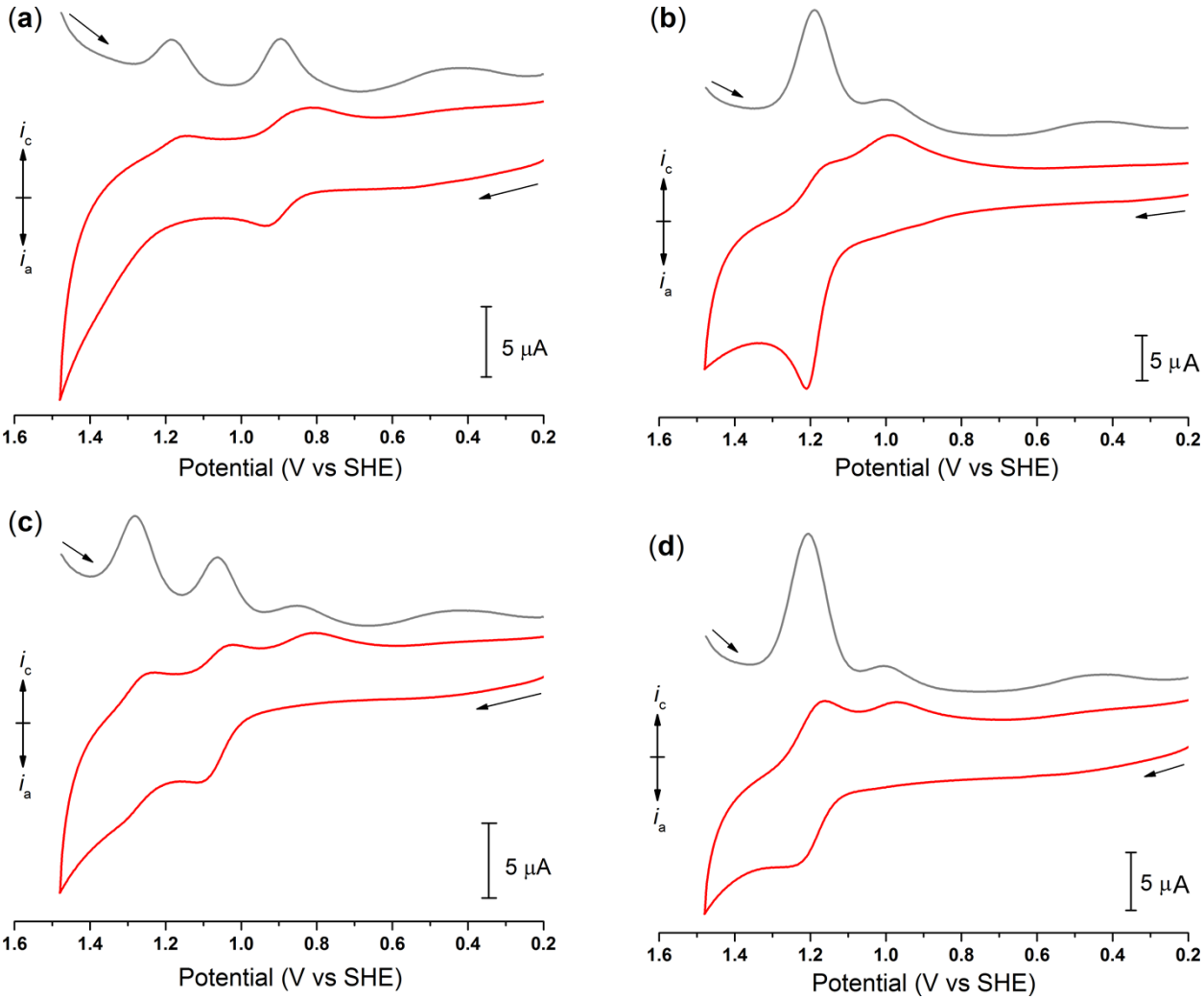

Figure S7. CV (red curve) and SW (grey curve) of **4a**$(PF_6)_2$ (0.25 mM, **a**), **4b**$(PF_6)_2$ (0.5 mM, **b**), **5**$(PF_6^-)_2$ (0.5 mM, **c**), and **6**$(OCl_4)_2$ (0.5 mM, **d**) in CF_3CH_2OH/HNO_3 (20/80, pH =1); glass carbon working electrode, scan rate = 100 mA/s.

