Journal of Photochemistry and Photobiology A: Chemistry 321 (2016) 151–160

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

# Photochemical water oxidation system using ruthenium catalysts embedded into vesicle membranes

Yoichi Sato[a], Shin-ya Takizawa[b], Shigeru Murata[b,*]

[a] Department of Chemistry, Graduate School of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan
[b] Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Meguro-ku, Tokyo 153-8902, Japan

ARTICLE INFO

*Article history:*
Received 3 October 2015
Received in revised form 29 January 2016
Accepted 1 February 2016
Available online 4 February 2016

*Keywords:*
Water oxidation
Vesicle
Ruthenium
Oxygen production

ABSTRACT

Vesicles, approximately spherical bilayer membranes formed by self-organization of phospholipids, have been employed as reaction fields to construct artificial systems capable of converting light energy into chemical potential. To gain information about the performance of water oxidation catalysts in vesicular membranes, the complex [Ru(bda)(pyCO$_2$Ocd)(pyCO$_2$Me)] ($H_2$bda = 2,2′-bipyridine-6,6′-dicarboxylic acid, pyR = pyridine having a substituent R at the 4-position, Ocd = $(CH_2)_{17}CH_3$) was newly synthesized, and photochemical water oxidation using the complex embedded into vesicle membranes as a catalyst was investigated in an aqueous solution containing a sensitizer $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) and a sacrificial electron acceptor $S_2O_8^{2-}$. At first, the dependence of the initial rate of $O_2$ production, $v_i$, on the concentration of $[Ru(bpy)_3]^{2+}$, as well as $S_2O_8^{2-}$, was investigated to find optimum conditions to examine the performance of the catalyst. Subsequently, the dependence of $v_i$ on the catalyst concentration was examined in the vesicular system, indicating that $v_i$ increased approximately linearly with the catalyst concentration up to ~30 μM, and declined after that. The turnover frequency for $O_2$ production with respect to the catalyst was evaluated to be 39.1 $h^{-1}$, which was larger than that in similar systems in a homogeneous solution by a factor of more than two. The reason for the linear dependence of $v_i$ on the catalyst concentration, as well as the superior performance of the catalyst in the vesicular system, was discussed on the basis of the mechanism accepted generally for the water oxidation catalyzed by related Ru complexes.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

In naturally occurring photosynthesis in green plants, algae, or bacteria, the following endoergic redox reaction with a positive free-energy change is driven by solar energy [1,2].

$$2H_2O + 2NADP^+ \rightarrow O_2 + 2NADPH + 2H^+ \quad (1)$$

The resulting reduced nicotinamide adenine dinucleotide phosphate (NADPH) is then used in the Calvin cycle for reduction of $CO_2$ to carbohydrates. To meet the global energy demands, research on the construction of an artificial photosynthetic system capable of converting solar energy into fuels becomes increasingly important [3,4]. In particular, much effort has been devoted to developing systems capable of splitting $H_2O$ into $H_2$ and $O_2$ using solar energy [5–7]. Typically, in a photochemical water-splitting system, a sensitizer can absorb a photon to form a charge-separated state by transferring an electron to a catalyst for reduction of $H^+$ to $H_2$, and regenerate by transfer of an electron from a catalyst for oxidation of $H_2O$ to $O_2$. Although significant progress has been made in the field of molecular catalysts for both reduction [8] and oxidation [9] of $H_2O$ during the past decade, there still remains much to be done for the construction of molecular-based photochemical water splitting systems.

In natural photosynthetic systems, the photoinduced redox reaction denoted by Eq. (1) proceeds using the phospholipid bilayer membranes as a reaction field. Solar energy is absorbed by sensitizers embedded in the membranes, and induces an electron transfer from a water oxidation catalyst located at the membrane-water interface close to the inner aqueous phase to a hydrogenase catalyst for the $NADP^+$ reduction in an outer aqueous phase. The total electron transfer proceeds across the bilayer membranes, which causes the oxidative and reductive reactions in different phases separated by the bilayer membranes. Thus, the photosynthetic membranes play an essential role in natural photosynthesis, which not only support molecules that participate in light absorption and charge separation, but also

