Visible Light-Driven Water Oxidation Promoted by Host−Guest Interaction between Photosensitizer and Catalyst with A High Quantum Efficiency

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S *Supporting Information*

ABSTRACT: A highly active supramolecular system for visible light-driven water oxidation was developed with cyclodextrin-modified ruthenium complex as the photosensitizer, phenyl-modified ruthenium complexes as the catalysts, and sodium persulfate as the sacrificial electron acceptor. The catalysts were found to form 1:1 host−guest adducts with the photosensitizer. Stopped-flow measurement revealed the host−guest interaction is essential to facilitate the electron transfer from catalyst to sensitizer. As a result, a remarkable quantum efficiency of 84% was determined under visible light irradiation in neutral aqueous phosphate buffer. This value is nearly 1 order of magnitude higher than that of noninteraction system, indicating that the noncovalent incorporation of sensitizer and catalyst is an appealing approach for efficient conversion of solar energy into fuels.

Photocatalytic oxygen evolution (water oxidation) is a crucial step for solar water splitting.[1] Despite significant efforts to develop semiconductor-based photocatalyst, recent research progresses demonstrate that it is promising to construct artificial photosynthetic systems through molecular approach.[2−4] To date, ruthenium and iridium complexes have been identified as the most active molecular catalysts for water oxidation. Other catalysts based on earth-abundant metals such as cobalt, iron, copper, and manganese have also been developed.[5] Although these catalysts are efficient in oxygen evolution driven by chemical oxidant or electricity, light-driven water oxidation with high quantum efficiency (QE) is still a great challenge for molecular system.[6] In literature, photocatalytic water oxidation is widely studied in a system consisting of a catalyst, a photosensitizer, and a sacrificial electron acceptor.[7] For example, we have reported the use of $[Ru(bpy)_3]^{2+}$ (bpy = 2, 2′-bipyridine) as the photosensitizer and $[Ru(bda)(Br-py)_2]$ (H_2bda = 2, 2′-bipyridine-6,6′-dicarboxylic acid, Br-py = 4-bromo pyridine) as the catalyst to obtain a 34% QE in visible light-driven water oxidation.[8] Puntoriero et al. employed a $[Ru(bpy)_3]^{2+}$-based dendrimeric sensitizer and a polyoxometalate tetraruthenium catalyst to gain a QE of 60%.[9] A similar QE value was obtained by using a polyoxometalate tetracobalt catalyst.[10] To date, the highest QE

value was reported by Sartorel et al. to be 80% with a system containing $[Ru(bpy)_3]^{2+}$ and a tetracobalt cubane catalyst (molar ratio 55:1). The use of a 1:1 CH_3CN/aqueous borate buffer mixed solvent at pH 8 was proposed to be the key to accelerate photoinduced electron transfer from catalyst to sensitizer and lead to high QE.[11]

Recently, supramolecular assemblies based on covalently linked light-absorbing and catalytic components have been demonstrated to facilitate water oxidation by facile intramolecular electron transfer. For instance, ruthenium dyads that incorporate $[Ru(bpy)_3]^{2+}$ and a mononuclear ruthenium catalyst through an amide or a pyrazine-based linker have been developed by Meyer and Thummel, respectively.[12−14] We envisioned that the construction of suitable photosensitizer-catalyst assembly would be an efficient approach to improve the QE for water oxidation.

We have previously prepared a triad by covalent incorporation of two $[Ru(bpy)_3]^{2+}$ sensitizers and a water oxidation catalyst $[Ru(bda)(pic)_2]$ (pic = picoline). The triad system promoted visible light-driven water oxidation activity by 5-fold with respect to the analogous intermolecular system.[15] However, mass spectrometry revealed the dissociation of sensitizer moiety from the assembly during photocatalysis, resulting in a low turnover number (TON) of 38 for oxygen evolution. It was thus anticipated that the reversible combination of photosensitizer and catalyst would address the stability issue and eventually lead to high QE that demanded by artificial photosynthesis. In this work, we report the success of this concept by noncovalent incorporation of $[Ru(bpy)_3]^{2+}$ and $[Ru(bda)(pic)_2]$ into a supramolecular system. The oxidation of water by noncovalent system achieved a remarkable QE of 84% under visible light irradiation under benign conditions.

