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Visible light-driven oxygen evolution using a binuclear Ru-bda catalyst

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ABSTRACT

Binuclear ruthenium complexes bearing the 2,2'-bipyridine-6,6'-dicarboxylate (bda) ligand have been demonstrated to be highly active catalysts towards water oxidation with Ce^{IV} as an oxidant. However, the catalytic properties of ruthenium dimers have not yet been explored for visible light-driven water oxidation. Herein, the photocatalytic performance of a dipyriddy propane-bridged ruthenium dimer **2** was investigated in comparison with its monomeric precursor, [Ru(bda)(pic)₂] (**1**), in CH₃CN/phosphate buffer mixed solvent in a three-component system including a photosensitizer and a sacrificial electron acceptor. Experimental results showed that the activity of each catalyst was strongly dependent on the content of CH₃CN in the phosphate buffer, which not only affected the driving force for water oxidation, but also altered the kinetics of the reaction, probably through different mechanisms associated with the O–O bond formation. As a result, dimer **2** showed significantly higher activity than monomer **1** in the solvent containing a low content of CH₃CN, and comparable activities were attained with a high content of CH₃CN in the solvent. Under the optimal conditions, complex **2** achieved a turnover number of 638 for photocatalytic O₂ evolution.

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1. Introduction

Artificial photosynthesis represents a sustainable approach toward conversion of solar energy into chemical fuels, for example, the production of hydrogen via water splitting [1,2]. The overall water splitting reaction consists of two half reactions, namely, water oxidation and proton reduction [3]. Oxidation of water is generally considered to be a difficult transformation because of the requirement of multiple electron transfer processes coupled with the removal of multiple protons from water molecules, which altogether impose a great challenge to artificial photosynthesis [4,5]. While numerous heterogeneous

and homogeneous catalysts have been developed to facilitate the oxygen evolution from water, most of them suffer from slow reaction rate and low stability [6–10]. In comparison with the conventional heterogeneous metal oxide catalysts, molecular water oxidation catalysts (WOCs) based on transition metal complexes have shown advantages in structural tunability and ease of mechanistic studies [6,11]. Since the first molecular WOC *cis,cis*-[(bpy)₂(H₂O)Ru(μ-O)Ru(H₂O)(bpy)₂]⁴⁺ (bpy = 2,2'-bipyridine) (blue dimer) was reported in 1982 [12], numerous efforts have been made to enhance the activity of molecular WOCs [13]. Recently, Sun and co-workers [14] developed a series of mononuclear ruthenium catalysts based on

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2,2'-bipyridine-6,6'-dicarboxylic acid (bda) ligand, which exhibited superior water oxidation activity in comparison to previously reported WOCs. Kinetic and DFT calculations revealed a bimolecular radical coupling mechanism of the O–O bond formation during the catalytic cycle [15,16]. Based on this understanding, we developed a class of dinuclear ruthenium catalysts, [(4-pic)(bda)Ru^{II}(μ-L)Ru^{II}(bda)(4-pic)] (pic = picoline, L = bridge ligand), by covalently connecting two mononuclear units with organic bridge ligands. Using this strategy, the O–O bond formation changed from an intermolecular manner to a more facile intramolecular manner, resulting in the greatly enhanced activity over that of the mononuclear species, especially at low catalyst concentrations [17].

However, the systems mentioned above are driven by either a chemical oxidant or electric power, and the visible-light induced water oxidation is less studied despite its fundamental importance to solar fuel utilization [18–24]. Specifically, the performance of the bda-based ruthenium dimer in photocatalytic water oxidation has not yet been fully explored, even though these complexes demonstrate highly efficient O₂ evolution with TONs > 10000 in chemical water oxidation with (NH₄)₂Ce(NO₃)₆ as the oxidant [17]. To fill this gap, in this work, we have discussed the photocatalytic water oxidation activity of a binuclear ruthenium complex [(4-pic)(bda)Ru^{II}(μ-L)Ru^{II}(bda)(4-pic)] (L = 1,3-(dipyridin-4-yl)propane, **2**) under visible light irradiation. The performance of **2** was compared with that of the monomeric complex [Ru^{II}(bpa)(pic)₂] (**1**). In addition, a dependence of the reaction mechanism on the reaction solvent has been discussed.

