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

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Two monomeric ruthenium molecular catalysts for water oxidation have been prepared, both of them show high activities in pH 1.0 aqueous solutions, with an initial rate of over 1000 turnover s^{-1} by complex 1, and a turnover number of more than 100 000 by complex 2.

Splitting water into dioxygen and dihydrogen driven by visible light is a promising, sustainable method to convert solar energy to chemical energy.[1-3] This process consists of two half reactions: (1) water oxidation [$2H_2O \rightarrow O_2 + 4e^- + 4H^+$, $E = 1.23 - 0.059 \times pH$ V vs. normal hydrogen electrode (NHE)], and (2) proton reduction ($2H^+ + 2e^- \rightarrow H_2$, $E = -0.059 \times pH$ V vs. NHE).[4] Water oxidation has been considered as the key step of water splitting, which involves the release of 4 electrons and 4 protons.

Since the report of "blue dimer" (*cis,cis*-[(bpy)$_2$(H$_2$O)Ru^{III}ORu^{III}(OH$_2$)(bpy)$_2$]$^{4+}$, bpy = 2,2′-bipyridine) as molecular water oxidation catalyst by Meyer group,[5] significant progresses have been made on the development of Ru-based water oxidation catalysts (WOCs), thanks to their high stability and suitability for detailed mechanistic investigations on the water oxidation reaction. A handful polypyridyl Ru complexes have been reported recent years as molecular water oxidation catalysts by the research groups of Meyer,[6, 7] Thummel,[8, 9] Berlinguette,[10, 11] Llobet[12-16], Sakai,[17, 18] and others,[19-23] and the catalytic pathways of these catalysts have been well studied by spectroscopic techniques and electrochemical methods. However, turnover frequencies of these reported molecular catalysts are much lower than that of the natural oxygen evolving complex (OEC) in the photosystem II.[24]

In 2009, our research group reported a mononuclear Ru complex [Ru^{II}(bda)(pic)$_2$] (H$_2$bda = 2,2′-bipyridine-6,6′-dicarboxylic acid, pic = 4-picoline) containing carboxylate groups in the ligand that showed a high catalytic activity for water oxidation.[25, 26] On the basis of the mechanistic studies of this Ru-bda complex, isoquinoline (isoq) and phthalazine (ptz), which have large π systems, were introduced into the Ru-bda catalysts as axial ligands instead of 4-

picoline.[27, 28] This small change caused a dramatic increase of the water oxidation catalytic activity with the initial turnover frequency (TOF) reaching up to 300 s^{-1} and turnover number (TON) up to 50 000. Another interesting finding is that both hydrophobic effect and electron withdrawing effect enhance the activities of the catalysts.[29]
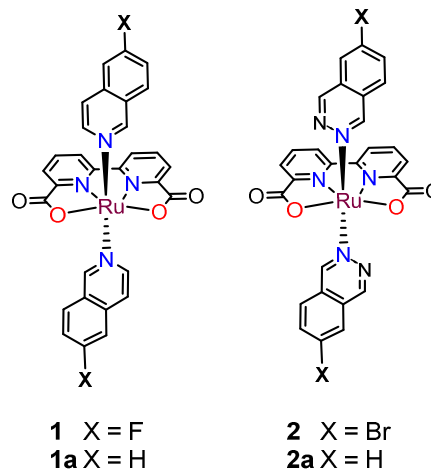

Fig 1. The chemical structures of Ru(II) complexes **1** and **2** together with the earlier reported complexes **1a** and **2a** as references.

On the basis of our earlier work, we reasoned that the introduction of halogen substitutes on the isoquinoline/phthalazine might further improve the performance of superior active catalysts [Ru^{II}(bda)(isoq)$_2$]/[Ru^{II}(bda)(ptz)$_2$]. We have now synthesized two new Ru-bda catalysts (**1** and **2**, Fig 1) with axial ligands bearing halogen substitutes and referenced to those non-halogen analogues (**1a** and **2a**), in order to develop more efficient and robust water oxidation catalysts. The location of the halogen substitutes on the axial ligands was selected far from the coordination sites in order to minimize the electronic effect (induction effect). In addition, the

present work also outlines how a co-solvent significantly influences the water oxidation performance.

