



## Priority Communication

## Visible light-driven water oxidation catalyzed by mononuclear ruthenium complexes

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## ABSTRACT

A series of mononuclear ruthenium water oxidation catalysts (WOCs) [Ru(bda)L<sub>2</sub>] (H<sub>2</sub>bda = 2,2'-bipyridine-6,6'-dicarboxylic acid; L = N-cyclic aromatic ligands) were investigated in three-component light-driven water oxidation systems composed of photosensitizers, a sacrificial electron acceptor, and WOCs. A high turnover number of 579 for water oxidation was achieved in the homogeneous system using complex **4** ([Ru(bda)(4-Br-pyridine)<sub>2</sub>]) as the WOC, and a high quantum efficiency of 17% was found which is a new record for visible light-driven water oxidation in homogeneous systems.

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## 1. Introduction

Artificial photosynthesis system that can split water to molecular hydrogen and oxygen by using solar energy has been considered as one of the most attractive options in the solar energy conversion respect [1–5]. Basically, such a system is comprised of the following units: (i) a light harvesting antenna; (ii) a charge separation part; (iii) water splitting catalysts (both oxygen and hydrogen evolution catalysts) [6,7]. Developing efficient catalysts for water oxidation are challenging because water oxidation is an extreme uphill reaction that involves multiple electron/proton transfer steps and the O–O bond formation. As regards homogeneous systems, one of the urgent tasks is to develop water oxidation catalysts and photosensitizers with a view of combining them into one molecular system to realize photo-induced water oxidation. Some related works have been published recently based on the so-called single-component metallosupramolecular system [8–14].

Our previous study focused on a series of [Ru(bda)L<sub>2</sub>] complexes (H<sub>2</sub>bda = 2,2'-bipyridine-6,6'-dicarboxylic acid; L = N-cyclic aromatic ligands) which had been proved highly active toward water oxidation in homogeneous system using Ce<sup>IV</sup> ((NH<sub>4</sub>)<sub>2</sub>-Ce(NO<sub>3</sub>)<sub>6</sub>) as an oxidant [15–18]. As show in Scheme 1, complexes **1–4** are capable catalyzing Ce<sup>IV</sup>-driven water oxidation with high

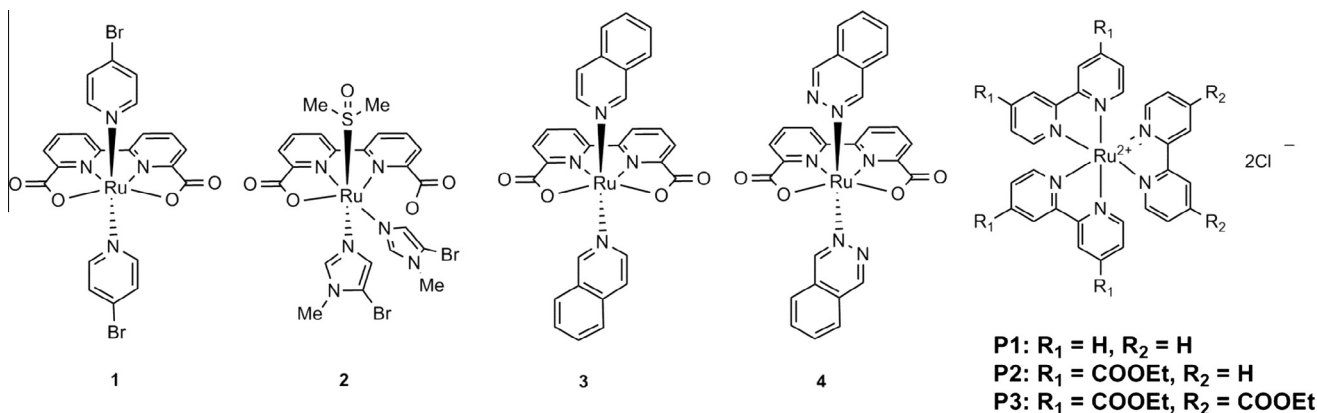
TONs up to 50,000 and high TOFs up to 300 s<sup>-1</sup> [17,18]. One of the advantages of these complexes is the small overpotentials at pH 7.0 (Table S1). All of the onset potentials of **1–4** at pH 7.0 are lower than 1.25 V vs. NHE which is lower than the potential of Ru<sup>3+/2+</sup> of the commonly used photosensitizer [Ru(bpy)<sub>3</sub>]<sup>2+</sup>. This indicates that water oxidation catalyzed by **1–4** could be thermodynamically driven by photo-generated [Ru(bpy)<sub>3</sub>]<sup>3+</sup>.

