Water Splitting

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Promoting the Activity of Catalysts for the Oxidation of Water with Bridged Dinuclear Ruthenium Complexes**

Yi Jiang, Fei Li, Biaobiao Zhang, Xiaona Li, Xiaohong Wang, Fang Huang, and Licheng Sun**

Water splitting is a promising way to supply sustainable fuel by producing hydrogen as an ideal energy carrier.[1] Of the two half reactions, water oxidation and proton reduction coupled in water splitting, the oxidation of water is envisioned as the bottleneck of artificial photosynthesis.[2] Although nature has solved this problem by employing the Mn_4O_5Ca cluster in the oxygen-evolving complex (OEC) of photosystem II as an efficient water oxidation catalyst,[3] development of highly active synthetic analogs to the OEC remains a fundamental chemical challenge. Recently, extensive efforts devoted to molecular organometallic catalysts led to a rapid progress in this field.[4] To date, the state-of-the-art molecular catalysts are those ruthenium and iridium complexes that show superior catalytic activity relative to those based on the first-row transition metals.[4,5] However, the observed activities limited to thousands of turnover numbers (TONs) are insufficient to meet the criteria for application as a catalyst in water-splitting devices. In this regard, new catalysts with improved structural and catalytic properties are desired.

We have previously reported a mononuclear ruthenium complex [Ru(bpa)(pic)$_2$] (H_2bpa = 2,2′-bipyridine-6,6′-dicarboxylic acid; pic = picoline) (Figure 1), which was found to be an efficient catalyst towards the oxidation of water.[6] Very recently, by replacing the axial picoline ligand of [Ru(bpa)(pic)$_2$] with isoquinoline (Figure 1), a high oxygen-evolving rate, approaching that of the naturally occurring OEC in homogeneous oxidation of water, was acquired with $(NH_4)_2[Ce(NO_3)_6]$ (Ce^{IV}) as oxidant.[7] However, the reactivity of the above catalysts was observed to intensively depend on the concentration of the catalyst because of the intrinsic bimolecular coupling of $Ru^{V}{=}O$ active species in the O−O bond formation.[7,8] This obviously limits their practical application either in solution or on the surface of the electrode of the water-splitting device. On the other hand, development of a bimetallic catalyst through covalently linking monomeric catalysts is a winning strategy in many organic transformation reactions.[9] This concept has been well applied in bimetallic salen system where two proximate metals in appropriate orientation serve as cooperatively reactive centers.[10–12] Inspired by the bimolecular reaction nature of [Ru(bpa)(pic)$_2$] and bimetallic metal salen, we attempt to extend this strategy to the oxidation of water with the aim of creating a highly effective dinuclear catalyst. It was envisioned that properly bridging two [Ru(bpa)(pic)$_2$] units may break the concentration limit by forcing the oxidative intermediate Ru(V)=O into facile intramolecular radical coupling. Though a related bimetallic system has been developed,[13–15] successful experimental proof on this strategy is still lacking. Herein, we present the first success in this approach. A series of oxygen-evolving dimeric catalysts was prepared based on [Ru(bpa)(pic)$_2$] and showed significantly enhanced catalytic activity with respect to their monomeric precursor in homogeneous solution.

We have noted that many dinuclear catalysts for the oxidation of water in literature were based on rigid ligands, which raised the complexity in synthesis and structure modification. To avoid tedious synthesis and to perturb less the original structural and electronic features of [Ru(bpa)(pic)$_2$], dimer **1** (Figure 1) was prepared by directly linking monomeric units using a methylene spacer through a three-step synthetic route (see the Supporting Information for details). The structure of dimer **1** was fully characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, and high-resolution mass spectrometry (Figures S2, S5, and S9). The cyclic voltammogram (CV) of dimer **1** in acidic aqueous solution shows two reversible redox couples at 0.86 and 1.10 V vs. NHE (the normal hydrogen electrode), which are assigned to two sets of one-electron processes $Ru^{II/III}$ and $Ru^{III/IV}$ for each metal center (Figure S15).[7,16] Similar to the independent manner observed for the pacman ruthenium dimers, this electrochemical behavior indicates no electronic communication between two metals.[14] The onset of a water oxidation peak comparable to that of the monomeric precursor was observed at 1.21 V (Figure S15).[16]

