doi:10.1246/cl.2011.345

Hydrogen Generation Using a Photoinduced Electron-transport System with a Molecular Catalyst in Vesicles

Kentaro Watanabe, Shin-ya Takizawa, and Shigeru Murata*
Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo,
Meguro-ku, Tokyo 153-8902

(Received December 15, 2010; CL-101063; E-mail: cmura@mail.ecc.u-tokyo.ac.jp)

We constructed a novel H_2 generation system mimicking natural photosynthesis, in which an electron is transported photochemically from ascorbate entrapped in the inner waterpool of vesicles to MV^{2+} dissolved in the outer aqueous solution and relayed to a Pt(II) complex embedded in the vesicle membrane that acts as a molecular catalyst.

Artificial molecular systems capable of converting light energy into chemical potential attract great interest relating to current energy and environmental problems.[1] Among these systems is a photochemical system for the generation of H_2 by reduction of water. Numerous studies have been done on photoinduced H_2 generation systems composed of a photosensitizer (usually $[Ru(bpy)_3]^{2+}$), methyl viologen (MV^{2+}) as an electron mediator, a sacrificial electron donor such as triethanolamine (TEOA), and a colloidal metal catalyst.[2] Recently, photochemical H_2 generation systems using a Pt(II)- and Co(III)-based molecular catalyst in place of metal colloids have been reported.[3,4] However, systems using sacrificial electron donors are of no significance from the viewpoint of light energy conversion and storage, because a large amount of chemical energy would be lost by an irreversible decomposition of oxidized donors. To construct photochemical systems for H_2 generation using electron donors capable of undergoing reversible redox cycles, a design to prevent charge recombination would be required.

Recently, we reported that pyrene derivatives embedded in phosphatidylcholine vesicle bilayers induced photochemically electron transport from ascorbate (Asc^-) entrapped in the inner waterpool to MV^{2+} dissolved in the outer aqueous solution.[5] Asc^- undergoes a reversible redox reaction with semidehydroascorbate ($Asc^\bullet$), which disproportionates to give dehydroascorbate and Asc^-.[6] The free-energy change for the total redox reaction of our electron-transport system is estimated to be $+12.7\,\mathrm{kcal\,mol^{-1}}$.[7] Thus, although this system cannot work using visible light, it appears to be one of the most faithful models of natural photosynthesis in that an electron is transferred with the aid of light energy between two reversible redox couples in the energetically uphill direction through lipid bilayer walls preventing charge recombination. Attempts to construct a photochemical system for H_2 generation by linking this system with a colloidal platinum catalyst gave unsatisfactory results, which were due to undesirable interaction between the vesicle membrane and the surfactants protecting the surface of platinum particles.[8] After examination of various conditions to link the photoinduced electron-transport system with a catalytic H_2 generation reaction, we found that certain Pt(II) complexes served as efficient catalysts. In this paper, we report a novel photochemical H_2 generation system, which is made up by the photoinduced electron-transport system using an electron donor capable of undergoing reversible redox cycles and a newly designed Pt(II)-based molecular catalyst embedded into the vesicle membrane.

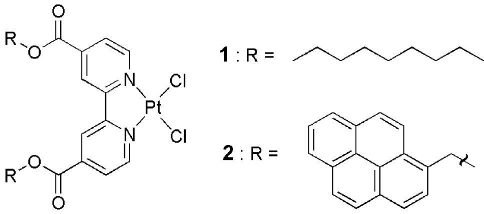

Chart 1.

