

Hydrogen Evolution Using the Visible-light-induced Metal-to-polyoxometalate Multiple Electron Transfer

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A tetranuclear cerium-containing polyoxometalate, $\text{TBA}_6\text{-}[\{\text{Ce}(\text{H}_2\text{O})\}_2\{\text{Ce}(\text{CH}_3\text{CN})\}_2(\mu_4\text{-O})(\gamma\text{-SiW}_{10}\text{O}_{36})_2]$ (**I**, TBA: tetra-*n*-butylammonium), showed a unique intramolecular multiple electron transfer (Ce^{3+} -to- $\text{POM}(\text{W}^{6+})$) on irradiation of visible light ($\lambda > 400$ nm). This could induce hydrogen (H_2) evolution using alcohols as the electron donors, and a high turnover number (TON) of 1960 was achieved. Moreover, **I** could be reused without an appreciable loss in its catalytic performance.

Photocatalytic conversion of light energy into chemical fuels has attracted much attention because of increasing energy demand and environmental issues.^{1,2} Over the past few decades, significant progress has been made in the development of metal oxide- and metal-based photocatalysts.² Compared with these heterogeneous catalysts, the structures and catalytic activities of organometallic complexes and organocatalysts can finely be controlled.³ However, there are concerns about their durability and recyclability. The transformations concerning fuel productions and energy conversions (for example, hydrogen evolution, water oxidation, and CO_2 reduction) generally involve multi-electron processes; therefore, development of efficient molecular systems that can store and release multiple electrons is in great demand.

Polyoxometalates (POMs) are a class of structurally well-defined anionic molecular metal oxide clusters consisting of the group V and VI metals in their highest oxidation states, such as W^{6+} , Mo^{6+} , V^{5+} , and Nb^{5+} .⁴ They are thermally and oxidatively stable in comparison with organometallic complexes and organocatalysts, and their chemical and physical properties can precisely be controlled by their structures and constituent elements. In addition, they can store multiple electrons and reversibly be reduced and reoxidized. Based on these unique properties, POMs are attractive candidates as catalysts for multi-electron systems. Although it has been reported that POMs show good electrocatalytic and photocatalytic performance for hydrogen evolution,^{5,6} to date there have only been a few systems using visible light and the catalytic activities are low (Table S1).⁷ Therefore, there is still room for improvement. Because the O-to-W (ligand-to-metal) charge transfers in POMs are commonly responsive only to ultraviolet light, the development of visible-light-responsive photocatalytic systems based on the O-to-W charge transfers has been considered very difficult.

Very recently, we have reported the visible-light-responsive tetranuclear cerium-containing POM, $\text{TBA}_6\text{-}[\{\text{Ce}(\text{H}_2\text{O})\}_2\{\text{Ce}(\text{CH}_3\text{CN})\}_2(\mu_4\text{-O})(\gamma\text{-SiW}_{10}\text{O}_{36})_2]$ (**I**), synthesized by the reaction of a lacunary $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ POM with $[\text{Ce}(\text{acac})_3]$ (acac: acetylacetonato).^{8,9} In response to visible light ($\lambda > 400$ nm), **I** showed a unique Ce^{3+} -to- $\text{POM}(\text{W}^{6+})$ charge transfer^{10,11} and the reversible reduction–oxidation with preserving the structure. Notably, **I** was the first efficient visible-light-responsive POM-

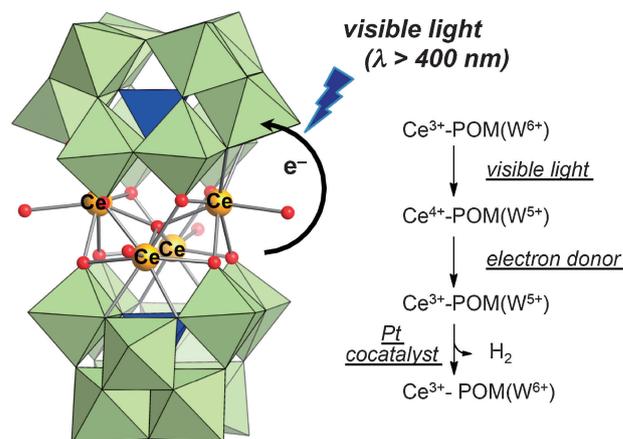


Figure 1. Schematic representations of the visible-light-induced intramolecular charge transfer of **I** and hydrogen evolution.

