Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

A ruthenium water oxidation catalyst containing a bipyridine glycoluril ligand

*Vishwanath Mane, Avinash Kumbhar * and Randolph Thummel*

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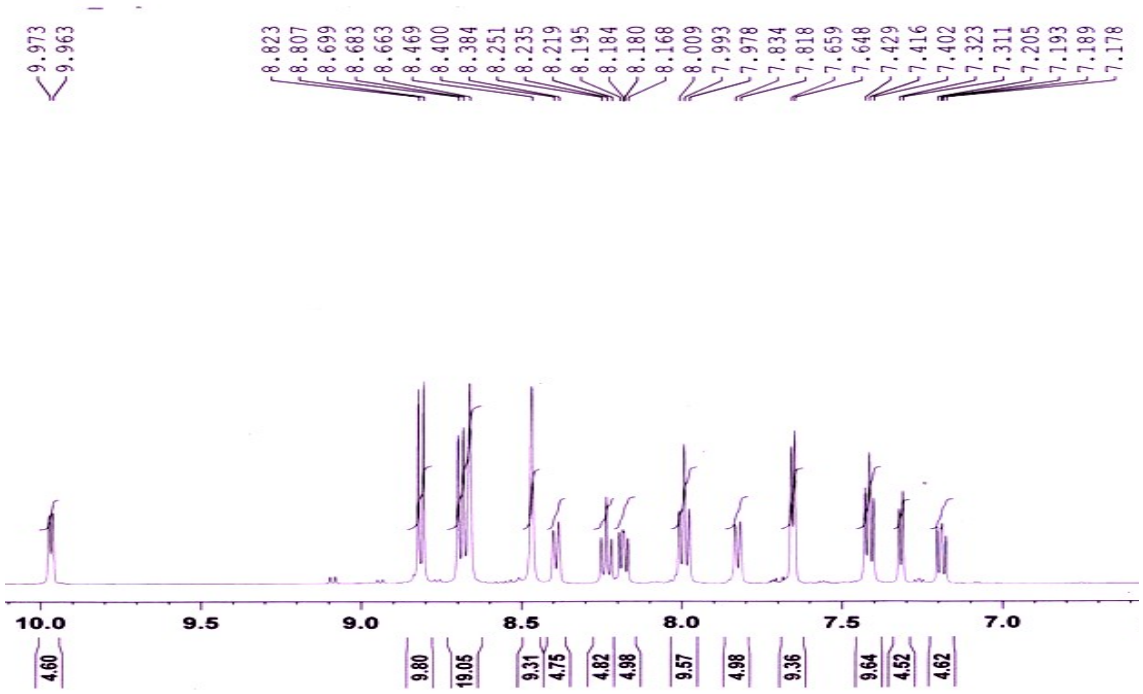


