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Water Splitting

Towards A Solar Fuel Device: Light-Driven Water Oxidation Catalyzed by a Supramolecular Assembly**

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Direct utilization of sunlight to split water into oxygen and hydrogen by artificial photosynthesis is an ideal way to convert solar energy into a fuel.[1] In principle, development of photoelectrochemical (PEC) cells that combine a photoanode, at which the photooxidation of water occurs, and a cathode, where the hydrogen is produced, is a promising strategy for overall water splitting.[2] Since water oxidation as a half-reaction is considered to be the energy demanding bottleneck in the construction of such solar fuel devices, artificial photosynthetic systems for light-driven water oxidation with high efficiency is highly desirable.

Recently, light-driven water oxidation catalyzed by molecular ruthenium complexes[3–8] as well as earth-abundant-metal complexes[9–11] has been demonstrated by our group and others using the photochemically generated oxidant $[Ru(bpy)_3]^{3+}$ (bpy = 2,2′-bipyridine) in homogeneous systems in the presence of sacrificial electron acceptors. However, almost all systems reported so far were based on three components: catalyst, photosensitizer, and acceptor. There may be complex problems such as charge transport kinetics when such an intermolecular system moves to a PEC cell. In this respect the synthetic supramolecular assembly of a covalently linked photosensitizer and catalyst has practical advantages in constructing light-driven water splitting devices. Such assemblies are expected to provide fast intramolecular electron transfer, and be convenient for immobilization on electrodes.[12–14] Mallouk has made a PEC cell wherein $[Ru(bpy)_3]^{2+}$ is modified with malonate ligands and covalently connected with IrO_2 nanoparticles. The rate of electron transfer in this dye/IrO_2 assembly was shown to be significantly faster than it is for the unbound dyes and IrO_2 colloids.[15] However, an active molecular photosensitizer/catalyst assembly for light-driven water oxidation is still not achievable even though great efforts have been made in past years.[2]

Our recent research work on water oxidation showed that the mononuclear Ru^{II} complex $[RuL(pic)_2]$ (H_2L = 2,2′-bipyridine-6,6′-dicarboxylic acid; pic = 4-picoline) is a highly active catalyst with Ce^{IV} as the chemical oxidant, and it can drive water oxidation by visible light in a three-component system which includes a photosensitizer and a sacrificial electron acceptor.[16,8a] As a result of the strong electron-donating character of the ligand, the onset potential for water oxidation catalyzed by $[RuL(pic)_2]$ was observed at approximately 1.0 V vs. NHE at pH 7 by means of cyclic voltammetry, and is significantly lower than that for the Ru^{II}/Ru^{III} redox couple of the ruthenium diimine photosensitizer (for example $E_{1/2} = 1.26$ V vs. NHE for $[Ru(bpy)_3]^{2+}$). Thus, light-driven water oxidation activated by $[RuL(pic)_2]$ is favorable in view of the thermodynamics. These results prompted us to build the supramolecular photosensitizer catalyst assembly by coupling the ruthenium diimine chromophore with the $[RuL(pic)_2]$ catalyst. Herein, we present the preparation and photocatalytic properties of two supramolecular assemblies (Figure 1), one of which demonstrates activity for water splitting in a homogeneous solution.

For synthetic simplicity, we decided to introduce the photosensitizer to the catalyst from its axial ligands. Firstly, the $[Ru(bpy)_3]^{2+}$ derivative was chosen as a photosensitizer unit for the assembly design of **1** (Figure 1). Through a known procedure,[17] pyridine was attached to $[Ru(bpy)_3]^{2+}$ through a methylene amide bridge. Two equivalents of this precursor

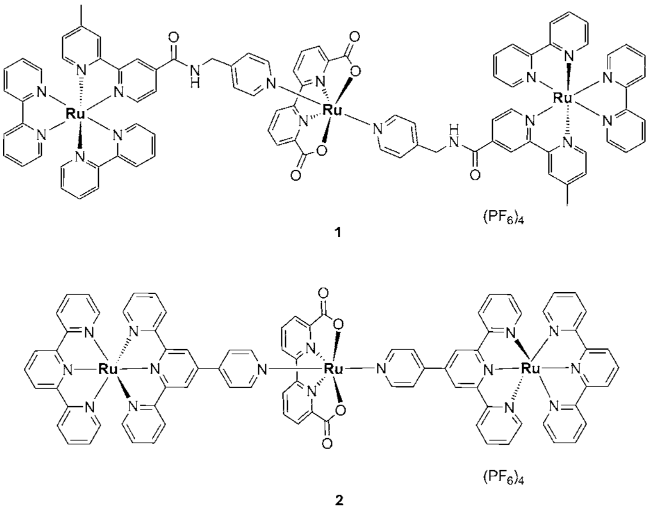

Figure 1. Structures of ruthenium molecular assemblies **1** and **2**.