The catalytic activity of dimer **1** towards the oxidation of water was evaluated by using Ce^{IV} as a chemical oxidant. For the purpose of comparison, a former reaction condition was

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[*] Y. Jiang, Dr. F. Li, B. Zhang, X. Wang, F. Huang, Prof. L. Sun
State Key Laboratory of Fine Chemicals
DUT-KTH Joint Education and
Research Center on Molecular Devices
Dalian University of Technology (DUT), 116024 Dalian (China)
E-mail: lifei@dlut.edu.cn
Dr. X. Li
Key Laboratory of Industrial Ecology and
Environmental Engineering (MOE)
School of Environmental Science and Technology
Dalian University of Technology (DUT), 116024 Dalian (China)
Prof. L. Sun
Department of Chemistry
School of Chemical Science and Engineering
KTH Royal Institute of Technology, 10044 Stockholm (Sweden)
E-mail: lichengs@kth.se

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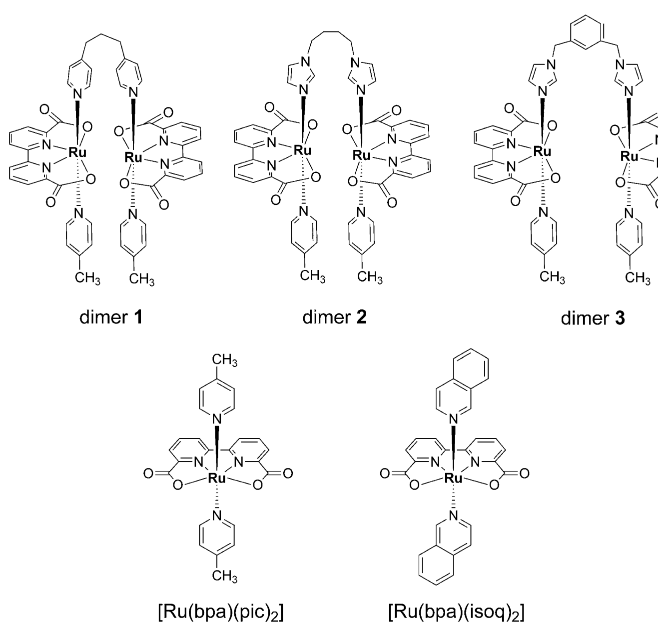


Figure 1. Structures of ruthenium monomers and dimers studied in this work.

employed,[17] that is, the oxidation of water was initiated by injection of a 20 μL catalyst solution (10^{-4} M) into a 40 mL pH 1 triflic acid solution containing 5×10^{-3} M Ce^{IV}. Once the catalyst was added, a large amount of oxygen gas bubbles evolved. The oxygen release completed in less than one hour and produced 41 μmol oxygen as determined by gas chromatography, corresponding to a TON of 20780 (10390 per ruthenium atom, Figure 2). According to this TON value, at least 83% of Ce^{IV} were consumed, consistent with the observation of rapid color bleaching of the reaction solution.[18] In comparison, replacement of dimer **1** with its monomeric precursor [Ru(bpa)(pic)$_2$] merely gave a TON of 1550 under the same conditions except that the concentration of the catalyst was doubled to maintain an equal concentration of Ru^{II} in solution (Figure 2). Furthermore, a TON less than 3000 and an initial turnover frequency (TOF) of 1.7 s^{-1} (Figure 2) were shown by [Ru(bpa)(isoq)$_2$] (isoq = isoquinoline) under the testing conditions containing a low concentration of the catalyst (10^{-7} M based on ruthenium) though a TOF value of 303 s^{-1} was recorded for [Ru(bpa)(isoq)$_2$] at a higher catalyst concentration.[7] These data provide strong experimental evidence that the oxygen-evolving activity of the monomer is allowed to be greatly enhanced by forming a dimer.