Figure S1.[1]H NMR of complex **9a** in DMSO-d_6

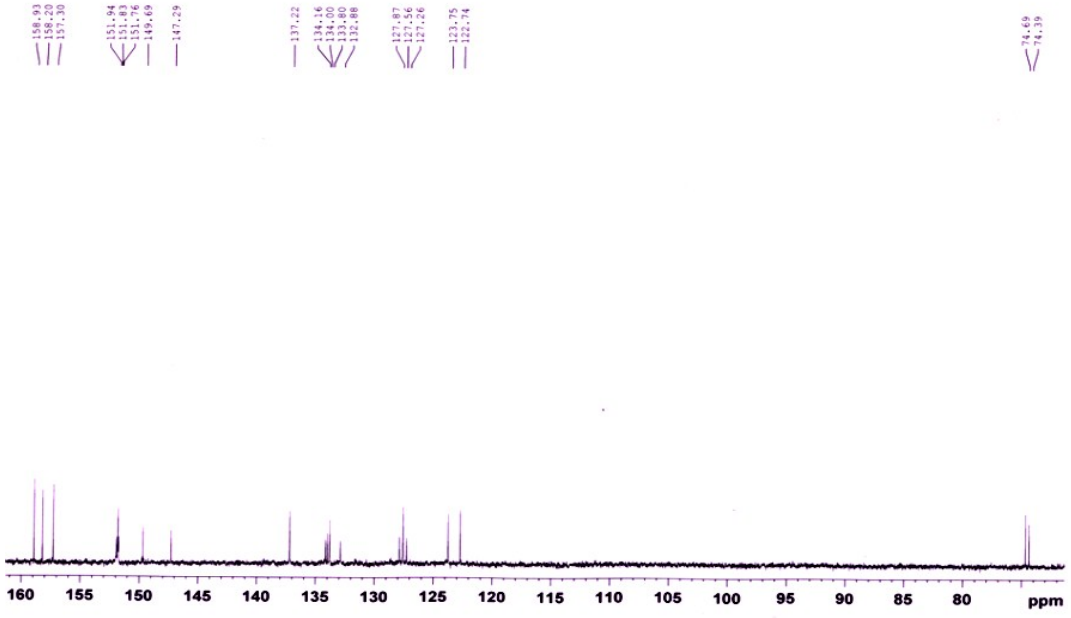


Figure S2.[13]C-NMR of complex **9a** in DMSO-d_6

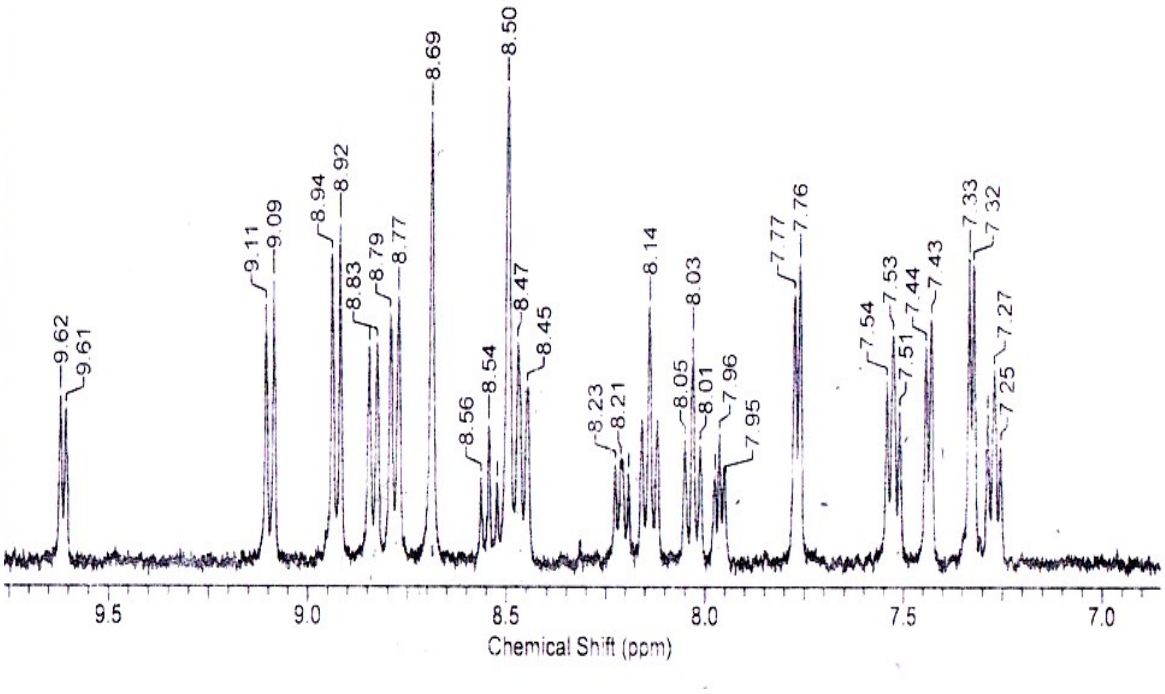
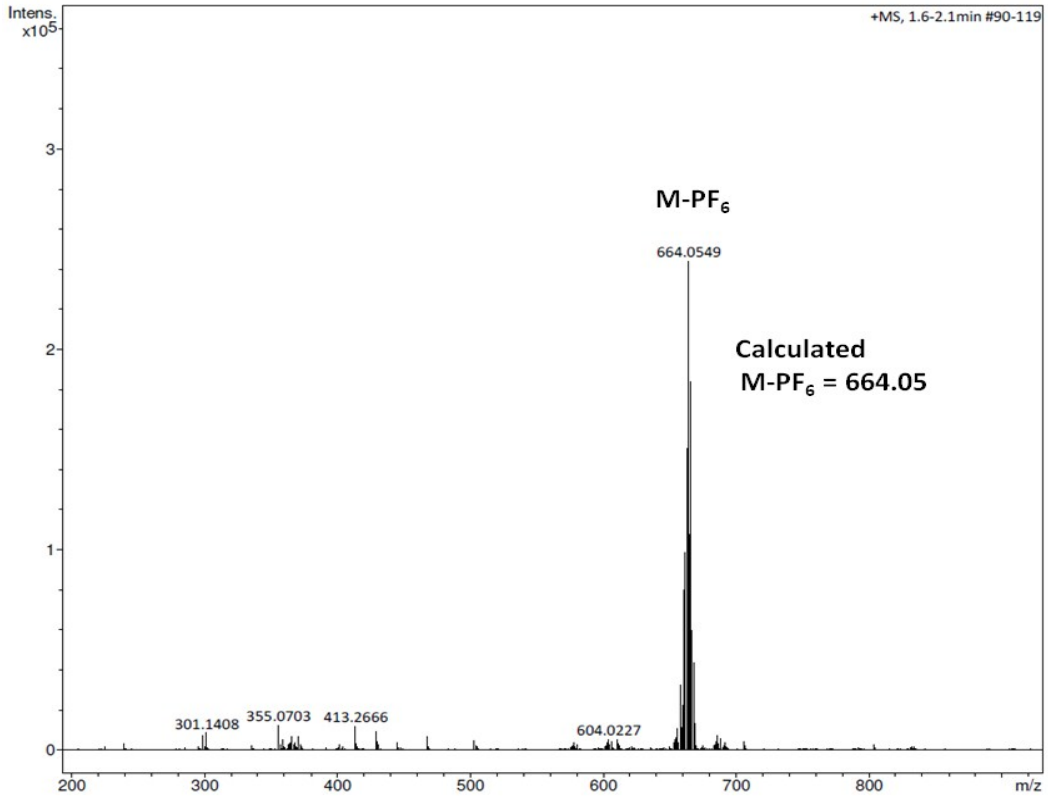


Figure S3. ^{1}H NMR of complex **9b** in DMSO-d_6

a)