In order to build such a system, a photosensitizer was prepared by functionalization of β-cyclodextrin (β-CD) onto $[Ru(bpy)_3]Cl_2$ through an ester bond ($[CD-Ru(bpy)_3]^{2+}$).[16] On the other hand, the picoline ligands in $[Ru(bda)(pic)_2]$ were replaced with more hydrophobic 4-phenylpyridine (ppy) to obtain a catalyst $[Ru(bda)(ppy)_2]$ (**1**). The molecular structures of $[CD-Ru(bpy)_3]^{2+}$ and complex **1** are shown in

Figure 1, and they were fully characterized by NMR, ESI-MS, and elemental analysis. Owing to the host−guest interaction
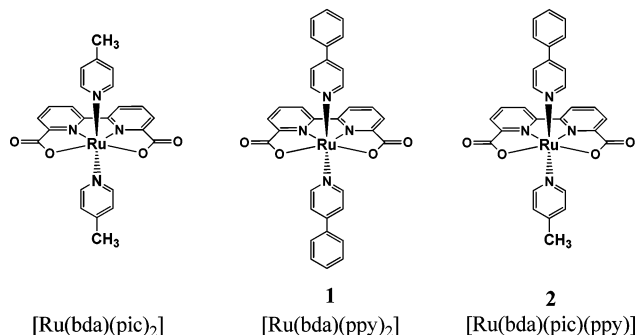
Photosensitizers:

[Ru(bpy)$_3$]Cl$_2$ [CD-Ru(bpy)$_3$]Cl$_2$

Catalysts:

[Ru(bda)(pic)$_2$]   1 [Ru(bda)(ppy)$_2$]   2 [Ru(bda)(pic)(ppy)]
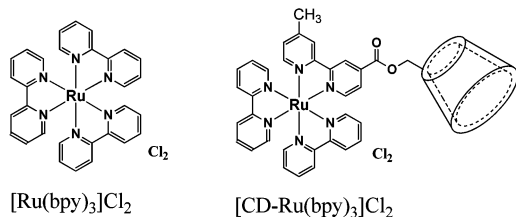
Figure 1. Structures of photosensitizers and catalysts used in this study.

between the hydrophobic cavity of [CD-Ru(bpy)$_3$]$^{2+}$ and the phenylpyridine ligands on **1**, these two components were expected to self-assemble into supramolecular adduct in aqueous solution.[17] The formation of inclusion complex in a mixture of [CD-Ru(bpy)$_3$]$^{2+}$ and **1** was identified by ESI-MS spectrometry (Figure S9). Signals consistent with both {[CD-Ru(bpy)$_3$]$^{2+}$-[Ru(bda)(ppy)$_2$]}$^{2+}$ (*m/z* 1199.2) dyad and {[CD-Ru(bpy)$_3$]$^{2+}$-[Ru(bda)(ppy)$_2$]-[CD-Ru(bpy)$_3$]$^{2+}$}$^{4+}$ (*m/z* 1036.0) triad were detected under the operating conditions. The difference between the UV−vis spectrum of the mixture of [CD-Ru(bpy)$_3$]$^{2+}$ and **1** and the addition spectrum of two components gave another clue to the formation of inclusion complex (Figure S11). The cyclic voltammogram (Figure S13) of the mixture of **1** and [CD-Ru(bpy)$_3$]$^{2+}$ showed the aggregation of individual components, indicating the properties of the constituents remain unchanged.

Photocatalytic oxygen evolution was carried out in a neutral phosphate buffer solution (50 mM) containing 10% CH$_3$CN in the presence of sensitizer, catalyst, and sacrificial electron acceptor (sodium persulfate). Under visible light irradiation ($\lambda > 400$ nm), the evolved oxygen was analyzed by gas chromotography. It was found that no reaction occurs in the absence of any of the following factors: light, electron acceptor, sensitizer, and catalyst (Figure S14). To optimize the reactivity, the molar ratios between [CD-Ru(bpy)$_3$]$^{2+}$ and **1** were varied from 1 to 20 with the concentrations of the other components kept constant. As shown in Figure S15, the best result was received at the sensitizer/catalyst ratio of 15:1. Under this condition, oxygen was produced with a TON of 267, corresponding to the consumption of 85% persulfate (Table 1 and Figure S16). Effort to further improve TON by employing higher concentration of persulfate failed because the unfavorable shift of the thermodynamic potential for water oxidation in concomitance with the accumulation of protons,

Table 1. Photocatalytic Water Oxidation by Combination of Different Photosensitizers and Catalysts in the Presence of Sodium Persulfate

photosensitizer	catalyst	TON[a]	QE (%)[b]
[CD-Ru(bpy)$_3$]$^{2+}$	**1**	267	84
[Ru(bpy)$_3$]$^{2+}$	**1**	28	10
[CD-Ru(bpy)$_3$]$^{2+}$	Ru(bda)(pic)$_2$	32	12
[CD-Ru(bpy)$_3$]$^{2+}$	**2**	65	21
[Ru(bpy)$_3$]$^{2+}$	**2**	14	4