The synthesis of these Ru^{II} complexes followed the well described procedures reported earlier from our lab.[27] All these complexes have been characterized unambiguously by ^{1}H NMR, elemental analysis and MS. Taking complex **1** for example, ^{1}H NMR (Fig S1) shows three peaks at 8.67 (d, 2H), 8.04 (d, 2H) and 7. 92 (t, 2H) ppm representing the proton resonances of bda^{2-} ligand; the other signals at 8.65(s, 2H), 7.98 (s, 2H), 7.61 (d, 2H), 7.57 (d, 2H) 7.51(dd, 2H) and 7.45(td, 2H) ppm are assigned to the aromatic protons of two isoquinoline ligands. Since the axial ligand 6-bromophthalazine in complex **2** is unsymmetrical and has two potential N binding sites, three isomers of complexes **2** could be involved. It is likely to obtain a mixture of several isomers due to the unsymmetrical ligand, and hard to identify the exact isomeric complex in the final product just base on the NMR spectral analysis. However, according to density functional theory calculations (Fig S2), the isomer of complex **2** as shown in Fig 1 is the most favored structure.

Electrochemical experiments were carried out by means of cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Fig 2 displays the CVs ($Ru^{III/II}$ couples only) of the four Ru complexes. The variation of these $E_{1/2}(Ru^{III/II})$ values reflects different electron-donating ability of the axial ligands: phthalazine > 6-bromophthalazine > isoquinoline > 6-fluoroisoquinoline. The halogen substitutes only show minor electronic effects on the oxidation levels of these Ru-bda complexes. Take complexes **1** and **1a** for example, their $E_{1/2}$ values of $Ru^{III/II}$ differ by just 0.01 V, and a similar feature is also observed for $Ru^{IV/III}$ and $Ru^{V/VI}$ (no more than 0.01 V). Moreover, all of these complexes show similar onset potentials for water oxidation under the same conditions (Fig S3), indicating that the introduction of the halogen atoms will not increase the overpotential for water oxidation catalyzed by these Ru-bda complexes.
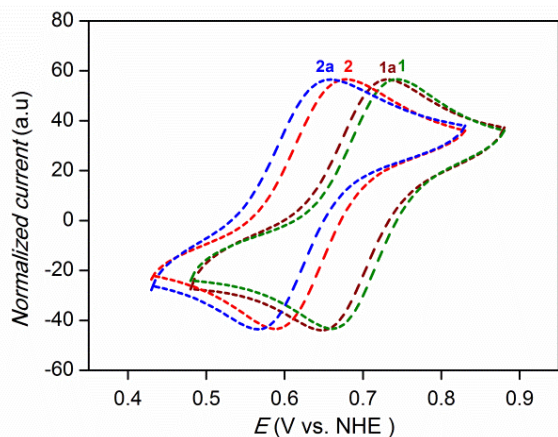
Fig 2. Normalized CVs of complexes **1**, **1a**, **2** and **2a** in pH 1 (0.1 M CF_3SO_3H) aqueous solutions containing 20% CF_3CH_2OH.