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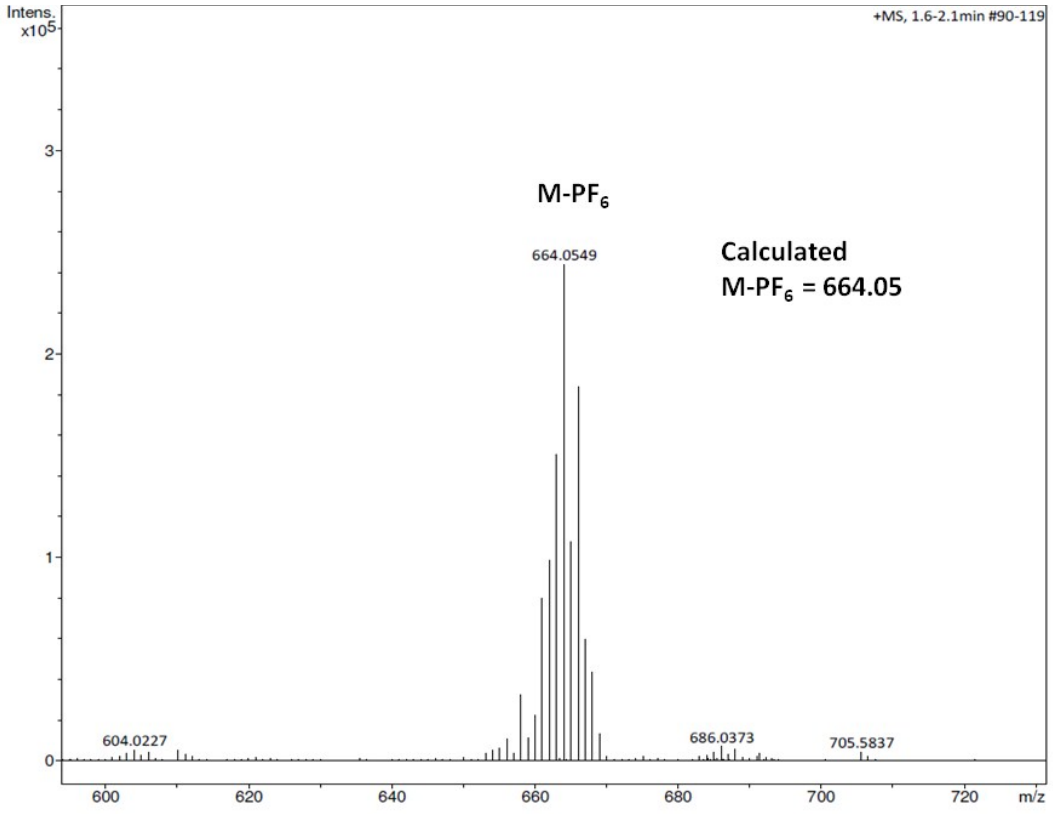
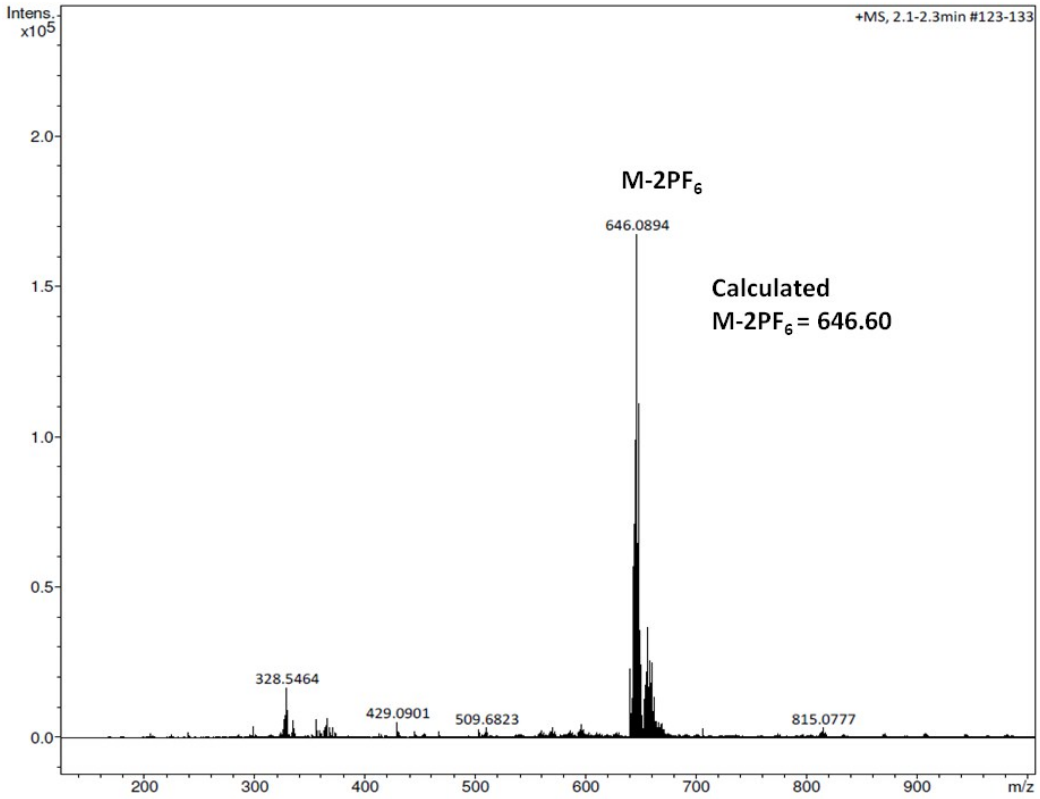
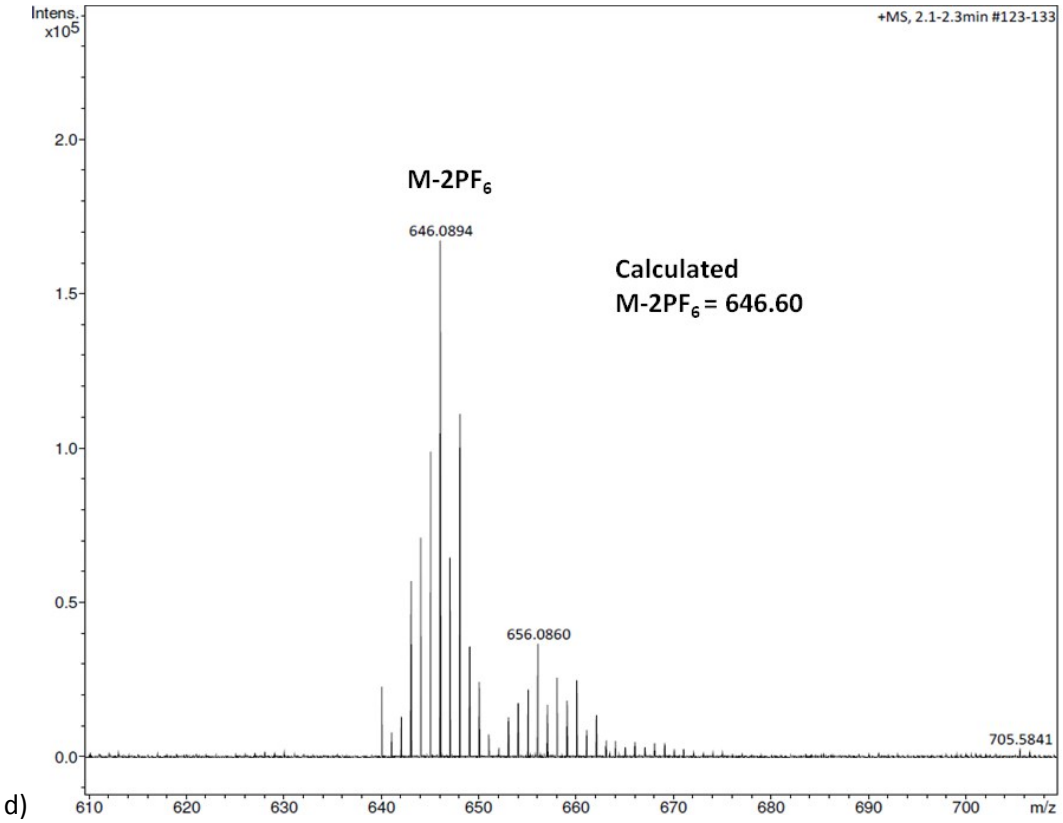