On the basis of the fact that some mononuclear Pt(II) complexes bearing a *cis*-$[PtCl_2(pyridine)_2]$ unit are active as catalysts for H_2 generation,[3] we designed two types of novel Pt(II) complexes. The complex **1** has hydrophobic alkyl chains to increase solubility in vesicle membranes, while in the complex **2** photosensitizing pyrene moieties are connected with the catalytic unit, which would be expected to act as a single-component system for photochemical H_2 generation (Chart 1). Both complexes **1** and **2** were obtained by the reaction of the corresponding 2,2′-bipyridyl-4,4′-dicarboxylates with *cis*-$[PtCl_2(DMSO)_2]$ in $CHCl_3$ as orange granules that melted at 183–184 and 241–242 °C, respectively, and showed satisfactory spectroscopic properties (Supporting Information, Figures S1 and S2).[9]

Vesicle solutions used for H_2 generation experiments using a photoinduced electron-transport system were prepared as follows: a mixture of complex **1** and 1-(hydroxymethyl)pyrene ($PyCH_2OH$) that acts as a photosensitizer or complex **2** alone was suspended with 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) in 1.0 M Tris-HCl buffer (pH 7.5) containing AscNa (1.0 M). The suspension was sonicated for 2 h at 60 °C and developed by chromatography on a Sephadex G-50 column with a buffer solution containing NaCl (1.0 M). To the solution $MVCl_2 \cdot 3H_2O$ was added to give a vesicle solution with MV^{2+} (10 mM) in an outer aqueous solution. Incorporation of the Pt(II) complex and $PyCH_2OH$ into the vesicle solution was monitored by their characteristic UV absorptions with maxima at 440 and 345 nm, respectively.

A degassed solution (3.0 mL) of vesicles containing **1** (1.4 µM) and $PyCH_2OH$ (17.9 µM) was irradiated with a 500-W xenon arc lamp through a cutoff filter (>350 nm), and the headspace of the cell (1.5 mL) was analyzed by GC equipped with a thermal conductivity detector and an activated carbon column. After an induction period of up to 30 min, H_2 was produced at a constant rate of $0.138\,\mathrm{\mu L\,h^{-1}}$ (Figure S3).[9]

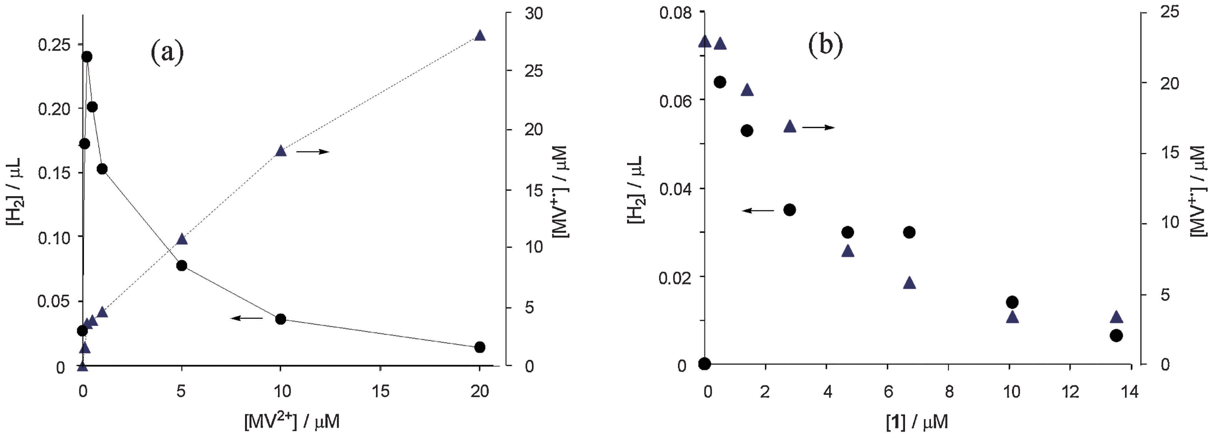

Figure 1. H_2 generation (circle) and $MV^{+•}$ formation (triangle) by irradiation (>350 nm, 2.0 h) of a solution (3.0 mL) of DPPC vesicles containing $PyCH_2OH$ (ca. 20 μM) in hydrophobic bilayers and AscNa in the inner waterpool (1.0 M): (a) Effect of the initial concentration of MV^{2+} dissolved in the outer aqueous phase ([**1**] ≈ 5 μM). (b) Effect of the initial concentration of **1** embedded in vesicle bilayers ($[MV^{2+}] = 10$ mM).