2. Experimental

2.1. Equipment

¹H NMR spectra were collected at 298 K using a Bruker DRX-400 instrument. Electrospray ionization mass spectra and high-resolution mass spectra were recorded on a Q-ToF Micro-mass spectrometer (Manchester, England). UV-Vis absorption measurements were carried out on an Agilent 8453 spectrophotometer. Oxygen evolution were analyzed on a Techcomp GC 7890T instrument equipped with a 5 Å molecular sieve column and a thermal conductivity detector with argon as the carrier gas. The electrochemical measurements were recorded on a CHI 660D electrochemical potentiostat. The light power was measured with a CEL-NP 2000 laser power meter.

2.2. Synthesis of complexes **1** and **2**

Ruthenium complexes **1** and **2** were prepared according to previously reported procedures and characterized by ¹H NMR and mass spectrometry [17]. The synthesis of all ruthenium complexes in this study were performed under N₂ atmosphere. The solvents were purified by standard methods. All other chemicals were used as received.

2.3. Photocatalytic water oxidation

In a typical experiment, [Ru(bpy)₃]Cl₂ (1 mmol/L), Na₂S₂O₈ (10 mmol/L), and the ruthenium catalyst (20 μmol/L for **1** and 10 μmol/L for **2**) dissolved in the phosphate buffer solution (5 mL, pH = 6.8) with a desired amount of CH₃CN were added to a 50-mL Schlenk flask. Prior to the photo-reaction, the solution was degassed with Ar for 20 min. The reaction was initiated by irradiation with a 300-W Xe lamp (λ > 400 nm; UV filter) under Ar atmosphere and at room temperature. The amount of generated O₂ was quantified by gas chromatography (TCD, MS-5A) at time intervals of 5 min.

2.4. Cyclic voltammetry measurements

Cyclic voltammetry measurements were obtained using a three-electrode setup with a glassy carbon (GC) working electrode, Ag/AgCl reference electrode, and a platinum wire counter electrode. For accurate evaluation, ferrocene was added as an internal standard. Cyclic voltammograms were obtained in phosphate buffer solutions (pH = 6.8) containing a specified amount of CH₃CN. The potentials were reported versus Fc⁺/Fc.

2.5. Kinetic study experiments

In a typical experiment, different amounts of **1** and [Ru^{III}(bpy)₃]³⁺ (0.125 mmol/L) were added into 2 mL of 5% or 60% CH₃CN aqueous solution, and the changes in the UV-Vis absorbance of [Ru^{II}(bpy)₃]²⁺ at 450 nm were recorded. The observed reaction rates (*k*_{obs}) at various concentrations of **1** were obtained according to the absorbance curves at 450 nm. A linear fitting of *k*_{obs} with [**1**]² in 5% CH₃CN indicated second order kinetics and a linear fitting of *k*_{obs} with [**1**] in 60% CH₃CN suggested that first order kinetics was operative.

2.6. Determination of quantum efficiency

In a typical experiment, [Ru(bpy)₃]Cl₂ (1 mmol/L), Na₂S₂O₈ (10 mmol/L), and ruthenium catalyst **1** (20 μmol/L) dissolved in phosphate buffer solution (5 mL, pH = 6.8) containing 60% CH₃CN were added to a 50 mL Schlenk flask. The solution was degassed using Ar for 20 min and then irradiated by a monochromatic light source (λ = 450 nm). The light power (*P*) was modulated to reach an optical density of 14 for the reaction solution. Under these conditions, the light entering the reaction solution was considered to be fully absorbed by the photosensitizers according to the Beer-Lambert law. The values of *P* were measured with a CEL-NP 2000 laser power meter at a point right in front of the reactor. The amount of generated O₂ (*n*_{O₂}) was quantified by gas chromatography (TCD, MS-5A) in the first 15 min of the reaction. The number of moles of photons absorbed (*n*_p) were determined by the following equation.

$$n_p = Pt\lambda / N_A hc$$

where *P* is the absorbed power of the light (W), and *t* is the irradiation time (900 s). The parameter λ refers to the irradiation wavelength (450 nm), *N_A* is the Avogadro constant (6.022 × 10²³ mol^{−1}), *h* is the Planck constant (6.63 × 10^{−34} J·s), and *c* is the speed of the light (3 × 10⁸ m/s). The quantum yield, Φ was evaluated by the following equation.

Fig. 1. Molecular structures of catalysts **1** and **2**.

$$\Phi = n_{O_2} / n_p$$

The quantum efficiency (QE) was derived from the quantum yield of O_2 as follows.

$$QE = (\Phi / \Phi_{\max}) \times 100\%$$

where Φ is the experimental value and $\Phi_{\max}$ is the theoretical maximum value. In the $[Ru(bpy)_3]^{2+}/S_2O_8^{2-}$ system, $\Phi_{\max}$ is 0.5 because two photons are needed to produce one oxygen molecule. Therefore, QE could be described as $QE = 2 \times \Phi \times 100\%$.