Figure S4.ESI-MS of a) and b) complex **9a** in methanol

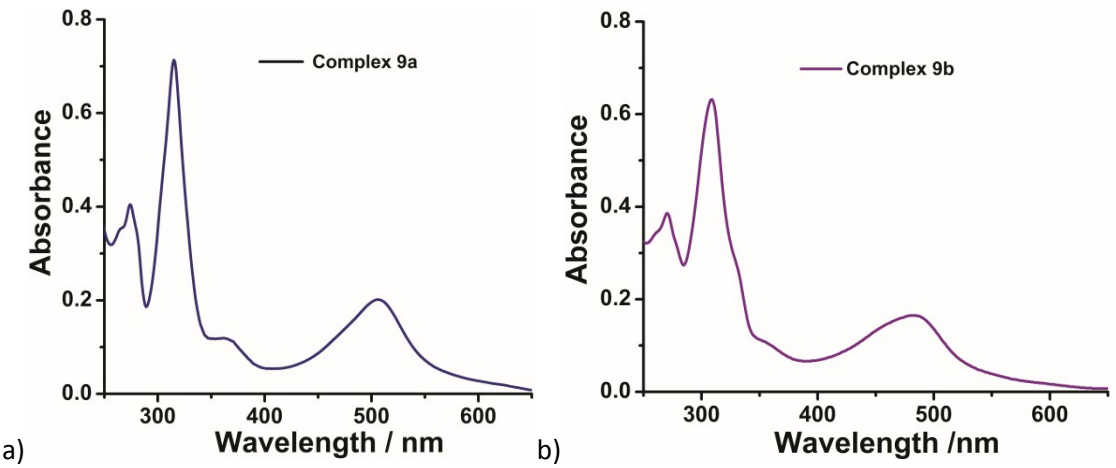
c)





d)

Figure S5.ESI-MS of c) and d) complex**9b** in methanol



a) b)

Figure S6.Uv-Visible spectra of a) complex **9a** (20μM) and b) complex **9b** (20μM) in water at 25 ˚C

Table S1. Photophysical properties of complex **9a** and **9b**

Complex	MLCT	Ligand based transition	
	nm (L mol^{-1} cm^{-1})	nm (L mol^{-1} cm^{-1})	
9a	506 (10125)	315 (35600)	274 (20000)
9b	483 (8255)	309 (31640)	270 (19260)