To evaluate the catalytic performance of catalysts **1** and **2** and to fairly compare with catalysts **1a** and **2a**, as well as to obtain a better understanding of the chemical aspects of the water oxidation catalysis, all measurements were conducted under the same conditions as our previously reported.[26,27] In a typical experiment, acetonitrile-water mixed solvents were used to dissolve the poorly water-soluble catalysts, and then the catalyst solution was injected into a pH 1 aqueous solution of Ce^{IV} to measure the catalytic activity. Surprisingly, complex **2** shows a TON around 10 000 (blue curve in

Fig S4), which is much lower than the TON of complex **2a** (55000 in our previous study[27]), even though the two complexes have similar structural and electrochemical properties. We therefore thought that the co-solvent acetonitrile might play a negative role during the Ce^{IV}-driven water oxidation catalyzed by the Ru-bda catalysts. Therefore, we replaced the coordinating CH_3CN co-solvent by the less coordinating solvent CF_3CH_2OH. Indeed, a very dramatic solvent effect was observed. For every catalyst a better performance was observed in the CF_3CH_2OH containing aqueous solution than in the CH_3CN containing aqueous solution (see Fig S5 and Table 1).

**Table 1.** The performance of water oxidation catalysts

Complex	[a] TOF (s^{-1})	[b]TON	[c] TON
1	1000 ± 58	24000±880	19600 ± 360
1a	780 ± 35	11300±640	8300 ± 280
2	380 ± 12	101000±870	15100 ± 410
2a	530 ± 36	61300±990	55000 ± 370

[a,b] H_2O containing CF_3CH_2OH (~ 2%) as solvent. [c] H_2O containing CH_3CN (~2%) as solvent. Reaction conditions: [a], 0.365 M Ce^{IV}, 6.25×10^{-5} M catalyst; [b, c], 0.365 M Ce^{IV}, [**1**] = [**1a**] = 2.469×10^{-6} M; [**2**] = [**2a**] = 0.933×10^{-6} M.

When commencing this study we did not expect such dramatic deactivation effects by CH_3CN, as reflected not only by the low TONs but also the decreased TOFs. We believe that it could be due to the CH_3CN molecule competing with the substrate H_2O molecule for a coordination site at the Ru center. We used DFT calculations to investigate the relative free energies of complexes binding the three different solvent molecules Ru^{II}-bda: CH_3CN, H_2O and CF_3CH_2OH. Using complex **1** as a model complex, we studied the relative Gibbs free energies of the complexes where one of the carboxylate groups is de-coordinated and a solvent molecule coordinates to the Ru ion (Fig S6). In order to catalyze the oxidation of water, the WOC needs to bind a water substrate molecule at the Ru center of catalyst **1**. We clearly see that only CH_3CN can replace a carboxylate with a favorable free energy (-5.3 kcal mol^{-1}), which is consistent with our NMR experiments (Fig S1). The CF_3CH_2OH-coordinate Ru-bda complex is less stable than the H_2O-coordinate one by 1.0 kcal/mole, which indicated that CF_3CH_2OH does not compete with H_2O for the coordination site at the catalyst. CF_3CH_2OH therefore displays no negative effect on the performance of these Ru-bda water oxidation catalysts.

Two outstanding results have to be mentioned. First, the record fast water oxidation initial rate of ∼1000 turnovers per second was obtained by using **1** as a WOC under given conditions (Fig 3). In comparison to the OEC in photosystem II (with rate 100–400 s^{-1}), the water oxidation activity of this molecular ruthenium catalyst is extremely impressive although the driving forces are different (ca 1.2 V in Photosystem II and ca 1.7 V with Ce^{IV}). Second, 300 μmol of O_2 was produced using complex **2** as catalyst after a reaction time of 3 hours, which equates to a champion TON of 101 000 (Fig S5). It is worth noting that catalysts **1a** and **2a** show higher initial TOFs even at lower concentration in comparison with our previous results.[27, 28] At the first glance, this appears inconsistent with the proven second-order kinetic behavior of the catalysts. However, this