Simultaneously, the reduction of MV^{2+} occurred to yield $MV^{+•}$, which was readily identified by its characteristic dark-blue color. The induction period of the H_2 generation may be due to the fact that sufficient $MV^{+•}$ is not yet accumulated to generate H_2. No significant consumption of $PyCH_2OH$ was observed after irradiation for at least 2 h. The rate of H_2 evolution gradually decreased after continuous irradiation for 12 h, and the dark-blue color of $MV^{+•}$ faded away. On the basis of the total volume of photogenerated H_2 (1.53 μL), the number of turnovers was calculated to be 30 relative to complex **1**.

In order to obtain conditions for efficient H_2 generation, the influence of the initial concentration of MV^{2+} and complex **1** was examined. As shown in Figure 1a, although a small amount of H_2 is detected in the absence of MV^{2+}, the electron-relay species MV^{2+} plays an important role in this H_2 generation system. However, the addition of MV^{2+} in high concentrations retards the H_2 generation, although the photoinduced electron transport across vesicle bilayers proceeds efficiently to yield large amounts of $MV^{+•}$, indicating that the electron discharge from $MV^{+•}$ to complex **1** is not necessarily a rate-limiting step in the total sequence of the H_2 generation. Figure 1b depicts the effect of the concentration of **1** embedded in the vesicle membrane, which could be controlled in the vesicle preparation, on the efficiency of the H_2 generation and $MV^{+•}$ formation at a given concentration of MV^{2+}. Although H_2 is not produced in the absence of **1**, the addition of a small amount of **1** into the vesicle membrane results in effective H_2 generation, and the efficiency of the H_2 generation, as well as the $MV^{+•}$ formation, decreases with an increase in the concentration of **1**. This observation can be interpreted in terms of the quenching of the excited state of $PyCH_2OH$ by **1**, which retards the $MV^{+•}$ formation that is mainly initiated by the reductive quenching of the $PyCH_2OH$ excited state by Asc^- in the inner waterpool.[5]

Figure 2 illustrates the proposed mechanism of the H_2 generation in this system. As discussed previously,[5] the irradiation of $PyCH_2OH$ embedded in the vesicle bilayers induces endoergic electron transport across vesicle bilayers from Asc^- in the inner waterpool to MV^{2+} in the outer aqueous solution to produce $MV^{+•}$. It is supposed that H_2 is formed by the reduction of H_2O catalyzed by the Pt(II) complex **1** embedded in the vesicle membrane using the electrons relayed to **1** by $MV^{+•}$.

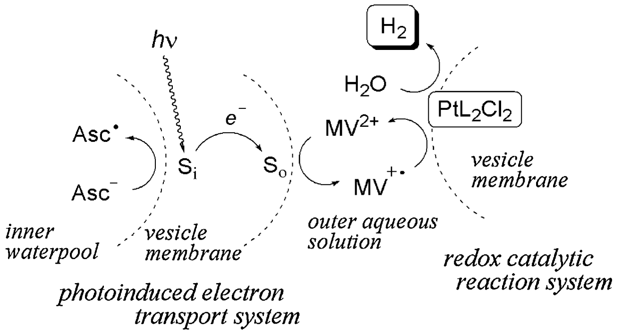

Figure 2. Proposed mechanism for H_2 generation using a photoinduced electron-transport system and a Pt(II) complex in vesicles. S_i and S_o stand for the sensitizers ($PyCH_2OH$) located in the vesicle bilayer close to the inner waterpool and the outer aqueous solution, respectively, and PtL_2Cl_2 stands for the Pt(II) complex **1** embedded in the vesicle membrane.