Taking the high activities and low onset potentials of these complexes into account, we employed these Ru-bda complexes in a three-component visible light-driven water oxidation system in the presence of a proper photosensitizer and electron acceptor (Scheme 2). Polypyridyl ruthenium complexes such as Ru(bpy)<sub>3</sub><sup>2+</sup> derivatives have attracted considerable attention recently because their capability of driving both photo-induced water oxidation to produce oxygen and proton reduction to generate molecular hydrogen [19–22]. Three different Ru(bpy)<sub>3</sub><sup>2+</sup> derivatives **P1–P3** (Scheme 1), which have oxidation potentials respectively, spanning from 1.26 to 1.55 V and to 1.69 V vs. NHE (Table S1), were employed as photosensitizers for light-driven water oxidation. In comparison with **P1**, the introduction of ethyl ester group in **P2** and **P3** can greatly shift their oxidation potential to anodic direction.

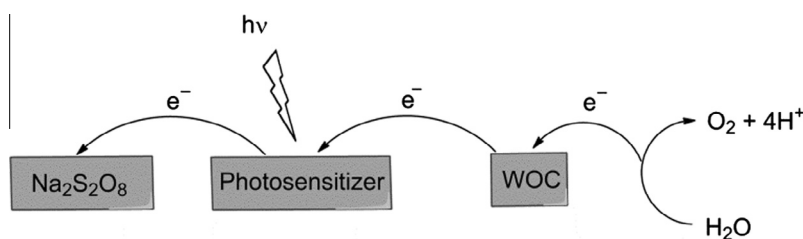
Sodium persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) as an efficient sacrificial electron acceptor had been used in homogenous systems for light-driven water oxidation [22–24]. The working principle is as follows: (1) [Ru(bpy)<sub>3</sub>]<sup>2+</sup> absorbs one photon and gets to the excited state [Ru(bpy)<sub>3</sub>]<sup>2+\*</sup>, (2) the excited dye and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> then react with each other, generating [Ru(bpy)<sub>3</sub>]<sup>3+</sup>, sulfate and sulfate radical, (3) the highly oxidizing sulfate radical oxidizes another equivalent of

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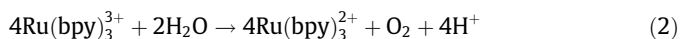


**Scheme 1.** Structures of complexes **1–4** and photosensitizers **P1–P3**.



**Scheme 2.** Visible light-driven water oxidation using three-component molecular systems.

$[\text{Ru}(\text{bpy})_3]^{2+}$  to  $[\text{Ru}(\text{bpy})_3]^{3+}$ . In total, one persulfate ( $\text{S}_2\text{O}_8^{2-}$ ) and one photon can generate two equivalents of  $\text{Ru}(\text{bpy})_3^{3+}$  (Eq. (1)), and four equivalents of  $\text{Ru}(\text{bpy})_3^{3+}$  are used to drive a catalyst to oxidize water to molecular oxygen (Eq. (2)).



The reaction conditions of a three component light-driven water oxidation system were optimized using complex **1** as the catalyst and **P1** as the photosensitizer. Firstly, two different buffer solutions, phosphate buffer and borate buffer, were tested [23,25]. The three component system  $\mathbf{1}/\mathbf{P1}/\text{S}_2\text{O}_8^{2-}$  exhibited better performance in borate buffer than in phosphate buffer (Fig. S1). This is probably due to the difference in anionation of the Ru cation in two buffers: the phosphate anion coordinates to the Ru cation stronger than the borate anion. As a result, the phosphate buffer inhibits the Ru catalyst more than the borate buffer, leading to a lower performance.