Determination of *p*K$_a$ value

The acid/base spectrophotometric titration was performed in B. R. Buffer to determine the *p*K$_a$ values of **9b** at room temperature. The pH value of the 0.1 mM **9b** buffer solution was adjusted by drop wise addition of concentrated NaOH solution. The *p*K$_a$ values were obtained by plotting the absorbance versus pH profile at specific wavelength, fitted with equation (1). In which absorbance of the starting complex is A_o and A_∞ is the absorbance of the final product. From the average absorbance values A_o and A_∞ of the fitted curve, the *p*K$_a$ value was determined as the corresponding pH value.[1]

$$A = A_o + K_a[\frac{A_\infty - A_o}{K_a + 10 - pH}] \quad (1)$$

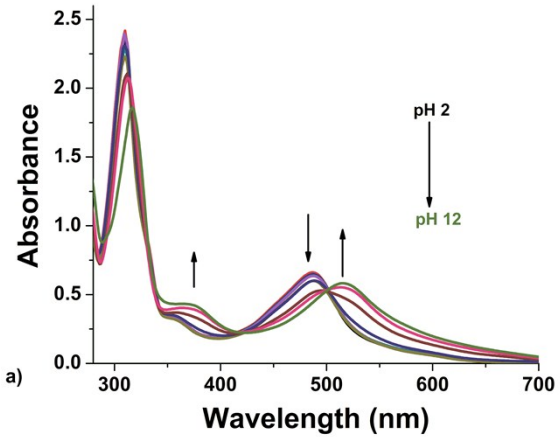


Figure S7. Absorption spectra of aqueous solutions of complex **9b** in B. R. buffer solution at a) pH 2-12 at 25 °C

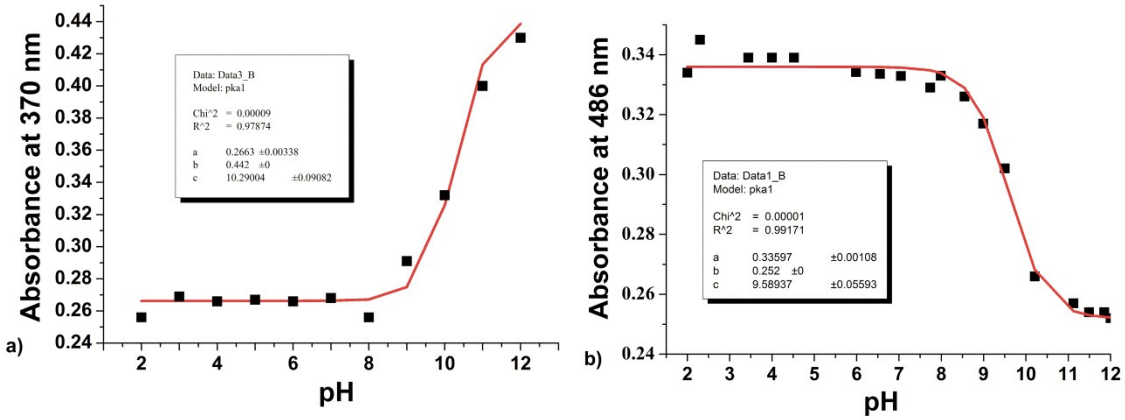


Figure S8. The dependence of the absorbance of complex **9b** at a) 370 nm and b) 486 nm on pH 2-12 at 25 ˚C

Table S2. Crystallographic collection and refinement Data

Parameters	Complex 9c	Complex 9d
Empirical formula	C29 H31 Cl2 N9 O7 Ru	C31 H27 F6 N9 O11 Ru S2
Formula weight	789.60	980.80
Temperature	250(2) K	296(2) K
Wavelength	1.54178 Å	1.54178 Å
Crystal system	Orthorhombic	Orthorhombic
Space group	P b c a	P c a 21
Unit cell dimensions	a = 14.1145(2) Å; α= 90°	a = 18.8901(8) Å; α= 90°
	b = 16.1624(2) Å; β= 90°	b = 8.5910(4) Å; β= 90°
	c = 28.6960(3) Å; γ = 90°	c = 22.5655(10) Å; γ = 90°
Volume	6546.25(14) $Å^3$	3662.0(3) $Å^3$
Z	8	4
Density (calculated)	1.602 Mg/m^3	1.779 Mg/m^3
Absorption coefficient	5.902 mm^{-1}	5.476 mm^{-1}
F(000)	3216	1976
Crystal size	0.36 x 0.28 x 0.07 mm^3	0.394 x 0.124 x 0.072 mm^3
Theta range for data collection	3.080 to 68.226°.	3.918 to 68.298°.
Index ranges	-9<=h<=16, -19<=k<=19, -33<=l<=34	-22<=h<=22, -10<=k<=9, -27<=l<=27
Reflections collected	21904	35302
Independent reflections	5820 [R(int) = 0.2129]	6538 [R(int) = 0.0578]
Completeness to theta = 67.679°	97.7 %	99.6 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.662 and 0.172	0.674 and 0.465
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5820 / 0 / 442	6538 / 31 / 593
Goodness-of-fit on F^2	1.207	1.017
Final R indices [I>2sigma(I)]	R1 = 0.1104, wR2 = 0.2809	R1 = 0.0333, wR2 = 0.0848
R indices (all data)	R1 = 0.2675, wR2 = 0.3908	R1 = 0.0347, wR2 = 0.0860
Absolute Structure parameter	n/a	0.089(12)
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	1.391 and -2.868 $e.Å^{-3}$	0.616 and -0.713 $e.Å^{-3}$