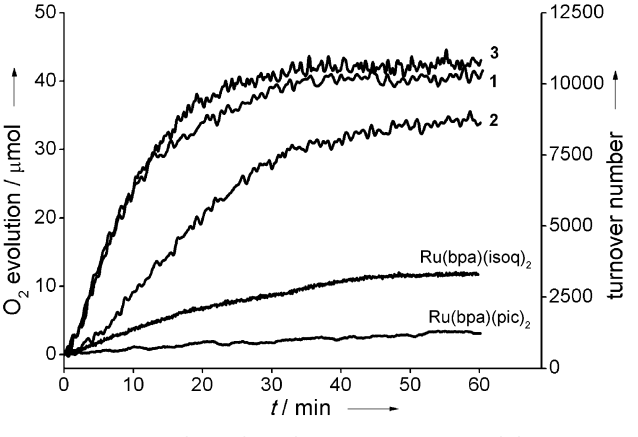


Figure 2. Oxygen evolution by ruthenium monomers and dimers versus time. The catalytic oxidation of water was performed by using 5×10^{-8} M ruthenium dimer or 1×10^{-7} M ruthenium monomer as catalyst and 5×10^{-3} M Ce^{IV} as oxidant in CF$_3$SO$_3$H solution (pH 1.0, 40 mL) at 20 °C. These data were collected by an oxygen sensor and calibrated by GC. Turnover numbers were calculated based on ruthenium.

Encouraged by these results, we decided to study the effect of various bridging spacers on the catalytic activity. Taking into account that the modification of imidazole is much easier than that of pyridine, imidazole was selected as an axial coordination ligand and -(CH$_2$)$_4$- and -CH$_2$PhCH$_2$- as spacers. Consequently, dimers **2** and **3** were prepared following a synthetic route similar to that of dimer **1** (Figure 1). As expected, both complexes exhibit similar electrochemical behaviors to **1** (Figures S16 and S17). To our delight, the variation of the spacer does not reduce the reactivity towards water oxidation. Under the conditions subjected to dimer **1**, dimers **2** and **3** gave TONs of 16690 and 21660 (8345 and 10830 based on ruthenium), respectively (Figure 2). Being the most active catalyst in this series, dimer **3** shows seven-fold and four-fold increases in activity relative to monomeric [Ru(bpa)(pic)$_2$] and [Ru(bpa)(isoq)$_2$], respectively, and exceeds prior reported most active dinuclear ruthenium catalyst [Ru$_2$(bpz)(pic)$_4$Cl]$^+$ (H$_2$bpz = 1,4-bis(6′-COOH-pyrid-2′-yl) phthalazine; 10400 TON) under identical reaction conditions.[17] Remarkably, the high TON was achieved in less than one hour, which is in sharp contrast to the reported twenty hours for [Ru$_2$(bpz)(pic)$_4$Cl]$^+$ to achieve a maximum TON.[17] The robustness of dimer **3** was explored by recharging the reaction solution with an equal amount of oxidant when the oxygen evolution had ceased. It was found that the large excess of Ce^{IV} could slowly decompose the catalyst, leading to a reduced activity for each run, whereas the oxygen evolution could be completely resumed using less Ce^{IV} for each aliquot (Figures S20–22).