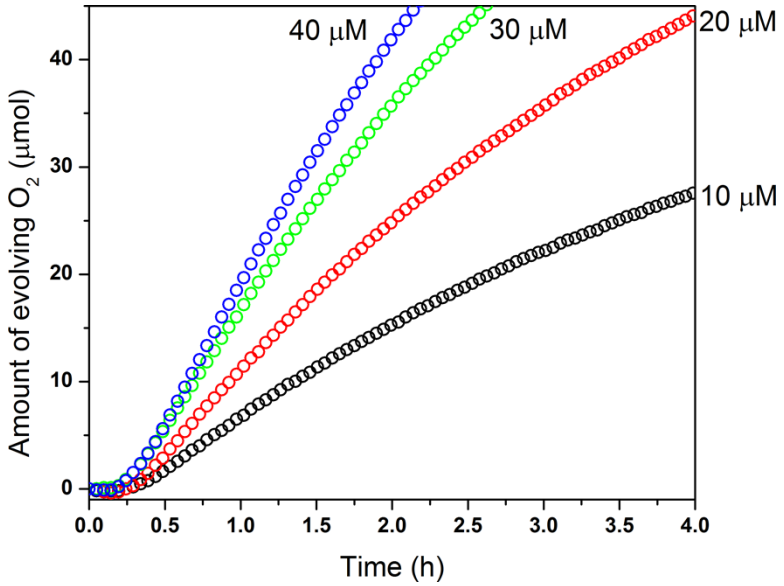

Figure S8. O_2 evolution vs time plots by **3** at various concentrations. Conditions: 0.2 M CAN in 10 mL HNO_3 (pH 1.0). Only one data point of every 35 recorded points is shown for clarity.

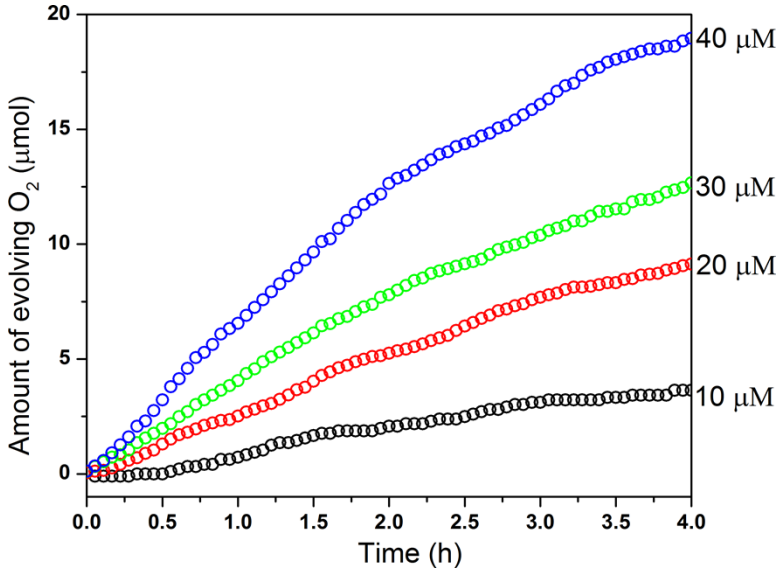

Figure S9. O_2 evolution vs time plots by **4a** at various concentrations. Conditions: 0.2 M CAN in 10 mL HNO_3 (pH 1.0). Only one data point of every 35 recorded points is shown for clarity.