* Corresponding author. Fax: +81 3 5454 6998.
*E-mail address:* cmura@mail.ecc.u-tokyo.ac.jp (S. Murata).

http://dx.doi.org/10.1016/j.jphotochem.2016.02.003
1010-6030/© 2016 Elsevier B.V. All rights reserved.

act as a barrier to inhibit the recombination reaction between photogenerated oxidizing and reducing species. Therefore, bilayer membranes are thought to be a fascinating reaction field to construct artificial systems mimicking a natural photosynthetic system. In fact, since 1970s, studies of photoinduced electron transport across bilayer membranes converting light energy into electrochemical energy of a persistent charge-separated state have been done using vesicles as a reaction field [10–12]. Vesicles are approximately spherical bilayer membranes formed by self-organization of amphiphiles, such as phospholipids, in an aqueous medium [13]. Moreover, vesicular systems for photocatalytic hydrogen production [14–16] and photochemical reduction of $CO_2$ [17] in aqueous solutions have recently been reported. By the use of vesicles, sensitizers and catalysts insoluble in water can be dispersed in a bulk aqueous solution by incorporating them into hydrophobic membranes of vesicles. Furthermore, the incorporation of sensitizers and catalysts into vesicle membranes causes a high local concentration of these molecules, which may enhance the efficiency of electron transfer processes among them.

In order to construct a molecular-based photochemical water splitting system using vesicles as a reaction field, it is absolutely necessary to explore molecular catalysts for water oxidation which can be incorporated into vesicle membranes and exhibit a good performance under photochemical conditions. Very recently, Sun and König reported the first vesicular system for photocatalytic water oxidation, in which both $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) and $[Ru(pda)(mpy)_3]$ ($H_2pda$ = pyridine-2,6-dicarboxylic acid, mpy = 4-methylpyridine) derivatives having hydrophobic alkyl chains acting as a photosensitizer and a water oxidation catalyst, respectively, are embedded into the phospholipid bilayer membranes of vesicles [18,19]. They demonstrated that the photochemical production of $O_2$ in this vesicular system is comparable to similar systems in homogeneous solutions, but superior at low concentration of the catalysis. Although their pioneering work suggests that clustering of the complexes in the bilayer membranes might facilitate the electron transfer process, we need more information on the performance of water oxidation catalysts in bilayer membranes to construct vesicular systems capable of splitting water using light energy. Here, we report on another vesicular system for photocatalytic water oxidation, in which only a catalyst is embedded into bilayer membranes, and a sensitizer and a sacrificial electron acceptor are located in an outer aqueous phase. Compared with the precedent system where a catalyst is co-embedded with a sensitizer into bilayer membranes [18], our system is favorable for understanding the effect of incorporation of the catalysts into bilayer membranes on the photochemical $O_2$ production. In order to gain information on the mechanism of the photocatalytic reaction and to search for optimum conditions for the $O_2$ production, we examined the dependence of the reaction efficiency on the concentrations of sensitizer, sacrificial electron acceptor, and catalyst.

## 2. Experimental

### 2.1. General information

$^1$H NMR spectra were recorded on a Bruker AVANCE 500 spectrometer. Chemical shifts were referenced to tetramethylsilane ($SiMe_4$). Melting points (m.p.) were recorded on YAZAWA BY-2. Elemental analysis was performed using a YANACO CHN corder MT-6 at the Microanalytical Laboratory (Department of Chemistry, The University of Tokyo). Electrospray ionization time-of-flight (ESI-TOF) mass spectra were obtained using a Waters Xevo G2-S Tof mass spectrometer. UV–vis absorption spectra were recorded on a JASCO V-560 spectrometer. Emission spectra were recorded on a JASCO FP-777 spectrofluorometer with a 200 nm min$^{-1}$ scanning speed and a 1.5 nm bandwidth. Emission lifetime measurements were carried out on a compact fluorescence lifetime spectrometer (Quantaurus-Tau C11367-01, Hamamatsu Photonics). Gas chromatography (GC) was performed using GC7000TF (J-Science Lab. Co., Ltd.) with a thermal conductivity detector and an activated carbon column (3 m × 3 mm).