[a]Reaction conditions for determination of TONs: catalyst 10^{-4} M, photosensitizer 1.5×10^{-3} M, and sodium persulfate 6.67×10^{-2} M in 5 mL phosphate buffer solution (pH 7.1, 50 mM) containing 10% acetonitrile under visible light irradiation. TON = moles of O$_2$ produced/moles of catalyst. [b]QEs were determined under the same conditions described above except for irradiation at 450 nm. QE = 2 × moles of O$_2$ produced/moles of photons absorbed × 100%.

which terminated the oxygen evolution before consumption of all sacrificial reagent.[18] However, oxygen evolution was able to be resumed by neutralizing the reaction solution with NaOH solution (step a in Figure S17) or the addition of persulfate at the same time (step b in Figure S17). Thereafter, the activity could only be recovered by the addition of [CD-Ru(bpy)$_3$]$^{2+}$ (step c in Figure S17), indicating the degradation of sensitizer rather than catalyst being the limit of our system.

Noncovalently assembled system exhibited greatly enhanced activity with respect to either the former one bearing covalent linker[15] or the related separate systems without host−guest interaction. For example, replacing [CD-Ru(bpy)$_3$]$^{2+}$/**1** pair with either [Ru(bpy)$_3$]$^{2+}$/**1** or [CD-Ru(bpy)$_3$]$^{2+}$/[Ru(bda)-(pic)$_2$], the amount of generated oxygen reduced by 9-fold (∼30 TON for each pair, Table 1). It was found that the TON of [CD-Ru(bpy)$_3$]$^{2+}$/**1** dropped to 48 in the presence of a large amount of β-CD that competed with [CD-Ru(bpy)$_3$]$^{2+}$ to interact with **1** (Figure S18). Control experiments excluded the possibility of the cyclodextrin moiety as a proton relay in catalysis (Figure S20 and S21). In addition, the superiority of the supramolecular system relative to separate system was maintained by replacing Na$_2$S$_2$O$_8$ with [Co(NH$_3$)$_5$Cl]$^{2+}$ as the sacrificial oxidant (Figure S19). These results consistently imply the crucial role of the noncovalent interaction on light-driven water oxidation.

To further reveal the influence of noncovalent interaction of sensitizer and catalyst on water oxidation, [Ru(bda)(pic)(ppy)] (**2**) with picoline as one axial ligand and 4-phenylpyridine as the other (see structure in Figure 1) was prepared as a reference catalyst. Again, photocatalytic activity of **2** was evaluated under the above conditions, exhibiting a moderate TON of 65 (Figure S16). From a structural point of view, a single binding site is available for **2** to combine with [CD-Ru(bpy)$_3$]$^{2+}$, which could possibly account for the drastically varied activities shown by **2** and **1**.

This hypothesis was identified by using isothermal titration calorimetry (ITC) to assess the binding affinity and binding mode between sensitizer and catalyst. The ITC data for both **1** and **2** were best fitted to an one-site binding model consistent with a 1:1 stoichiometry for the complexation of [CD-Ru(bpy)$_3$]$^{2+}$ to catalyst (Figure 2).[19] The related thermodynamic parameters were summarized in Table S1. The binding constants were determined to be 3.8×10^4 M^{-1} for **1** and 1.1×10^4 M^{-1} for **2**, confirming that catalyst **1** can form a more stable adduct with [CD-Ru(bpy)$_3$]$^{2+}$.

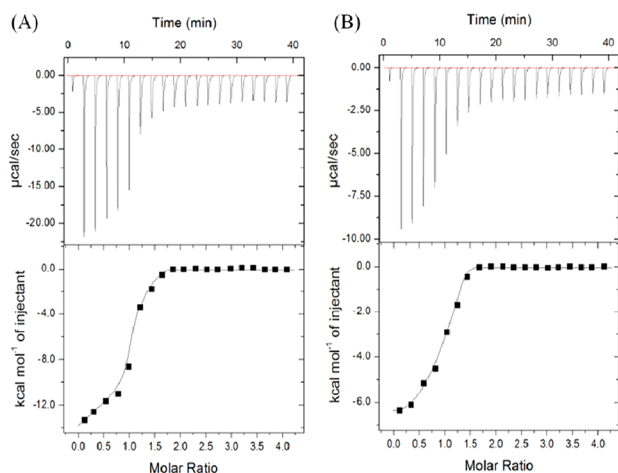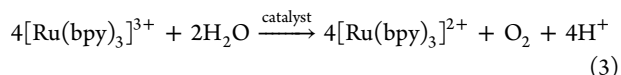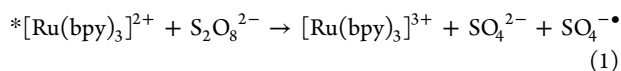**Figure 2.** Isothermal titration calorimetric curves for the interaction of catalysts **1** (A) and **2** (B) (0.1 mM) with $[CD\text{-}Ru(bpy)_3]^{2+}$ (stock concentration 3 mM) in 10% CH_3CN phosphate buffer solutions (pH = 7.1) at 298 K. The top panels show the raw data of the titration, and the bottom panels show the normalized integrated peaks against molar ratio (squared symbols) and best fit assuming 1:1 complexation (lines). All the data points were corrected for the heat of dilution.