With **3** as catalyst the oxygen evolution was found to be susceptible to the concentrations of both oxidant and catalyst. Tuning the concentrations of Ce^{IV} in a range of 5 to 20 mM, the highest TON of 38340 was obtained at 10 mM (Table 1, entry 2). By variation of the catalyst concentration in a range of 1.25×10^{-8} to 6.25×10^{-8} M and maintaining the concentration of Ce^{IV} at 10 mM, the best result was received at a concentration of 2.5×10^{-8} M for dimer **3**, showing an excellent TON as high as 42840 (Table 1, entry 6 and Figure S23). Under the optimized conditions, an initial TOF reached 40 s^{-1} based on the time-dependent oxygen evolution profile (Figure S23). This is an impressive value considering that TOFs for most artificial water oxidation systems are generally less than 1 s^{-1}.[4,5]

The kinetics of oxygen evolution was investigated under catalytic conditions. The initial rates of oxygen evolution catalyzed by **3** show a linear dependence on the catalyst

Table 1: Impacts of the catalyst (dimer **3**) and oxidant (Ce^{IV}) concentrations on the water oxidation.

Entry[a]	Catalyst [$\times 10^{-8}$ M]	Oxidant [$\times 10^{-3}$ M]	TON
1	5	5	21660
2	5	10	38340
3	5	15	24630
4	5	20	22580
5	1.25	10	31510
6	2.5	10	42840
7	3.75	10	39570
8	6.25	10	33550

[a] The catalytic reactions were carried out in aqueous CF_3SO_3H solutions (pH 1.0, 40 mL) with $(NH_4)_2[Ce(NO_3)_6]$ as oxidant. The amount of evolved oxygen was determined by GC and converted to turnover numbers according to the equation of turnover number = mol oxygen/mol catalyst.

concentrations with a first-order rate constant of 39 s^{-1} (Figure S24). The first-order kinetics was also found by monitoring the decay of Ce^{IV} at 360 nm at a low Ce^{IV} concentration (Figure S25). In contrast to the kinetic behavior of monomeric $[Ru(bpa)(pic)_2]$ that is second-order in catalyst concentration,[6] the observed first-order behavior of dimer **3** suggests that only one molecule is involved in the rate-determining step and thus opens the possibility that the crucial O–O bond formation may occur through intramolecular interaction or at a single-metal site.[13,14] As a result, high reactivity was permitted even at a very low catalyst concentration. A further reason for the high reactivity may relate to the structural particularity of the dimer. In contrast to the rigid framework, the soft spacer gives rise to a flexible molecular cleft, which can accommodate dynamically changed distances between metal centers over an entire catalytic cycle.[8]

The electrochemical characteristics of the supported catalysts also give clues to intramolecular mechanisms. Though an efficient method for stable immobilization of the ruthenium dimer on an electrode is lacking, dimer **3** was modified on the surface of tin-doped indium oxide (ITO)-coated glass slide to form a composite anode by a drop-casting method.[19] The preliminary results of cyclic voltammetry showthat dimer **3** sustains its reactivity towards water oxidation on the electrode surface and shows a relatively low overpotential (100 mV) in neutral aqueous solution (Figure 3).[20,21] On the contrary, the monomers lose their solution activity without showing any oxygen evolution current upon immobilization. Despite a thorough electrochemical investigation, for example, the extended periods of controlled-potential electrolysis were prevented by fast detachment of the drop-casted catalyst from the electrode surface, the striking different behaviors of the ruthenium monomer and the dimer strongly suggests a cooperative interaction between ruthenium centers in the oxygen evolution. It is possible that this interaction was blocked by loading the monomer on an electrode surface. This result bears a resemblance to the system by Tanaka and co-workers, where the electrocatalytic water oxidation was carried out by a ruthenium dimer instead of the monomeric analog.[19,22] Thus this result indicates the potential advantages of using the ruthenium dimer for the fabrication of a hybrid electrode in a functional device.