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were additioanly reacted with bipyridine dicarboxylic acid and $[Ru(DMSO)_4Cl_2]$ (DMSO = dimethylsulfoxide) in the presence of a base to obtain the target trinuclear ruthenium assembly **1**. Secondly, for comparison, $[Ru(tpy)_2]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine) was used as a photosensitizer to couple to the catalyst (**2**, Figure 1) since a related report by Rocha et al. has shown that $[Ru(tpy)_2]^{2+}$ is an efficient metal-to-ligand charge-transfer (MLCT) pump in an assembly including a photosensitizer catalyst and dyads for photocatalytic oxidation of alcohols involving a two-electron/two-proton coupled process.[18] The trinuclear ruthenium assembly **2**, having a relatively rigid structure, was synthesized through a similar procedure as described for **1** with functionalization of pyridyl group at the 4′-position of the terpyridine ligand as a precursor.

Both assemblies were fully characterized by ^{1}H NMR spectroscopy, as well as ESI/MS and elemental analysis (see Figures S2–S7 in the Supporting information). The ^{1}H NMR spectrum of **1** shows that the proton resonances of the equatorial ligand, L, are embedded in a series of aromatic resonances arising from the sensitizer fragment. In **2**, protons on the equatorial ligand are assigned to the doublet and triplet at $\delta = 8.88$ and 8.05 ppm, respectively, by comparison to the NMR spectrum of the precursor $[Ru(tpy)(py\text{-}tpy)](PF_6)_2$ (py-tpy = 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine). In both cases, the pattern and integration of the ^{1}H NMR signals agree well with C_2-symmetric structures of each catalytic unit linked to two photosensitizers from axial positions. For **1**, the ESI/MS signals at $m/z = 444.89$, 641.51, and 1034.76 are assigned respectively to the species of $[M{-}4PF_6]^{4+}$, $[M{-}3PF_6]^{3+}$, and $[M{-}2PF_6]^{2+}$. A series of cationic species with different charges are also observed for **2** in the ESI/MS spectrum.

The electrochemistry of the two supramolecular assemblies was characterized in a phosphate buffer (pH 6.8) solution by cyclic voltammetry, which displays similar electrochemical behaviors. For **1**, a redox couple of $Ru_{cat}^{II}/Ru_{cat}^{III}$ is observed at 0.74 V vs. NHE (all potentials are reported versus NHE) (Figure 2). The onset potential for water oxidation starts at 0.96 V, which is very close to that of the catalyst alone and indicates that the catalytic property of the catalyst unit in the supermolecule is not perturbed much by linking it to photosensitizers.[8a] In addition, two anodic waves attributed to $Ru_{cat}^{III}/Ru_{cat}^{IV}$ at 1.0 V and $Ru_{cat}^{IV}/Ru_{cat}^{V}$ at 1.19 V are detected by differential pulse voltammetry (DPV). The $Ru_{ps}^{II}/Ru_{ps}^{III}$ redox couple of the photosensitizer unit occurs at 1.42 V at the onset of the catalytic water oxidation wave,[19] which is similar to that of sensitizer precursor alone (Figure 2), thus implying that the $[Ru(bpy)_3]^{3+}$ unit, as the oxidized form of the photosensitizer, is able to drive water oxidation in the supramolecular assembly with a driving force of over 400 mV. For **2**, the corresponding $Ru_{cat}^{II}/Ru_{cat}^{III}$ redox couple is observed at 0.79 V (see Figure S8 in the Supporting Information). The anodic waves of $Ru_{cat}^{III}/Ru_{cat}^{IV}$ at 1.04 V and $Ru_{cat}^{IV}/Ru_{cat}^{V}$ at 1.21 V, followed by $Ru_{ps}^{II}/Ru_{ps}^{III}$ which appears at higher potential (1.43 V), are observed at the onset of water oxidation. These data again demonstrate the thermodynamic feasibility of driving water oxidation by the photogenerated $[Ru(tpy)_2]^{3+}$ in **2**.