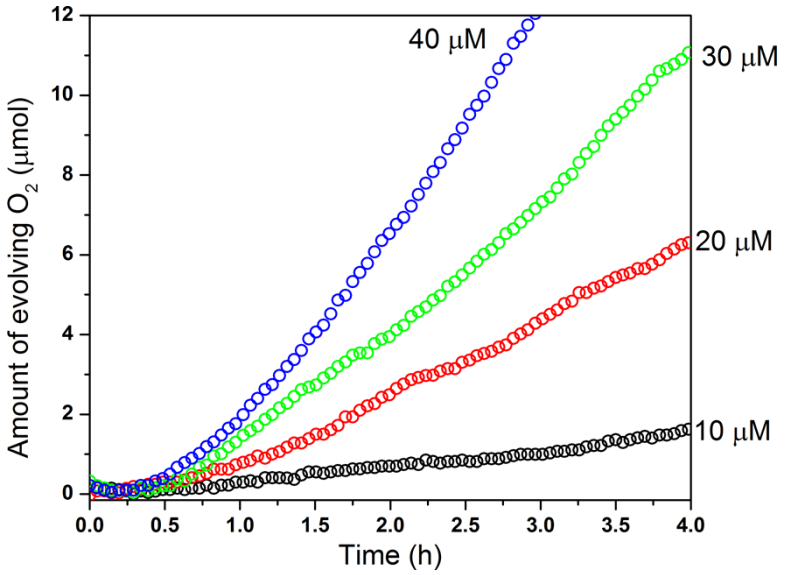

Figure S10. O_2 evolution vs time plots by **4b** at various concentrations. Conditions: 0.2 M CAN in 10 mL HNO_3 (pH 1.0). Only one data point of every 35 recorded points is shown for clarity.

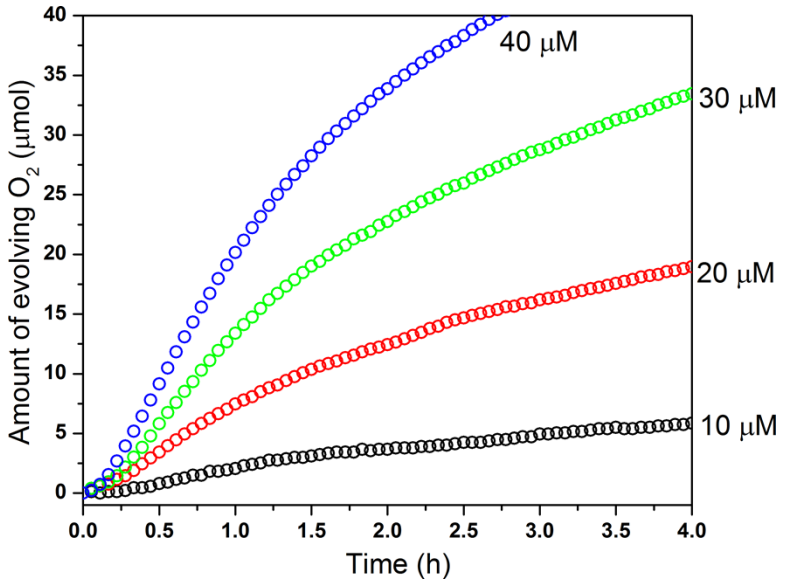

Figure S11. O_2 evolution vs time plots by **5** at various concentrations. Conditions: 0.2 M CAN in 10 mL HNO_3 (pH 1.0). Only one data point of every 35 recorded points is shown for clarity.

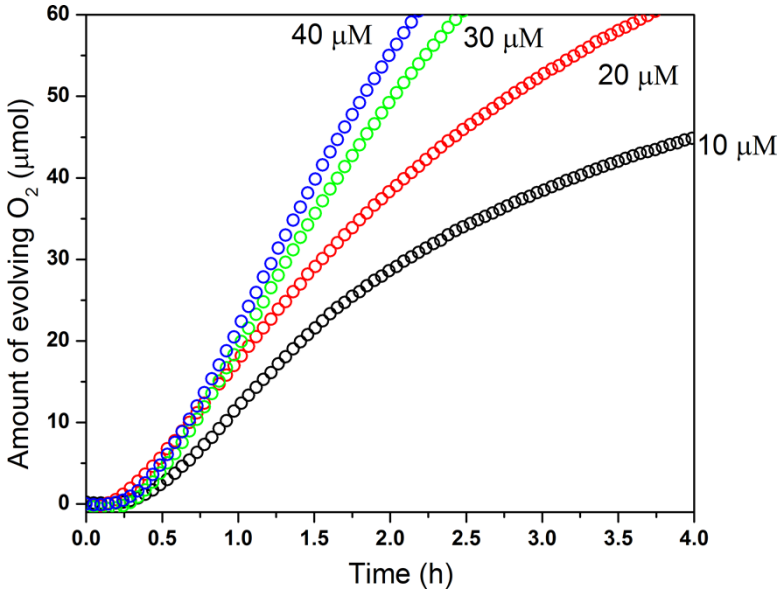

Figure S12. O_2 evolution vs time plots by **6** at various concentrations. Conditions: 0.2 M CAN in 10 mL HNO_3 (pH 1.0). Only one data point of every 35 recorded points is shown for clarity.