based photoredox catalyst for chemoselective functional group transformations without any additional sensitizers, and photocatalytic oxidation of primary, secondary, and tertiary amines smoothly proceeded in the presence of O_2 (1 atm) as the sole oxidant.⁸ Herein, we report that **I** shows intramolecular multiple (at least four) electron transfer in the presence of alcohols such as 4-methoxybenzyl alcohol and ethanol as the electron donors, resulting in the remarkable catalytic performance for hydrogen evolution on irradiation of visible light ($\lambda > 400$ nm; Figure 1). To the best of our knowledge, the present catalytic system showed the highest TON among the previously reported systems with visible-light-responsive POMs.⁷

First, we investigated the visible-light-responsive charge transfer in the presence of 4-methoxybenzyl alcohol as the electron donor. When visible light ($\lambda > 400$ nm, 300 W Xe lamp with a 400 nm cutoff filter) was irradiated onto an acetonitrile solution of a mixture of **I** and 4-methoxybenzyl alcohol under Ar (1 atm), the color of the reaction solution changed from reddish brown to dark blue (Figure 2a). The UV–vis spectra showed that the intensities of the absorption bands around 670 and 840 nm, which are assignable to the W^{5+} -to- W^{6+} intervalence charge transfer, increased ($\epsilon = 11900$ (670 nm) and $9400 \text{ M}^{-1} \text{ cm}^{-1}$ (840 nm) after 21 h; Figure 2b). The UV–vis spectrum of the photoreduced **I** (for 21 h) was almost the same as that of **I** electrochemically reduced by four electrons at -1.35 V (vs. NHE) (Figures 2b and S1). The above-mentioned results show that four-electron-reduced **I** is formed using 4-methoxybenzyl alcohol as the electron donor via the intramolecular Ce^{3+} -to- $\text{POM}(\text{W}^{6+})$ charge transfer by irradiation of visible light¹¹ and that electrons are stored in $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ units. After irradiation of visible light, the photoreduced **I** was readily reoxidized by exposure to air within 1 min, and the color of the

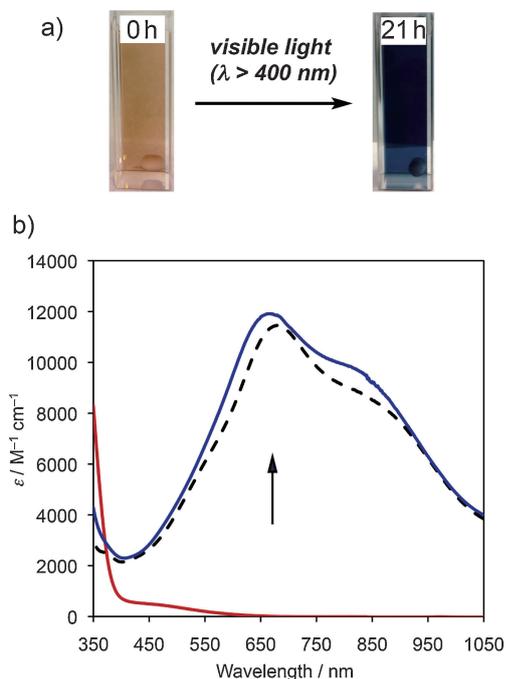


Figure 2. a) Photographs representing the color change of the solution upon irradiation of visible light ($\lambda > 400$ nm), b) UV-vis spectra of **I** (0.2 mM; red line), **I** (0.2 mM) upon irradiation of visible light for 21 h in the presence of 4-methoxybenzyl alcohol (4.5 M) in acetonitrile under Ar (1 atm; blue line), and **I** (0.1 mM) upon electrochemical reduction at -1.35 V (four-electron reduction, red line) in the presence of 4-methoxybenzyl alcohol (4.5 M; black broken line).

solution reverted to the original reddish brown back from dark blue. These results clearly indicate that the visible-light-induced four-electron reduction of **I** occurs and that the electrons can be transferred to O_2 .