As a key parameter to directly evaluate the efficiency of photoconversion, QE was determined under the irradiation of monochromatic light (λ = 450 nm) according to QE = (Φ/Φ_{max}) × 100%, where Φ is quantum yield termed as moles of O_2 evolved/moles of photons absorbed (see Supporting Information for experimental details). Photochemical water oxidation based on $[Ru(bpy)_3]^{2+}/S_2O_8^{2-}$ system has been known to proceed through the oxidative quenching of the excited sensitizer as indicated by eqs 1−3.[10,11,20] Given that two photons are required to produce one O_2, the Φ_{max} of our system is 0.5. Hence, QE can be described as QE = 2 × Φ × 100%.

$$*[Ru(bpy)_3]^{2+} + S_2O_8^{2-} \rightarrow [Ru(bpy)_3]^{3+} + SO_4^{2-} + SO_4^{-\bullet} \tag{1}$$

$$[Ru(bpy)_3]^{2+} + SO_4^{-\bullet} \rightarrow [Ru(bpy)_3]^{3+} + SO_4^{2-} \tag{2}$$

$$4[Ru(bpy)_3]^{3+} + 2H_2O \xrightarrow{catalyst} 4[Ru(bpy)_3]^{2+} + O_2 + 4H^+ \tag{3}$$

Due to the oxygen-evolving rate leveled off with the consumption of persulfate, we have determined QE over the first 30 min of the reaction.[9−11] To our delight, an unprecedented high value of 84% was afforded by $[CD\text{-}Ru(bpy)_3]^{2+}/\textbf{1}$ under the conditions applied for visible-light irradiation. Our result is comparable to the best QE value reported so far for visible light water oxidation.[11] Compared with $[Ru(bpy)_3]^{2+}$/cobalt cubane system, the current system clearly shows the advantage of benign reaction conditions, such as the neutral pH, reduced sensitizer/catalyst ratio (15:1 vs 55:1), and the use of less organic solvent (10% vs 50%).[11] The values of QE showed a dependence on the interaction between active components, consistent with the trend observed for TONs in different systems. For instance, only 21% was obtained by $[CD\text{-}Ru(bpy)_3]^{2+}/\textbf{2}$ system, and even lower QEs were found for the separate systems such as $[Ru(bpy)_3]^{2+}/\textbf{1}$ and $[Ru(bpy)_3]^{2+}/\textbf{2}$ (Table 1).

On the basis of eqs 1−3 and Hill's study on $[Ru(bpy)_3]^{2+}/S_2O_8^{2-}$ system, the quantum yield (Φ) as well as the QE can be related to the quenching efficency (Φ_q) and chemical yield (Φ_c) according to eqs 4 and 5.[10] Herein, Φ_2 and Φ_3 represent the efficiencies of eq 2 and 3, respectively.

$$\Phi = \Phi_q \Phi_c \tag{4}$$

$$\Phi_c = 0.5(1 + \Phi_2)\Phi_3 \tag{5}$$

The quenching efficiency of the excited $*[CD\text{-}Ru(bpy)_3]^{2+}$, which increases with the increasing of $Na_2S_2O_8$, was determined by steady-state luminescence to be 92% in the presence of 66.7 mM $Na_2S_2O_8$ (Figure S22). Although it has been reported that the static quenching of the emission of $*[Ru(bpy)_3]^{2+}$ within the closely interacted catalyst/sensitizer pair would compete with the primary photoreaction shown in eq 1,[21] in our case, only small fraction of $[CD\text{-}Ru(bpy)_3]^{2+}$ appears to bond with **1** (estimated to be 4% by spectrofluorimetry, Figure S23) at the molar ratio of 15:1, which imposes very little effect on Φ_q. In addition, the efficiency of $[CD\text{-}Ru(bpy)_3]^{2+}$ reacting with sulfate radical was also expected to be near unity (Φ_2).[10] The overall efficiency would thus be determined by the efficiency of the dark reaction (Φ_3).