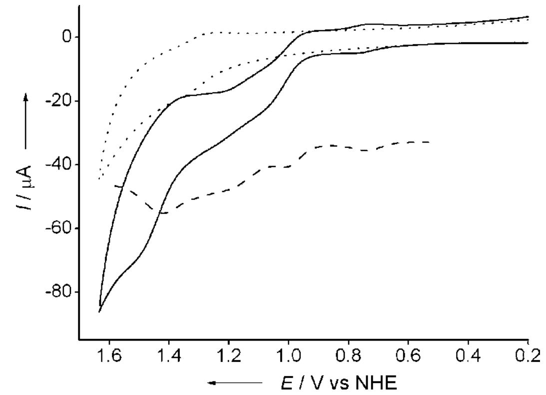

Figure 2. Cyclic voltammograms of **1** (solid line), its photosensitizer precursor $[Ru(bpy)_2(py\text{-}bpy)](PF_6)_2$ (dotted line), and differential pulse voltammogram of **1** (dashed line). Conditions: 5×10^{-4} M sample in 5 mL phosphate buffer solution (pH 6.8, containing 10% acetonitrile) at a scan rate of 100 mV s^{-1} for CV, and with a step potential of 5 mV and an amplitude of 50 mV for DPV.

The intensive electronic absorption bands at $\lambda = 460$ and 490 nm, assigned to the MLCT bands of the photosensitizer units, are observed in respective UV-Vis spectra of **1** and **2** in aqueous solution (see Figures S10–S13 in the Supporting Information). Since these bands strongly overlap with the absorptions of the catalytic unit, absorption spectra show no difference between the assembly and the corresponding precursor. The steady-state emissions of both assemblies show efficient excited state quenching (95%), which is typical for the supermolecules having strong interactions between different fragments.

The photocatalytic experiment was performed in a degassed phosphate buffer solution (pH 6.8, 10% acetonitrile) containing **1** (2.0×10^{-5} M) and sodium persulfate as the sacrificial electron acceptor (5.0×10^{-2} M). Upon irradiation with visible light ($\lambda > 400$ nm), molecular oxygen formed quickly from water and the oxygen evolution was monitored by a Clark-type oxygen electrode. According to an oxygen evolution versus time plot, the TOF (turnover frequency) in the liquid phase was calculated to be 4.7 min^{-1} (see Figure S14 in the Supporting Information). Control experiments confirm that all three factors of light, assembly, and sacrificial reagent are necessary for efficient water oxidation. It is also found that each unit in the assembly is essential to photocatalysis, since replacement of **1** with $[Ru(bpy)_2(py\text{-}bpy)]^{2+}$ (py-bpy = 2-(4-methyl-2-pyridyl)-*N*-(4-pyridylmethyl) isonicotinamide) or $[RuL(pic)_2]$ did not lead to oxygen evolution under the above-mentioned experimental conditions (Figure 3a).

An important question here is whether the assembly results in effective oxygen evolution by linking light-harvesting and water-oxidation components. To address this issue, comparison experiments were carried out by employing a combined system and a separate system, respectively (Figure 3b). Upon illumination of a solution containing 5.0×10^{-5} M of **1** and 5.0×10^{-2} M of sodium persulfate for 70 minutes, the evolved oxygen in the headspace of the reactor was quantified by gas chromatography to be 38 TN (turnover number). To make a reasonable comparison,