3. Results and discussion

The visible light-driven water oxidation was carried out in a homogeneous three-component system with $[Ru(bpy)_3]Cl_2$ as the photosensitizer, $Na_2S_2O_8$ as the sacrificial electron acceptor, and either complex **1** or **2** as the catalyst [25]. The phosphate buffer solutions (pH = 6.8) containing different amounts of CH_3CN were used as the solvents for photocatalysis. The addition of CH_3CN was necessary to improve the solubility of the catalyst and achieve a high activity. In such a three-component system, the ground state $[Ru(bpy)_3]^{2+}$ was excited to its excited state, and $[Ru(bpy)_3]^{3+}$ was subsequently generated by electron transfer from $[Ru(bpy)_3]^{2+}$ to $Na_2S_2O_8$. As a strong oxidant, $[Ru(bpy)_3]^{3+}$, in turn, accepted an electron from the catalyst. Once sufficient oxidative equivalents were accumulated at the active site of the catalyst, water was oxidized to molecular oxygen.

In Fig. 2(a), the TONs of oxygen evolution under visible light irradiation are plotted with respect to the volume percentage (%) of CH_3CN in phosphate buffer. This plot is associated with two important features. First, the oxygen evolution for both catalysts increased with a higher CH_3CN content in the phosphate buffer. For instance, a TON of 19 was obtained for **1** in the presence of 20% CH_3CN , which increased 10 times to a TON of 204 in the presence of 60% CH_3CN . Likewise, the TON increased from 57 to 215 when **2** was employed as the catalyst. Another notable feature in Fig. 2(a) is that catalyst **2** exhibits higher activities than **1** in the solvents containing less CH_3CN , although the activities of both catalysts became comparable in solvents containing more than 40% CH_3CN . Under the optimal conditions (60% CH_3CN), a quantum efficiency of 77% was attained with irradiation at 450 nm for water oxidation catalyzed by **2**, which is comparable to the best value reported in the literature [26]. It was found that acetonitrile not only promoted the amount of evolved oxygen, but also accelerated the reaction rate. As shown in Fig. 2(b), the photocatalytic rate of complex **2** increased from 0.07 to 0.33/s upon increasing the content of CH_3CN in the phosphate buffer from 20% to 60%.

With complex **2** as the catalyst, the effect of varying $Na_2S_2O_8$ concentrations on photocatalytic water oxidation was studied in phosphate buffer containing 60% CH_3CN (pH = 6.8) while keeping the concentrations of **2** (10 μ mol/L and $[Ru(bpy)_3]Cl_2$ (1 mmol/L) constant. The highest activity based on TON was obtained in the presence of 45 mmol/L $Na_2S_2O_8$. When the concentrations of $[Ru(bpy)_3]Cl_2$ and $Na_2S_2O_8$ were fixed, lowering the concentration of the catalyst also lowered the amount of evolved oxygen, but the corresponding TONs were increased. For example, a TON of 638 was obtained under the reaction condition of 45 mmol/L $Na_2S_2O_8$, 1 mmol/L $[Ru(bpy)_3]Cl_2$, and 2 μ mol/L catalyst.

In order to clarify the role of CH_3CN in promoting photocatalytic activity, the cyclic voltammetry (CV) of the photosensitizer $[Ru(bpy)_3]Cl_2$ was carried out in phosphate buffers with varying amounts of CH_3CN . As shown in Fig. 3(a), the onset potential for water oxidation was negatively shifted with the increase in CH_3CN content in the mixed solvent. For example, the onset potential of oxygen evolution decreased by 82.5 mV

Fig. 2. (a) Photocatalytic oxygen evolution by complexes **1** (20 μ mol/L) and **2** (10 μ mol/L) in phosphate buffer (pH = 6.8) containing different amounts of CH_3CN ; (b) Oxygen evolution-time plots of photocatalytic oxygen evolution by **2** (10 μ mol/L) in phosphate buffers containing 20% and 60% CH_3CN , respectively. All experiments were conducted in the presence of 1 mmol/L $[Ru(bpy)_3]Cl_2$ and 10 mmol/L $Na_2S_2O_8$ under visible light irradiation.