is attributed to the following reasons: (1) the solvent effect; CF_3CH_2OH is used instead of CH_3CN in this work which leads to a better catalytic performance; (2) the efficiency of the catalysts were underestimated in our previous work due to the limitation of the pressure sensor (the pressure sensor is not responding fast enough to detect the oxygen generation under high catalyst concentrations).
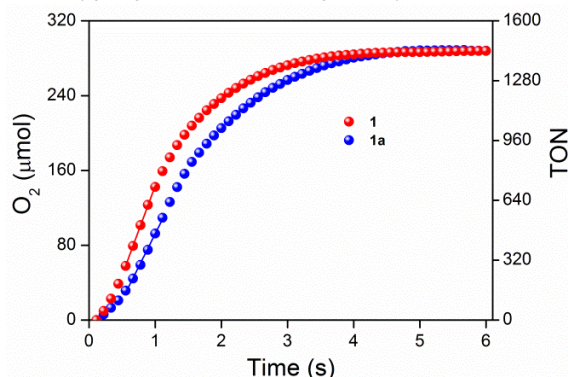

Fig 3. Catalytic performances of complexes **1** and **1a**, $[Ce^{IV}]$ = 0.365 M; $[1]$ = $[1a]$ = $6.25×10^{-5}$ M, in H_2O containing ~ 2% CF_3CH_2OH. The plots connected by solid line were used to calculate the initial TOFs. TONs are limited by the amount of oxidant. The O_2 yield based on Ce^{IV} is 96 ± 4% for both catalysts.

To provide some more insights into the high performance of water oxidation by these two new Ru complexes, a Pourbaix diagram (see Fig 4) of complex **1** was made to study the proton coupled electron transfer (PCET) processes of water oxidation catalysis. Further, the reaction kinetics of **1** was studied in order to see if the mechanism is follows the same bimolecular path as found in our previous reports. In the Pourbaix diagram, the aqua complex (Ru-OH₂) is proposed to be $[Ru(\kappa_3^{O,N,N}bda)(L)_2(OH_2)]$ (L= 6-F-isoquinoline).[29] A pH independent $Ru^{III/II}$ redox process was observed under acidic conditions, suggesting that no proton transfer is coupled with electron transfer and the pK_a of $Ru^{II}-OH_2$ is 6.9; in contrast, the redox processes of $Ru^{IV/III}$ and Ru^{IV}/Ru^V are 1e⁻/1H⁺ coupled, as evidenced by a slope of approximately 59 mV per pH unit. Accordingly, these two oxidation steps correspond to $Ru^{III}-OH_2/Ru^{IV}-OH$ and $Ru^{IV}-OH/Ru^V=O$, respectively. A new redox process following the $Ru^{IV}-OH/Ru^V=O$ step was observed for complex **1**, especially under basic conditions (see Fig 4 and Fig S7). We tentatively assign it to the oxidation of $[Ru^{IV}-O-O-Ru^{IV}]^{2+}$ to $[Ru^{IV}-O-O-Ru^{IV}]^{3+\bullet}$. To test if the oxidation potential of this complex can be expected in this region, we performed DFT calculations of the free energy of the process. The redox potential of $[Ru^{IV}-O-O-Ru^{IV}]^{2+}/[Ru^{IV}-O-O-Ru^{IV}]^{3+\bullet}$ was calculated to be 1.69 V, which is slightly higher than the experimentally determined value (< 1.40 V). However, in the oxidized species both O atoms in the peroxo bridge were calculated to have a spin density of around 0.5 (Fig S8), which shows that the oxidation event is mainly localized to the O-O bridge. Furthermore, the shortening of the O–O bond distance from 1.374 Å in $[Ru^{IV}-O-O-Ru^{IV}]^{2+}$ to 1.279 Å in $[Ru^{IV}-O-O-Ru^{IV}]^{3+\bullet}$ also indicates the formation of a stronger bond between the oxygen atoms. This is the first experimental evidence that supports the results from the previously published DFT calculations.[28] The kinetic results were shown in Fig S9, where second order kinetics were found for both complex **1** and **1a** with rate constants (k_{obs}) $2.54×10^5$ (LM⁻¹s⁻¹) and $1.52×10^5$ (LM⁻¹s⁻¹)