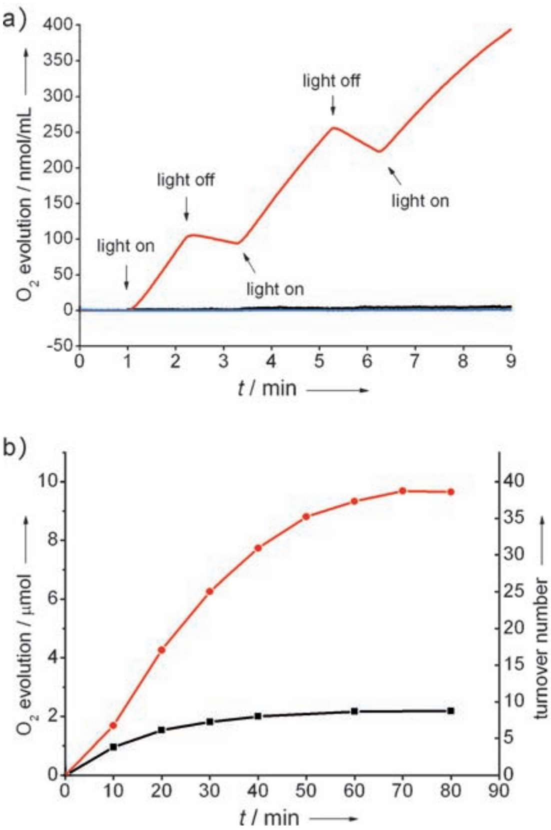

Figure 3. a) Control experiments of the photocatalytic water oxidation in 2 mL phosphate buffer solutions (initial pH 6.8) of **1** (2×10^{-5} M) (red), [RuL(pic)$_2$] (2×10^{-5} M) (blue), and [Ru(bpy)$_2$(py-bpy)](PF$_6$)$_2$ (4×10^{-5} M) (black) in the presence of $Na_2S_2O_8$ (5×10^{-2} M). The oxygen evolution was recorded by a Clark-type oxygen electrode. b) Oxygen evolution measured by GC in a 5 mL phosphate buffer solution (pH 6.8) employing either a combined system consisting of **1** (5×10^{-5} M) and $Na_2S_2O_8$ (5×10^{-2} M) (red) or a multicomponent system consisting of [RuL(pic)$_2$] (5.0×10^{-5} M), $[Ru(bpy)_3]^{2+}$ (10^{-4} M), and $Na_2S_2O_8$ (5.0×10^{-2} M) (black) under the same visible light illumination.

a separate system consisting of [RuL(pic)$_2$] (5.0×10^{-5} M), $[Ru(bpy)_3]^{2+}$ (10^{-4} M), and sodium persulfate (5.0×10^{-2} M) was illuminated under the same light source, and showed an activity of 8 TN, which is 5 times lower than that observed for the combined system. Based on these results, we attribute the superior activity of the molecular assembly to the intramolecular electron transfer between the catalytic center and the $[Ru(bpy)_3]^{3+}$ units that are generated through the oxidative quenching of the excited state $[Ru(bpy)_3]^{2+*}$ by $S_2O_8^{2-}$.[20] The photocatalytic reaction catalyzed by **1** was monitored by ESI/MS analysis, which indicates that the decrease of the water oxidation rate correlates to a slow decomposition process resulting from the dissociation of the sensitizer component $[Ru(bpy)_2(py\text{-}bpy)]^{2+}$ from the assembly (see Figure S15 in the Supporting Information). Therefore the improved activity for the combined system benefits from the integrated supermolecule but not from any decomposed species.

In contrast to **1**, no oxygen formation was detected in the system containing **2**. Additional experiments show that the light-driven water oxidation occurs upon addition of $[Ru(bpy)_3]^{2+}$ to the solution of **2** and persulfate. This means that the activity of **2** is limited by kinetic reasons. Since the lifetime of the $[Ru(tpy)_2]^{2+}$ excited state is known to be significantly short compared to that of $[Ru(bpy)_3]^{2+}$,[21] poor electron transfer between the photosensitizer and the external electron acceptor is likely to be responsible for the inactivity of **2** in photocatalysis. However, activity for water oxidation might change if a faster oxidative quenching process can be secured by, for example, immobilizing **2** on nanostructured TiO_2 surface. Work along these lines is in progress.

In conclusion, for the first time an active light-driven water oxidation assembly has been constructed by matching two light-harvesting sites and one catalytic site in a supramolecular system and exhibits enhanced photocatalytic activity compared with conventional multicomponent system. Although the photocatalytic activity is limited by ligand dissociation, this study demonstrates the possible application of such simple assembly in photocatalytic oxygen evolution and is very important to the development of visible-light-driven dye-sensitized PEC cells based on tunable molecular catalysts. The development of more stable photosensitizer/catalyst assemblies aiming at highly efficient visible-light-driven water oxidation on semiconductor electrode surfaces is currently under investigation in our lab.

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