Table S3. Selective bond distances [Å] of Complex **9c**

Ru(1)-N(2)	1.970(10)
Ru(1)-N(5)	2.007(10)
Ru(1)-N(3)	2.044(10)
Ru(1)-N(1)	2.055(10)
Ru(1)-N(4)	2.092(9)
Ru(1)-Cl(1)	2.429(5)
O(1)-C(28)	1.247(19)
O(2)-C(29)	1.241(19)
N(1)-C(1)	1.351(16)
N(1)-C(5)	1.371(17)
N(2)-C(10)	1.343(16)
N(2)-C(6)	1.368(16)
N(3)-C(15)	1.375(16)
N(3)-C(11)	1.382(16)
N(4)-C(16)	1.339(17)
N(4)-C(27)	1.352(17)
N(5)-C(17)	1.375(15)
N(5)-C(18)	1.381(16)
N(6)-C(28)	1.35(2)
N(6)-C(23)	1.463(16)
N(6)-H(6)	0.8700
N(7)-C(28)	1.337(18)
N(7)-C(22)	1.452(18)
N(7)-H(7A)	0.8700
N(8)-C(29)	1.371(19)
N(8)-C(22)	1.453(17)
N(8)-H(8)	0.8700
N(9)-C(29)	1.33(2)
N(9)-C(23)	1.446(16)
N(9)-H(9A)	0.8700

Table S4.Selective bond angle [°] of Complex **9c**

N(2)-Ru(1)-N(5)	96.9(4)
N(2)-Ru(1)-N(3)	78.6(4)
N(5)-Ru(1)-N(3)	91.5(4)

N(2)-Ru(1)-N(1)	79.7(4)
N(5)-Ru(1)-N(1)	90.3(4)
N(3)-Ru(1)-N(1)	158.3(4)
N(2)-Ru(1)-N(4)	174.9(5)
N(5)-Ru(1)-N(4)	78.4(4)
N(3)-Ru(1)-N(4)	103.4(4)
N(1)-Ru(1)-N(4)	98.1(4)
N(2)-Ru(1)-Cl(1)	89.2(4)
N(5)-Ru(1)-Cl(1)	173.9(3)
N(3)-Ru(1)-Cl(1)	89.5(3)
N(1)-Ru(1)-Cl(1)	91.1(3)
N(4)-Ru(1)-Cl(1)	95.5(4)
C(1)-N(1)-C(5)	115.4(13)
C(1)-N(1)-Ru(1)	129.7(10)
C(5)-N(1)-Ru(1)	114.9(9)
C(10)-N(2)-C(6)	124.0(11)
C(10)-N(2)-Ru(1)	118.7(9)
C(6)-N(2)-Ru(1)	117.3(9)
C(15)-N(3)-C(11)	116.5(12)
C(15)-N(3)-Ru(1)	128.8(9)
C(11)-N(3)-Ru(1)	114.8(9)
C(16)-N(4)-C(27)	119.6(12)
C(16)-N(4)-Ru(1)	114.3(10)
C(27)-N(4)-Ru(1)	126.0(10)
C(17)-N(5)-C(18)	113.4(12)
C(17)-N(5)-Ru(1)	117.5(10)
C(18)-N(5)-Ru(1)	129.1(8)
C(28)-N(6)-C(23)	111.4(13)
C(28)-N(6)-H(6)	124.3
C(23)-N(6)-H(6)	124.3
C(28)-N(7)-C(22)	112.1(15)
C(28)-N(7)-H(7A)	124.0
C(22)-N(7)-H(7A)	124.0
C(29)-N(8)-C(22)	111.8(15)
C(29)-N(8)-H(8)	124.1
C(22)-N(8)-H(8)	124.1

C(29)-N(9)-C(23)	111.5(14)
C(29)-N(9)-H(9A)	124.3
C(23)-N(9)-H(9A)	124.3
N(1)-C(1)-C(2)	123.2(16)
N(1)-C(1)-H(1)	118.4
C(2)-C(1)-H(1)	118.4
C(3)-C(2)-C(1)	119.7(17)
C(3)-C(2)-H(2)	120.1
C(1)-C(2)-H(2)	120.1
C(2)-C(3)-C(4)	119.5(16)
C(2)-C(3)-H(3)	120.3
C(4)-C(3)-H(3)	120.3
C(3)-C(4)-C(5)	119.2(15)
C(3)-C(4)-H(4)	120.4
C(5)-C(4)-H(4)	120.4
N(1)-C(5)-C(4)	123.0(15)
N(1)-C(5)-C(6)	113.5(12)
C(4)-C(5)-C(6)	123.5(14)
N(2)-C(6)-C(7)	118.3(14)
N(2)-C(6)-C(5)	114.6(11)
C(7)-C(6)-C(5)	127.1(14)
C(6)-C(7)-C(8)	119.0(14)
C(6)-C(7)-H(7)	120.5
C(8)-C(7)-H(7)	120.5
C(9)-C(8)-C(7)	120.3(12)
C(9)-C(8)-H(8A)	119.8
C(7)-C(8)-H(8A)	119.8
C(8)-C(9)-C(10)	120.5(13)
C(8)-C(9)-H(9)	119.8

Table S5.Selective bond lengths [Å] of complex **9d**

Ru(1)-N(2)	1.982(4)
Ru(1)-N(5)	2.029(4)
Ru(1)-N(4)	2.067(4)
Ru(1)-N(1)	2.083(5)
Ru(1)-N(3)	2.090(5)
O(5)-H(5O)	0.91(3)