respectively. All these findings further support the previously proposed radical coupling reaction mechanism by these Ru complexes, as shown in Fig 5 for complex **1**.
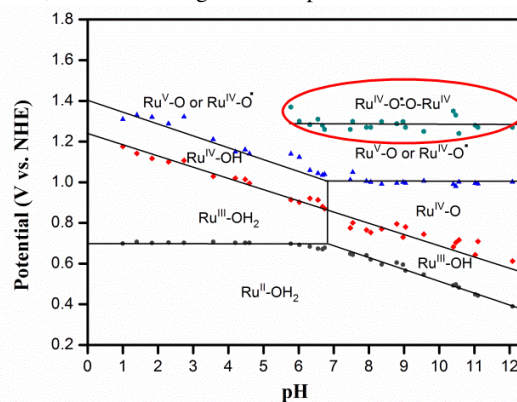
Fig 4. Pourbaix diagram of complex **1**. The black solid lines indicate trends in data.
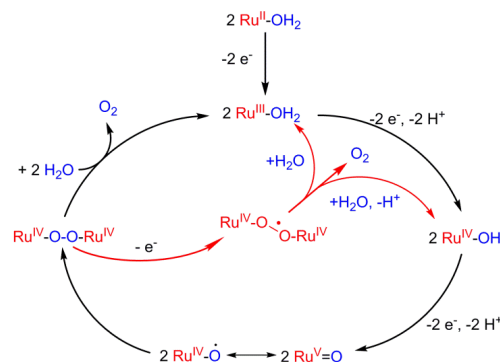
Fig 5. Proposed water oxidation pathways for complex **1** under the catalytic conditions.

In summary, the whole library of Ru complexes presented in this study provides compelling evidence for the dramatic effect of the hydrophobic halogen atoms in the catalyst structure on both the catalytic rate and the catalyst stability for water oxidation. By this design, complex **1**, $[Ru(bda)(6-fluoroisoquinoline)_2]$, achieves an extremely high catalytic activity with a TOF of 1000 s⁻¹, and complex **2**, $[Ru(bda)(6-bromophthalazine)_2]$, exhibits a high TON over 100 000. Since the electrochemistry data show a negligible electronic effect, we believe that the hydrophobic effect of the halogen-substituted axial ligands enhances the activity of the catalysts. Interestingly, it appears to be a fine balance between hydrophobic and hydrophilic nature. A co-solvent is needed to solvate the catalyst at the Ru(II) state, indicating that too high hydrophobicity can affect the reactivity negatively. At the same time highly hydrophobic axial ligands clearly has a favourable influence on the catalytic reaction rates, by favouring dimer formation in the aqueous solution. The assignment of the radical intermediate $[Ru^{IV}-O-O-Ru^{IV}]^{3+\bullet}$ observed in the electrochemistry experiments was supported by DFT calculations, lending credence to the proposed pathway of oxygen evolution based on previous DFT calculations.[28] In this study, it's also vital to note that the chosen organic medium for a better solubility of the catalysts directly determines the catalytic activity of water oxidation. Both

experiments and DFT calculations demonstrate the undesired coordination of acetonitrile to Ru center of the catalyst, resulting in inferior performance. In contrast, the poorly coordinating solvent trifluoroethanol can be considered as a good candidate.

Notes and references

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Electronic Supplementary Information (ESI) available: [synthesis route, NMR, MS, electrochemistry, kinetics and DFT calculation details]. See DOI: 10.1039/c000000x/

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TOC

Molecular catalyst Ru(bda)L$_2$ (H$_2$bda = 2,2′−bipyridine−6,6′−dicarboxylic acid, L= 6−bromophthalazine) shows excellent catalytic activity for water oxidation. By using Ce(NH$_4$)$_2$(NO$_3$)$_6$ as an oxidant, the catalyst reached a high turnover number TON = 100 000 in 3 hours.

$$2\ H_2O + 4\ Ce^{IV} \xrightarrow{\text{Catalyst}} O_2 + 4\ H^+ + 4\ Ce^{III}$$