Fig. 3. (a) CVs of complex **1** in phosphate buffers containing (20–70)% CH_3CN ; (b) CVs of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in phosphate buffers containing different amounts of CH_3CN (0–70)%. The potentials are reported versus Fc^+/Fc , which was used as an internal standard. Scan rate 0.1 V/s. Complex **1** was insoluble in pure phosphate buffer.

in an aqueous solution containing 50% CH_3CN in comparison with that in phosphate buffer containing 20% CH_3CN . In contrast, the redox potential of the photosensitizer $[\text{Ru}(\text{bpy})_3]^{3+/2+}$ ($E_{1/2}$) was not influenced by the content of CH_3CN in the reaction solution (Fig. 3(b)). Since $[\text{Ru}(\text{bpy})_3]^{3+}$ serves as a strong oxidant in photocatalysis, increasing the proportion of CH_3CN in the mixed solvent could increase the driving force for water oxidation, leading to higher activity for oxygen evolution [27]. This analysis agrees well with our observation that the TON increases with the increase in the relative content of CH_3CN in the phosphate buffer (Fig. 2(a)).

In another experiment, $[\text{Ru}(\text{bpy})_3]^{3+}$ was separately synthesized as a chemical oxidant to facilitate the kinetic study of water oxidation. The UV-Vis absorption changes at 450 nm were monitored upon addition of different concentrations of $[\text{Ru}(\text{bda})(\text{pic})_2]$ into 2 mL of $[\text{Ru}(\text{bpy})_3]^{3+}$ (0.125 mmol/L) phosphate buffer solutions containing either 5% or 60% CH_3CN . Based on the absorption-time plots shown in Fig. 4(a) and (c), k_{obs} was estimated as a function of catalyst concentration (Fig. 4(b) and (d)).

The value of k_{obs} was found to be proportional to the square of the concentration of **1** in 5% CH_3CN aqueous solution (Fig.

Fig. 4. Absorbance changes monitoring at 450 nm after the addition of $[\text{Ru}(\text{bpy})_3]^{3+}$ (0.125 mmol/L) and different amount of **1** into 5% (a) and 60% (c) CH_3CN aqueous solution; (b) k_{obs} as a function of $[\text{1}]^2$ in 5% CH_3CN solution; (d) k_{obs} as a function of $[\text{1}]$ in 60% CH_3CN solution.

Fig. 5. Two possible reaction mechanisms involved in catalytic water oxidation.

4(b)), which was indicative of second order kinetics involving two catalyst molecules in the rate-determining step. This feature is consistent with a radical coupling mechanism as previously reported [16,25]. In comparison, k_{obs} showed a linear dependence on the concentration of **1** in 60% CH_3CN solution, indicating first order kinetics with a single catalyst molecule in the rate-determining step [28]. Therefore, water oxidation in 5% and 60% CH_3CN solution may be governed by different reaction mechanisms.

On the basis of the manner of O–O bond formation, it was concluded that two different kinds of mechanisms were prevalent [29]. The first mechanism is the aforementioned bimolecular radical coupling, wherein oxygen is released through the interaction between two $\text{M}=\text{O}$ ($\text{M} = \text{Ru}, \text{Ir}, \text{Fe}, \text{Co}, \text{Mn}$, and so on) moieties. The second mechanism involves the nucleophilic attack of the water molecule on the single site of the $\text{M}=\text{O}$ intermediate to release molecular oxygen via the $\text{M}-\text{OOH}$ peroxide (Fig. 5). It is highly plausible that the reaction mechanism alters from intermolecular radical coupling to water nucleophilic attack upon increasing the relative content of CH_3CN . This assumption explains the trend observed in Fig. 2(a) that the catalytic activities of **1** and **2** only differ in the mixed solvent with a low content of CH_3CN , which become comparable in the solvent with a high content of CH_3CN . However, the possibility that the rate-determining step in the radical coupling pathway switches from O–O bond formation to a step that involves association with one Ru center cannot be excluded. The active intermediate of water oxidation in a mixed solvent of $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ (7/3 V/V) was characterized by mass spectrometry and ^1H NMR spectroscopy as $[\text{Ru}(\text{bda})(\text{pic})_2(\text{OH})]^+$, a seven-coordinate $\text{Ru}(\text{IV})$ ($S = 0$) species, consistent with that isolated in our previous study [14]. The subsequent one electron oxidation of $[\text{Ru}^{\text{IV}}(\text{bda})(\text{pic})_2(\text{OH})]^+$ gave either $[\text{Ru}^{\text{IV}}(\text{bda})(\text{pic})_2(\text{O})\cdot]^+$ ($\text{Ru}^{\text{IV}}\text{-O}\cdot$) or $[\text{Ru}^{\text{V}}(\text{bda})(\text{pic})_2(\text{O})]^+$ ($\text{Ru}^{\text{V}}=\text{O}$) as the key intermediate for bimolecular coupling and single-molecular water nucleophilic attack, respectively. Although we are not able to differentiate between two reaction pathways at the present stage, other methods such as DFT calculations may help us to reveal the detailed mechanism.