Ru(1)-N(2)	1.980(4)
Ru(1)-N(5)	2.027(4)
Ru(1)-N(4)	2.067(4)
Ru(1)-N(1)	2.083(5)
Ru(1)-N(3)	2.090(5)
Ru(1)-O(3)	2.125(4)
O(1)-C(28)	1.242(8)
O(2)-C(29)	1.213(9)
O(3)-H(3OA)	0.90(3)
O(3)-H(4OA)	0.90(3)
N(1)-C(1)	1.334(8)
N(1)-C(5)	1.367(7)
N(2)-C(10)	1.340(8)
N(2)-C(6)	1.348(8)
N(3)-C(15)	1.339(8)
N(3)-C(11)	1.359(7)
N(4)-C(27)	1.342(7)
N(4)-C(16)	1.352(7)
N(5)-C(18)	1.349(7)
N(5)-C(17)	1.357(6)
N(6)-C(28)	1.349(8)
N(6)-C(23)	1.437(8)
N(6)-H(6)	0.8600
N(7)-C(28)	1.353(9)
N(7)-C(22)	1.446(7)
N(7)-H(7N)	0.8600
N(8)-C(29)	1.359(9)
N(8)-C(23)	1.450(8)
N(8)-H(8N)	0.8600
N(9)-C(29)	1.368(9)
N(9)-C(22)	1.443(9)
N(9)-H(9N)	0.8600

Table S6. Selective bond angle [°] of complex **9d**

H(6O)-O(5)-H(5O)	94(9)

N(2)-Ru(1)-N(5)	97.18(17)
N(2)-Ru(1)-N(4)	176.85(17)
N(5)-Ru(1)-N(4)	79.67(16)
N(2)-Ru(1)-N(1)	79.39(19)
N(5)-Ru(1)-N(1)	86.08(18)
N(4)-Ru(1)-N(1)	100.21(18)
N(2)-Ru(1)-N(3)	78.77(19)
N(5)-Ru(1)-N(3)	95.86(18)
N(4)-Ru(1)-N(3)	101.55(18)
N(1)-Ru(1)-N(3)	158.15(18)
N(2)-Ru(1)-O(3)	92.90(17)
N(5)-Ru(1)-O(3)	169.44(17)
N(4)-Ru(1)-O(3)	90.24(17)
N(1)-Ru(1)-O(3)	92.72(17)
N(3)-Ru(1)-O(3)	89.17(18)
Ru(1)-O(3)-H(3OA)	168(7)
Ru(1)-O(3)-H(4OA)	114(7)
H(3OA)-O(3)-H(4OA)	77(9)
C(1)-N(1)-C(5)	119.4(5)
C(1)-N(1)-Ru(1)	127.3(4)
C(5)-N(1)-Ru(1)	112.7(4)
C(10)-N(2)-C(6)	123.0(5)
C(10)-N(2)-Ru(1)	119.1(4)
C(6)-N(2)-Ru(1)	117.9(4)
C(15)-N(3)-C(11)	118.7(5)
C(15)-N(3)-Ru(1)	128.1(4)
C(11)-N(3)-Ru(1)	113.2(4)
C(27)-N(4)-C(16)	118.1(4)
C(27)-N(4)-Ru(1)	127.6(4)
C(16)-N(4)-Ru(1)	114.2(3)
C(18)-N(5)-C(17)	117.8(4)
C(18)-N(5)-Ru(1)	126.8(4)
C(17)-N(5)-Ru(1)	115.0(3)
C(28)-N(6)-C(23)	111.9(5)
C(28)-N(6)-H(6)	124.1
C(23)-N(6)-H(6)	124.1

C(28)-N(7)-C(22)	112.7(5)
C(28)-N(7)-H(7N)	123.7
C(22)-N(7)-H(7N)	123.7
C(29)-N(8)-C(23)	113.8(5)
C(29)-N(8)-H(8N)	123.1
C(23)-N(8)-H(8N)	123.1
C(29)-N(9)-C(22)	112.6(5)
C(29)-N(9)-H(9N)	123.7
C(22)-N(9)-H(9N)	123.7
N(1)-C(1)-C(2)	121.5(6)
N(1)-C(1)-H(1)	119.2
C(2)-C(1)-H(1)	119.2
C(3)-C(2)-C(1)	119.3(7)
C(3)-C(2)-H(2)	120.3
C(1)-C(2)-H(2)	120.3
C(2)-C(3)-C(4)	119.7(7)
C(2)-C(3)-H(3A)	120.2
C(4)-C(3)-H(3A)	120.2
C(3)-C(4)-C(5)	119.6(7)
C(3)-C(4)-H(4)	120.2
C(5)-C(4)-H(4)	120.2
N(1)-C(5)-C(4)	120.3(6)
N(1)-C(5)-C(6)	115.7(5)
C(4)-C(5)-C(6)	123.9(6)
N(2)-C(6)-C(7)	118.5(6)
N(2)-C(6)-C(5)	114.0(5)
C(7)-C(6)-C(5)	127.4(6)
C(8)-C(7)-C(6)	119.0(6)
C(8)-C(7)-H(5N)	120.5
C(6)-C(7)-H(5N)	120.5
C(9)-C(8)-C(7)	120.7(6)
C(9)-C(8)-H(3N)	119.7
C(7)-C(8)-H(3N)	119.7
C(8)-C(9)-C(10)	118.9(6)