In contrast to the successful H_2 generation using a $PyCH_2OH$-sensitized electron-transport system with complex **1** as a molecular catalyst, the complex bearing pyrene moieties **2** is found to be ineffective as a photocatalyst for H_2 generation in the vesicular system using Asc^- as an electron donor. Thus, irradiation of a vesicle solution containing **2** (5.5 μM) prepared in an identical manner to that described above, except for using **2** instead of **1** and $PyCH_2OH$ caused neither H_2 generation nor $MV^{+•}$ formation. Based on the fact that the H_2 generation is retarded in high-concentration ranges of **1** embedded in the vesicle membrane (Figure 1b), the ineffectiveness of **2** is probably due to rapid intramolecular quenching of the excited state of the pyrene moieties by the Pt(II) complex. However, we found that the complex **2** serves as a photocatalyst for H_2 generation in the vesicular system using a sacrificial electron donor. To a buffer solution (1.0 M Tris-HCl, pH 7.5, 2.5 mL) of DPPC vesicles, in which **2** (4.4 μM) was embedded in hydrophobic bilayers and AscNa was absent in the inner waterpool, was added MV^{2+} (5.0 mM) and TEOA (0.5 mL). Upon irradiation of the resulting vesicle solution (>350 nm), H_2 generation occurred, along with $MV^{+\bullet}$ formation. After irradiation for 10.5 h, the number of turnovers was estimated to be 51 relative to complex **2** (Figure S4).[9]

In conclusion, a novel H_2 generation system has been constructed using a photoinduced electron-transport system mimicking natural photosynthesis and the Pt(II) complex **1** acting as a molecular catalyst. Further studies on improving the efficiency of the system are now in progress in our laboratory.

References and Notes

1 M. Calvin, *Int. J. Energy Res.* **1979**, *3*, 73; T. J. Meyer, *Acc. Chem. Res.* **1989**, *22*, 163; D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **2001**, *34*, 40; D. Gust, T. A. Moore, A. L. Moore, in *Artificial Photosynthesis: From Basic Biology to Industrial Application*, ed. by A. F. Collings, C. Critchley, Wiley, Weinheim, **2005**, pp. 187–210.

2 M. Kirch, J.-M. Lehn, J.-P. Sauvage, *Helv. Chim. Acta* **1979**, *62*, 1345; J. Kiwi, M. Grätzel, *J. Am. Chem. Soc.* **1979**, *101*, 7214.

3 H. Ozawa, M. Haga, K. Sakai, *J. Am. Chem. Soc.* **2006**, *128*, 4926; H. Ozawa, Y. Yokoyama, M. Haga, K. Sakai, *Dalton Trans.* **2007**, 1197; K. Sakai, H. Ozawa, *Coord. Chem. Rev.* **2007**, *251*, 2753.

4 P. Du, K. Knowles, R. Eisenberg, *J. Am. Chem. Soc.* **2008**, *130*, 12576; T. Lazarides, T. McCormick, P. Du, G. Luo, B. Lindley, R. Eisenberg, *J. Am. Chem. Soc.* **2009**, *131*, 9192.

5 A. Yoshida, A. Harada, T. Mizushima, S. Murata, *Chem. Lett.* **2003**, *32*, 68; T. Mizushima, A. Yoshida, A. Harada, Y. Yoneda, T. Minatani, S. Murata, *Org. Biomol. Chem.* **2006**, *4*, 4336; R. Sasaki, Y. Nako, S. Murata, *Tetrahedron* **2009**, *65*, 7364.

6 D. Njus, P. M. Kelley, *Biochim. Biophys. Acta, Bioenerg.* **1993**, *1144*, 235.

7 For the calculation of free-energy change for the total redox reaction, +0.09 and −0.46 V were emplyed for the redox potentials of $Asc^{\bullet}/Asc^{-}$ (pH 7.0)[6] and $MV^{2+}/MV^{+\bullet}$ (vs. SCE), respectively: S. L. Murov, I. Carmichael, G. L. Hug, *Handbook of Photochemistry*, 2nd ed., Marcell Dekker, New York, **1993**.

8 K. Watanabe, S. Murata, Annual Meeting on Photochemistry 2008, Sakai, Osaka, Japan, September 11–13, **2008**, Abstr., No. 1P99.

9 Supporting Information is available electronically in the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.