### 2.2. Chemicals

The known complex **2** [20], as well as 2,2′-bipyridine-6,6′-dicarboxylic acid ($H_2bda$) [21], $Ru(DMSO)_4Cl_2$ [22], methyl isonicotinate ($pyCO_2Me$) [23] and octadecyl isonicotinate ($pyCO_2Ocd$) [24], was synthesized according to literature procedures. $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ and sodium ascorbate (AscNa) were purchased from Tokyo Kasei Kogyo Co., Ltd., and $Na_2S_2O_8$ was purchased from Wako Pure Industries Ltd., and these reagents were used without purification. Spectrum grade organic solvents and distilled water used for spectroscopic measurements and water oxidation experiments were purchased from Wako Pure Industries Ltd.

### 2.3. Synthesis of [Ru(bda)(pyCO$_2$Ocd)(pyCO$_2$Me)] (1)

To a suspension of $H_2bda$ (48.9 mg, 200 μmol) and $[Ru(DMSO)_4Cl_2]$ (97.4 mg, 201 μmol) in MeOH (4 mL) degassed by $N_2$-bubbling, trimethylamine (160 μL, 1.1 mmol) was added under $N_2$ atmosphere. After refluxing for 7 h, the mixture was filtered and the residue was washed with cold MeOH to give brown solid containing $[Ru(bda)(DMSO)_2]$. To a suspension of the solid in THF (4 mL) degassed by $N_2$-bubbling was added a solution of $pyCO_2Ocd$ (148 mg, 394 μmol) and $pyCO_2Me$ (52.2 mg, 381 μmol) in THF (4 mL), and then the mixture was refluxed for 2 d under $N_2$ atmosphere. The resulting mixture was concentrated under reduced pressure, and the residue was developed on an aluminum column chromatography with $CH_2Cl_2$–methanol (50:1–20:1) eluent to give **1** (47 mg, 27%) as dark red powder: m.p. > 300 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.6 Hz, 2H), 8.12 (d, *J* = 7.6 Hz, 2H), 8.00 (d, *J* = 6.0 Hz, 2H), 7.99 (d, *J* = 6.0 Hz, 2H), 7.78 (t, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 6.0 Hz, 4H), 4.27 (t, *J* = 6.5 Hz, 2H), 3.89 (s, 3H), 1.69 (quin, *J* = 6.5 Hz, 2H), 1.25 (brs, 30H), 0.88 (t, *J* = 6.5 Hz, 3H); ESI-TOF mass *m/z* 857.29 $[M + H]^+$; Anal. Calcd for $C_{43}H_{54}N_4O_8Ru{\cdot}2H_2O$: C, 57.90; H, 6.55; N, 6.28. Found C, 57.81; H, 6.26; N, 6.14.

### 2.4. Vesicle preparation

A $CHCl_3$ solution of **1** (0.52 μmol) and DPPC (12 μmol) was concentrated under reduced pressure to form a thin film in a flask. The film was dried under vacuum overnight, and then dispersed in borate buffer (40 mM, pH 8.0) by vortex mixing (Shibata, TTM-1) at 50 °C. The dispersion was treated with ultrasonic process (Iwaki, USC-100Z38S-22) for 90 min at 55–60 °C under Ar. The resulting solution was developed on a column with Sephadex G-50 (Amersham Biosciences) equilibrated with borate buffer to remove **1** outside the vesicles, and the fraction containing the phospholipids was collected to give a vesicle solution (11.4 mL). The concentration of **1** in the vesicle solution was evaluated as follows; to the vesicle solution (3.00 mL) was added AscNa (13.1 mg, 66.1 μmol) and MeOH (*ca.* 3 mL), and the reaction mixture was extracted with $CH_2Cl_2$. After the organic layer was dried over $Na_2SO_4$, the solvent was removed under reduced pressure and the residue was dissolved in $CHCl_3$ (5.00 mL). The UV–vis absorption spectrum of the solution was recorded, and the concentration of **1** was calculated by the absorbance at the wavelength of its maximal absorption and its molar extinction coefficient (15,500 M$^{-1}$ cm$^{-1}$ at 462 nm).

Download English Version:

https://daneshyari.com/en/article/26263

Download Persian Version:

https://daneshyari.com/article/26263

Daneshyari.com