With the visible-light-responsive multielectron-transfer system in hand, we next investigated photocatalytic hydrogen evolution with **I**. As we expected, catalytic hydrogen evolution proceeded on irradiation of visible light ($\lambda > 400$ nm) in the presence of $H_2[PtCl_6]$ as the cocatalyst.^{12,13} Among the solvents examined (*N,N*-dimethylacetamide, *N,N*-dimethylformamide, dimethyl sulfoxide, and acetonitrile), *N,N*-dimethylacetamide was the best solvent (Table S2 and Figure S2). The order of the catalytic activity of **I** was as follows: *N,N*-dimethylacetamide > *N,N*-dimethylformamide > acetonitrile > dimethyl sulfoxide. This order was approximately the same as that of the W^{6+}/W^{5+} redox potential ($E_{1/2}$ (1st reduction)) of **I** in these solvents. These results showed that the higher reduction ability of **I** resulted in the higher catalytic activity in the present system.¹⁴ Under the present reaction conditions, the total amount of hydrogen evolved after 10 h was 249 μ mol, which corresponds to the 249 TON based on **I** (Table 1, Entry 1). 4-Methoxybenzaldehyde was also produced, and the amount (227 μ mol) was close to that of evolved hydrogen. The catalyst was highly durable; the catalytic activity was preserved over longer reaction times, and the TON reached up to 1960 after 80 h (Figure 3 and Table 1, Entry 2).^{12,15} In contrast, no hydrogen was evolved in the absence of **I** (Table 1, Entry 8) or the presence of $[Ce(acac)_3]$ (Table 1, Entry 9) or $TBA_4[SiW_{12}O_{40}]$ (Table 1, Entry 10). Additionally, the reaction did not proceed at all without

Table 1. Visible-light-induced photocatalytic hydrogen evolution^a

Entry	Catalyst (μ mol)	Time/h	H_2 TON ^b
1	I (1)	10	249
2	I (1)	80	1960
3 ^c	I (1)	10	252
4 ^d	I (1), dark	10	<0.1
5 ^e	I (1)	80	224
6 ^f	I (1)	10	<0.1
7 ^g	I (1)	10	<0.1
8	none	10	—
9	$[Ce(acac)_3]$ (4)	10	<0.1
10	$TBA_4[SiW_{12}O_{40}]$ (2)	10	<0.1

^aReaction conditions: Catalyst, $H_2[PtCl_6]$ (0.5 μ mol), 4-methoxybenzyl alcohol (50 mmol), *N,N*-dimethylacetamide (5 mL), visible light ($\lambda > 400$ nm), Ar (1 atm). Amount of hydrogen was determined by GC (TCD). ^bTON = (hydrogen evolved/mol)/(catalyst/mol). ^cThis experiment used the retrieved **I**. ^dWithout photoirradiation. ^eWith ethanol (103 mmol) as the electron donor. ^fWith 4-methoxybenzylamine (50 mmol) as the electron donor. ^gWithout $H_2[PtCl_6]$.

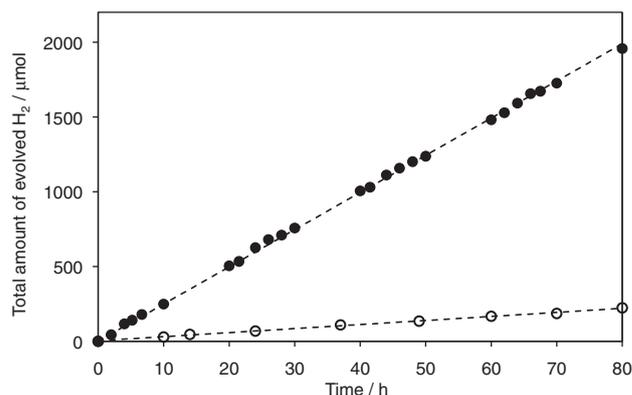


Figure 3. Time courses for hydrogen evolution from the *N,N*-dimethylacetamide (5 mL) solution of **I** (1 μ mol), $H_2[PtCl_6]$ (0.5 μ mol) and alcohol (filled circle, 4-methoxybenzyl alcohol (50 mmol); open circle, ethanol (103 mmol)) by irradiation of visible light ($\lambda > 400$ nm) under Ar (1 atm).

irradiation of visible light (Table 1, Entry 4). Even when less reactive ethanol was used as the electron donor, hydrogen was also evolved (TON 224; Table 1, Entry 5). In contrast, no hydrogen was produced when 4-methoxybenzylamine was used as the electron donor (Table 1, Entry 6).⁸