The kinetics of eq 3 were investigated by stopped-flow technique in the presence of 15 equiv $[CD\text{-}Ru(bpy)_3]^{3+}$ as the chemical oxidant. As shown in Figure 3, the reduction of [CD-
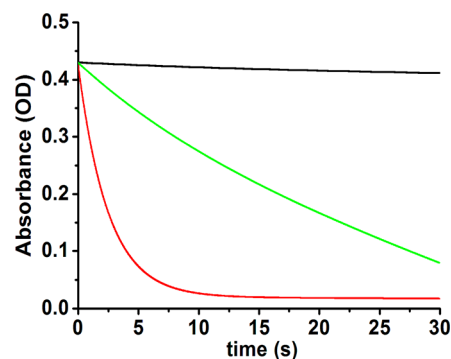

Figure 3. Stopped-flow kinetics of chemical oxidation of water with $[CD\text{-}Ru(bpy)_3]^{3+}$ as the oxidant in phosphate solutions (pH 7.1, 10% CH_3CN). The reduction of $[CD\text{-}Ru(bpy)_3]^{3+}$ (1.5 mM) to $[CD\text{-}Ru(bpy)_3]^{2+}$ was recorded as the decay at 675 nm in the absence of catalyst (black) and in the presence of 0.1 mM catalyst (green: $[Ru(bda)(pic)_2]$, red: **1**).

$Ru(bpy)_3]^{3+}$ to $[CD\text{-}Ru(bpy)_3]^{2+}$ was monitored by the decay of its characteristic absorption at 675 nm. In the absence of catalyst, $[CD\text{-}Ru(bpy)_3]^{3+}$ persists in the time scale of experiment (30 s) without significant decay. The decay of $[CD\text{-}Ru(bpy)_3]^{3+}$ is accelerated by the addition of $[Ru(bda)(pic)_2]$, showing a half-life of 12 s. A similar half-life was obtained for $[Ru(bpy)_3]^{3+}$ in the noninteraction system of $[Ru(bpy)_3]^{3+}/\textbf{1}$ (Figure S24). Upon the addition of **1** to $[CD\text{-}Ru(bpy)_3]^{3+}$, a much faster reaction takes place with the half-life greatly reduced to 1.5 s. Under above reaction conditions, oxygen was found to be nearly quantitatively produced by $[CD\text{-}Ru(bpy)_3]^{3+}/\textbf{1}$ with an initial TOF of 0.13 s^{-1}. In comparison, the initial TOF values for both noninteraction systems are close to 0.07 s^{-1}, and the produced oxygen is not quantitative, indicative of the presence of nonproductive routes such as the decomposition of sensitizer or catalyst that compete with catalytic oxygen evolution (Figure S25). From these results, the remarkable QE of supramolecular system could be reasonably attributed to its high chemical efficiency Φ_3. As $[Ru(bpy)_3]^{3+}$

has been known to be unstable at pH 7 and the catalyst is possible to be deactivated under the harsh oxidative conditions,[22] fast electron transfer from catalytic site to photogenerated oxidant within the assembly apparently offers advantage to minimize the decomposition of both components.[11,21] However, the inclusion behavior between catalyst and sensitizer occurs not only in their rest states but also in their oxidative states (e.g., $Ru^{III}-OH$ and $Ru^{IV}=O$). To fully understand the effect of host−guest binding on each step of the entire catalytic cycle, a more detailed study on the kinetics of electron transfer processes is clearly needed.

In summary, cyclodextrin modified $[Ru(bpy)_3]^{2+}$ and phenyl modified $[Ru(bda)(pic)_2]$ were self-assembled by host−guest interaction in neutral aqueous buffer solution. In the presence of electron acceptor, $[CD-Ru(bpy)_3]^{2+}/\mathbf{1}$ showed enhanced activity for visible light-driven water oxidation relative to the analogous noninteraction system. The high activity due to the facile electron transfer within photosensitizer-catalyst supermolecule is in line with a high QE of 84% at 450 nm. The noncovalent strategy developed here implies the potential application of sensitizer-catalyst assembly in a Z-scheme artificial photosynthetic system or a dye-sensitized photoelectrochemical cell for the purpose of overall water splitting.[23,24]

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Synthesis, characterization of the related complexes, and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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