4. Conclusions

In summary, the photocatalytic activity of bda-based binu-

clear ruthenium catalyst **2** was investigated in a three-component system and compared with that of its monomeric precursor **1**. It was found that the oxygen evolution activity of both catalysts increased with the amount of CH_3CN in the phosphate buffer as a result of a larger driving force provided by the photo-activated sensitizer $[\text{Ru}(\text{bpy})_3]^{3+}$. A notable finding here was that the kinetics of the water oxidation reaction by **1** switched from second order to pseudo-first order with the increasing CH_3CN content. Consequently, the binuclear catalyst **2** showed higher activity when the CH_3CN content was low, and comparable activities were attained by **1** and **2** with a high content of CH_3CN . This is probably because the pathway of O–O bond formation changes from the bimolecular radical coupling mechanism to the single-site nucleophilic attack of water. This study demonstrates the flexibility of the molecular catalysts in light-driven water oxidation. The solvent-tunable behavior of Ru-bda may also be applicable to electrochemical and photoelectrochemical water oxidation, enabling a deeper understanding and rational design of engineered molecular devices for highly efficient solar water splitting.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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Graphical Abstract

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A binuclear ruthenium catalyst exhibited higher activity than its monomeric precursor in photocatalytic water oxidation. However, the difference in the activity between the bi- and mononuclear catalysts was diminished with the increase in the amount of CH₃CN in the reaction solution.

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基于 Ru-bda 双核钌催化剂的可见光驱动水氧化

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摘要: 开发高效水氧化催化剂对于太阳能分解水制氢和 CO₂ 还原都具有重要意义。我们之前的研究表明, 基于 Ru-bda(bda = 2,2'-联吡啶-6,6'-二羧酸) 单体的双核钌催化剂在以 (NH₄)₂Ce(NO₃)₆ 为氧化剂的化学法水氧化反应中表现出良好的催化性能, 比相同条件下单核钌催化剂的活性高出一个数量级。然而, 该类双核钌催化剂的光催化水氧化性能尚未被系统研究。

因此我们考察了以丙烷桥双核钌配合物为催化剂、 $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ 为光敏剂、 $\text{Na}_2\text{S}_2\text{O}_8$ 为电子牺牲体组成的三组分体系的光催化性能, 并和相应的单核钌催化剂进行了对比, 同时考察了溶液中乙腈的含量对单、双核钌分子催化剂光催化产氧性能和产氧机理的影响。

实验结果表明, 无论是单核还是双核钌催化剂, 其催化活性与乙腈在磷酸缓冲溶液中的比例密切相关。乙腈的含量不仅影响了水氧化的驱动力, 而且影响 O-O 的形成机理, 改变反应的动力学和反应速率。单、双核钌催化剂的活性都随着乙腈比例的增加而增加, 然而双核钌催化剂在低乙腈含量的缓冲溶液中展现优于单核钌催化剂的光催化性能; 而在高乙腈含量的缓冲溶液中, 双核钌催化剂和单核钌催化剂的光催化性能趋于相当。在最优化条件 (60% 乙腈) 下, 双核钌的光催化产氧 TON 值达到 638, 在 450 nm 的光量子效率达到 77%。我们还发现, 当乙腈浓度较低时, 单核钌催化剂 Ru-bda 催化的水氧化反应为二级动力学; 当乙腈浓度较高时, 该催化剂在反应中表现为一级动力学。从而推测 O-O 键的形成机制由双分子自由基耦合转变成单分子亲核进攻, 也解释了为什么高乙腈含量下单核和双核钌催化剂的活性差别不大。本研究所展示的 Ru-bda 的溶剂效应可能同样适用于电化学和光电化学水氧化, 对深入理解和设计高效太阳能分解水器件具有重要意义。

关键词: 水氧化; 双核钌催化剂; 光催化; 溶剂效应; 动力学

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