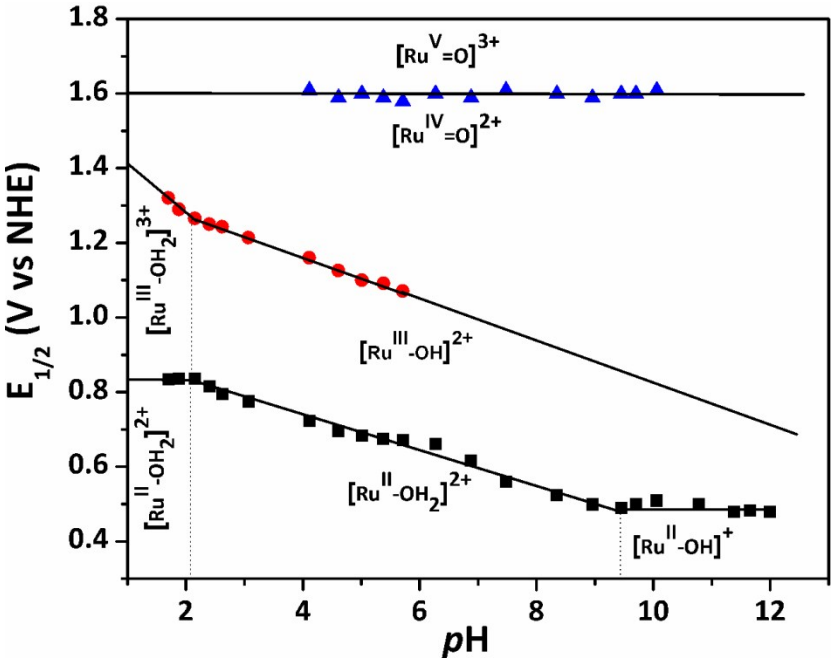


Figure S9. Pourbiax diagram for **9b** in aqueous B. R. Buffer solution (10 % Acetonitrile). The solid black lines indicate trends of redox potentials ($E_{1/2}$) depending on *p*H Values. The blue triangles, red circles and black squares are observed Ru^{V}/Ru^{IV}, Ru^{IV}/Ru^{III} and Ru^{III}/Ru^{II} redox couples respectively.

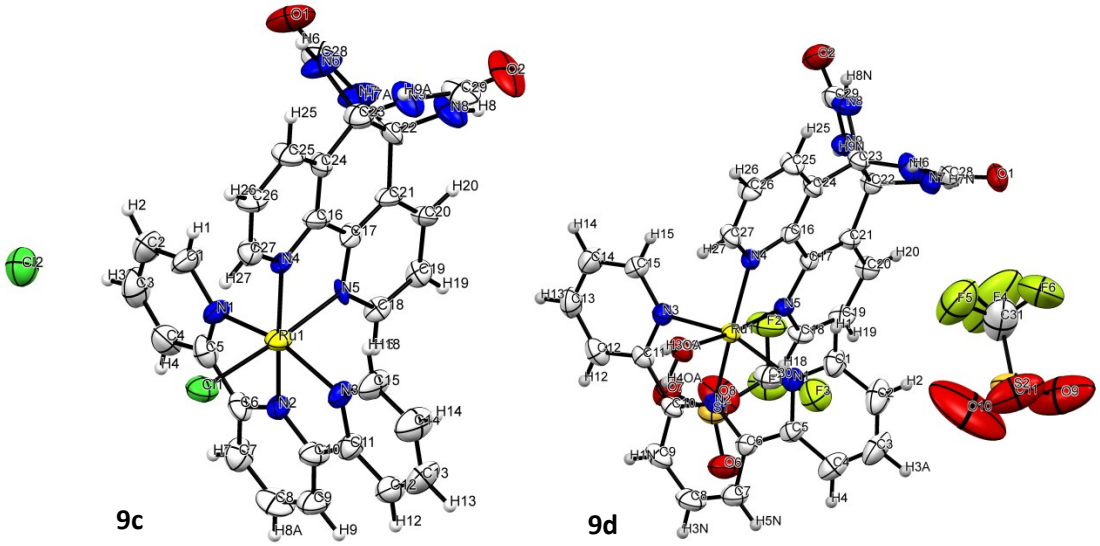


Figure S10. Crystal structure of **9c** and **9d** with anions Cl^{-} and CF_3SO^{3-}respectively

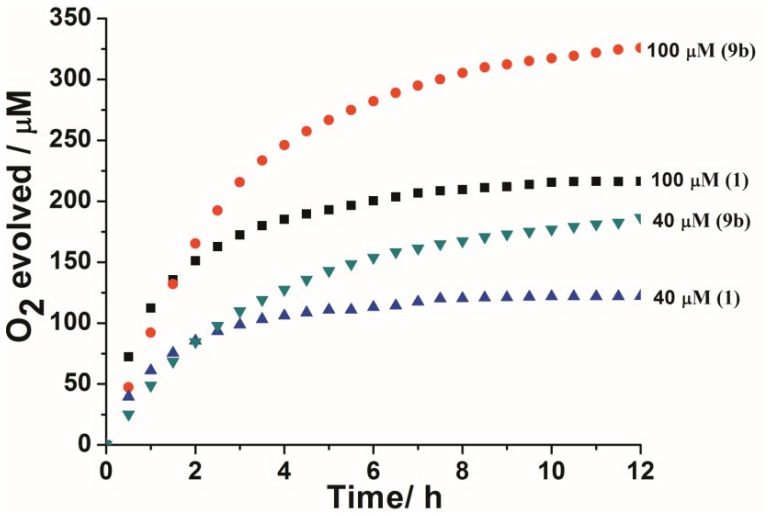


Figure S11. Comparative oxygen evolution of complexes **9b** and **1** at pH 1 at 25 ^{o}C

References:

1. J. Patel, K. Majee, E. Ahamad, B. Das and S. K. Padhi, *Eur. J. Inorg. Chem.* 2017, 160-171