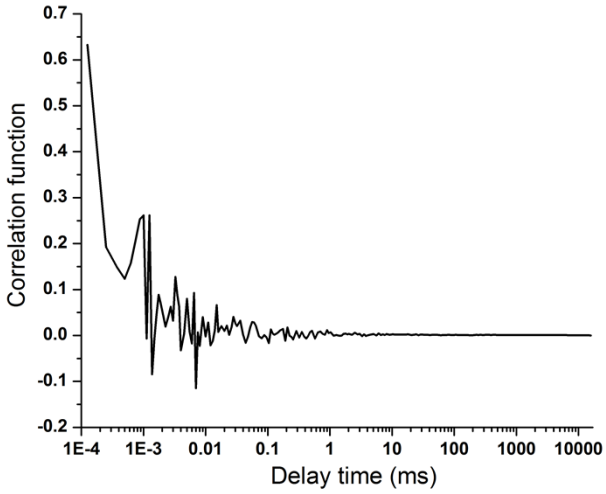

Figure S13. Raw spectrum of dynamic light scatting (DLS) showing no peak or spike corresponding the presence of particles were detected. Sample contains **3** (25 μM) and CAN (10 mM) in pH = 1.0 HNO_3, mixed for 1 h before measurement.

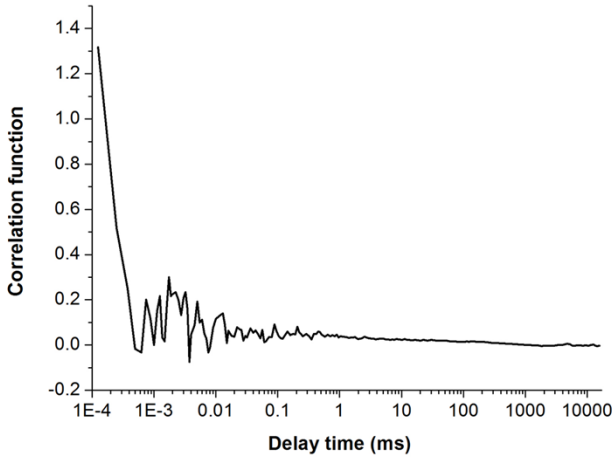

Figure S14. Raw spectrum of dynamic light scatting (DLS) showing no peak or spike corresponding the presence of particles were detected. Note the fluctuation was due to dust. Sample contains **6** (5 μM), $[Ru(bpy)_3]Cl_2$ (0.3 mM) and $Na_2S_2O_8$ (10 mM) in $Na_2SiF_6/NaHCO_3$ buffer (5 mL, pH 6.8, 0.01 M of Na_2SiF_6) and was irradiated for 10 min before measurement.