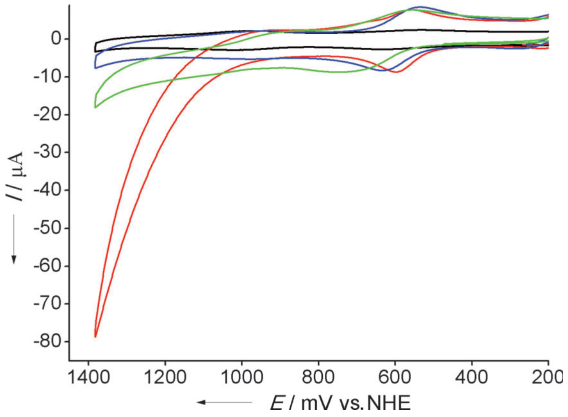
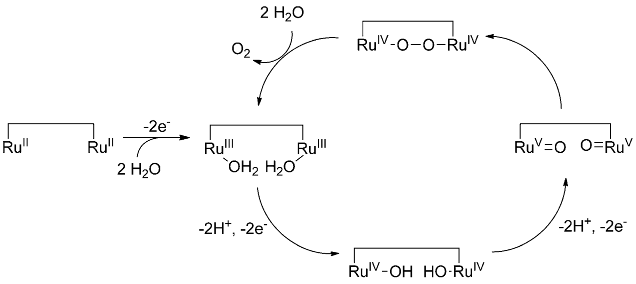


Figure 3. Cyclic voltammograms of a bare ITO electrode (black) and the ITO electrodes (4 cm^2) modified with the monomers $[Ru(bpa)(pic)_2]$ (blue), $[Ru(bpa)(isoq)_2]$ (green), and dimer **3** (red) in a phosphate buffer solution (pH 6.8) at a scan rate of 100 $mV s^{-1}$.



Scheme 1. Proposed catalytic cycle for water oxidation catalyzed by a ruthenium dimer.

On the basis of above investigations and the bimolecular radical coupling mechanism by monomeric $[Ru(bpa)(pic)_2]$,[8] the catalytic cycle for the dimer was proposed and shown in Scheme 1. With Ce^{IV} as oxidant, the initial Ru^{II} dimer is oxidized to dimeric Ru^{III} accompanied with water coordination. Ru^{IV}–OH and Ru^{V}=O dimers are subsequently generated by proton-coupled electron transfer (PCET). The Ru^{V}=O complex undergoes intramolecular O–O radical coupling, which in turn liberates the oxygen. Nevertheless, other mechanisms cannot be excluded at this stage. It was shown that the dinuclear complex *cis,cis*-$[(bpy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(bpy)_2]^{4+}$, known as the ruthenium “blue dimer” is much more reactive than its monomeric analogs under comparable conditions.[23] However, nucleophilic attack of water instead of radical coupling pathway dominates the reaction mediated by the blue dimer.[24]

In conclusion, dinuclear catalysts for the oxidation of water were developed by covalently linking monomeric ruthenium units with flexible linkages. The advantages of the ruthenium dimeric systems are: 1) Contrary to the conventional experience that rigid ligands are mandatory for bimetallic water oxidation, the dimers possess intrinsic ease in preparation and the choise of spacer. 2) The dimers show remarkable oxygen evolution activities, leading to a TON over 40000 with a TOF value as high as 40 s^{-1}. These findings promise that the dimeric catalysts will find extensive application in electrochemical as well as photo-electrochemical devices for overall water splitting.

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[18] The control experiments showed that the high reactivity of the ruthenium dimer is not a consequence of using a high concentration of Ce^{IV}. In fact, dimer **1** consumed all oxidant and nearly quantitatively produced oxygen when the 100-fold amount of Ce^{IV} was used (Figure S18). Furthermore, dimer **1** is active for the photocatalytic water oxidation with $[Ru(bpy)_3]Cl_2$ as photosensitizer and $Na_2S_2O_8$ as the sacrificial electron acceptor in neutral phosphate buffer solution (Figure S19). Therefore, the possibility of Ce^{IV} to take part in the water oxidation processes can be ruled out.

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