Next, we studied the influence of the buffer concentration on the catalytic activity. A higher activity of the three component system  $\mathbf{1}/\mathbf{P1}/\text{S}_2\text{O}_8^{2-}$  in the 20 mM borate buffer was observed in comparison with that in 10 mM borate buffer (Fig. S2). However, further increase in the buffer concentration from 20 mM to 50 mM led to successive deactivation of the three component system, which is likely due to the aforementioned anionation of the catalyst under highly concentrate buffer solutions.

The optimized experimental conditions were applied for all of the three photosensitizers, **P1** (excited state lifetime  $\tau = 0.6 \mu\text{s}$ ), **P2** ( $\tau = 1.6 \mu\text{s}$ ), and **P3** ( $\tau = 2.1 \mu\text{s}$ ) with increasing redox potentials of  $\text{Ru}^{3+/2+}$ . With **1** as the catalyst, the initial oxygen production rates were 2.5, 20.0, and  $15.2 \text{ min}^{-1}$  for **P1**, **P2**, and **P3**, respectively (Fig. S3). It is obviously that the weak driving force of **P1** caused the low activity of the three component  $\mathbf{1}/\mathbf{P1}/\text{S}_2\text{O}_8^{2-}$  system. For the lower activity of  $\mathbf{1}/\mathbf{P3}/\text{S}_2\text{O}_8^{2-}$  than  $\mathbf{1}/\mathbf{P2}/\text{S}_2\text{O}_8^{2-}$ , there might be many

reasons: (1) the electron-withdrawing ethyl ester groups decrease the stability of  $\mathbf{P3}^+$  state, as evidenced by the higher oxidation potential of  $\mathbf{P3}^+/\mathbf{P3}$  than  $\mathbf{P2}^+/\mathbf{P2}$ ; (2) the oxidized species  $\mathbf{P3}^+$  is a stronger oxidizing reagent than  $\mathbf{P2}^+$  and may cause faster decomposition of the catalyst. One coin has two sides: the introduction of ethyl ester groups to **P1** not only enhances the driving force for intermolecular charge transfer between catalyst and photosensitizer but also shows negative effect when too many are installed. Control experiments were carried out using the same system but absence of catalyst, almost no oxygen was observed. This result confirmed that light-driven oxygen evolution is catalyzed by the ruthenium catalyst (**1–4**).

We further investigated the photo-activity of three component systems using water oxidation catalysts **1–4** which possess the same equatorial ligand but different axial ligands<sup>5</sup>. As shown in Fig. 1 and Table 1, catalysts **1**, **3**, and **4** showed similar activities (TON and TOF values) while catalyst **2** displayed a relatively lower activity due to its instability. With this series of catalysts, the best light-driven water oxidation performance with a TOF =  $20.0 \text{ min}^{-1}$  and a TON = 251 was observed under the first run of illumination for the three component system  $\mathbf{1}/\mathbf{P2}/\text{S}_2\text{O}_8^{2-}$ .

As we observed previously with other three component systems, the pH value of the working solution dropped dramatically after the first run of illumination (from 7.0 to 1.94, see Fig. 2(a)). The increase in acidity would shift the onset potential of the catalytic curve to a positive direction, resulting in the evanescent of  $\text{O}_2$  generation. Hence, as clearly shown in Fig. S3, sensitizer **P2** and **P3** with relatively higher oxidation potential can work better in a more acidic medium. Representatively, **P2** was chosen for the repetitive reactivation experiment by alkalization. Fig. 2 highlights, respectively, the results of catalyst **1** (a) and **4** (b) under the same initial conditions. In both cases, the rate of  $\text{O}_2$  evolution decreased gradually with the concomitance of the decreasing pH; and both of them could be more or less retrieved after neutralizing the resulting acidic solutions to the original pH value. In the process of three  $\text{O}_2$  evolution cycles,  $\text{O}_2$  generation diminished after each cycle.

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