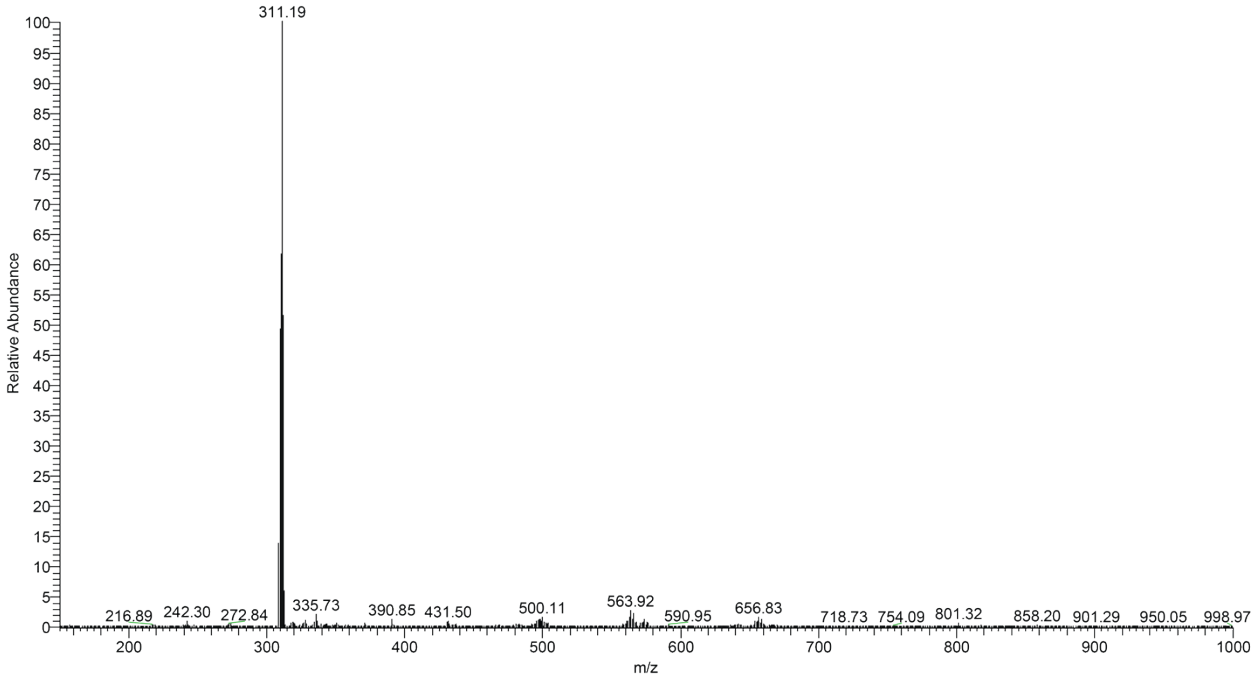

Figure S15. Mass spectra of **6** (in water).

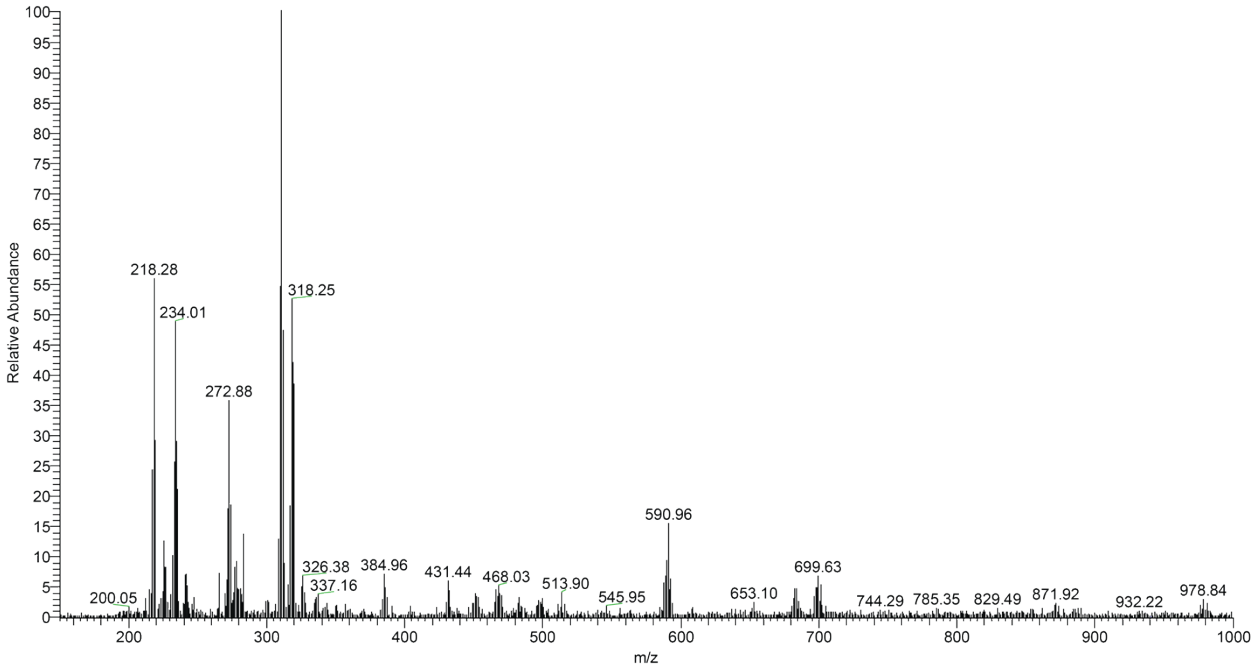

Figure S16. Mass spectra of **6** (in water) after treated with 4 equivalent of CAN.