The TON of **I** for hydrogen evolution was much higher than that of the previously reported visible-light-responsive POMs; $K_{11}H[Sn_4(SiW_9O_{34})_2]$ (TON 1.4),^{7a} $[Cu(eda)_2]_{11}K_4Na_2[KNb_{24}O_{72}H_9]_2$ (eda: ethylenediamine) (9.0),^{7b} and $TBA_6[P_2W_{17}O_{61}\{O(SiC_{36}H_{23}N_3O_2)Ir\}_2]$ (41)^{7c} (Table S1). Furthermore, the performance of the present system was even higher than those of the systems consisting of POMs with additional sensitizers such as $K_5[AlSiW_{11}O_{39}(H_2O)] +$ eosin Y (473),^{7d} and $[Mn_4(H_2O)_2(VW_9O_{34})_2]^{10-} + [Ru(bpy)_3]^{2+}$ (42)^{7e} (Table S1).

After the reaction, **I** could easily be retrieved as precipitates by addition of excess diethyl ether. The CSI-MS spectrum of the retrieved **I** showed the sets of signals assignable to $[TBA_7-Ce_4O(SiW_{10}O_{36})_2]^+$ (centered at m/z 7158) and $[TBA_8-Ce_4O-$

(SiW₁₀O₃₆)₂]²⁺ (*m/z* 3700) (Figure S3), and the IR spectrum was almost identical with that of the original **I** (Figure S4). These data show that the structure of **I** was preserved even after the reaction. In addition, the retrieved **I** could be reused without an appreciable loss in its remarkable catalytic performance for hydrogen evolution (252 μmol for 10 h; Table 1, Entry 3).

In conclusion, the tetranuclear cerium-containing POM **I** showed the intramolecular multiple electron transfer on irradiation of visible light ($\lambda > 400$ nm). Compound **I** could store up to four electrons and be reoxidized by O₂. Based on these photoresponsive properties, **I** efficiently catalyzed hydrogen evolution by irradiation of visible light in the presence of alcohols (4-methoxybenzyl alcohol and ethanol) as the electron donors. The present system did not require additional sensitizers, and **I** could be reused without an appreciable loss in its remarkable catalytic activity.

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Supporting Information is available electronically on J-STAGE.

References and Notes

- 1 P. D. Tran, L. H. Wong, J. Barber, J. S. C. Loo, *Energy Environ. Sci.* **2012**, *5*, 5902.
- 2 a) A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2009**, *38*, 253. b) K. Maeda, K. Domen, *J. Phys. Chem. Lett.* **2010**, *1*, 2655. c) A. Dhakshinamoorthy, S. Navalon, A. Corma, H. Garcia, *Energy Environ. Sci.* **2012**, *5*, 9217. d) Y. Shiraishi, Y. Sugano, S. Tanaka, T. Hirai, *Angew. Chem., Int. Ed.* **2010**, *49*, 1656. e) K. Mori, M. Kawashima, M. Che, H. Yamashita, *Angew. Chem., Int. Ed.* **2010**, *49*, 8598. f) M. Higashi, K. Domen, R. Abe, *J. Am. Chem. Soc.* **2012**, *134*, 6968.
- 3 A. J. Esswein, D. G. Nocera, *Chem. Rev.* **2007**, *107*, 4022.
- 4 a) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, **1983**. b) C. L. Hill, C. M. Prosser-McCartha, *Coord. Chem. Rev.* **1995**, *143*, 407. c) T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* **1996**, *41*, 113. d) N. Mizuno, M. Misono, *Chem. Rev.* **1998**, *98*, 199. e) R. Neumann, in *Progress in Inorganic Chemistry*, John Wiley & Sons, Inc., **1998**, Vol. 47, p. 317. doi:10.1002/9780470166482.ch3. f) I. V. Kozhevnikov, *Chem. Rev.* **1998**, *98*, 171. g) C. L. Hill, in *Comprehensive Coordination Chemistry II*, ed. by J. A. McCleverty, T. J. Meyer, Elsevier Pergamon, Amsterdam, **2004**, Vol. 4, p. 679. h) D.-L. Long, R. Tsunashima, L. Cronin, *Angew. Chem., Int. Ed.* **2010**, *49*, 1736.
- 5 a) B. Keita, U. Kortz, L. R. B. Holze, S. Brown, L. Nadjo, *Langmuir* **2007**, *23*, 9531. b) B. Keita, L. Nadjo, *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *217*, 287.
- 6 a) S. Li, S. Liu, S. Liu, Y. Liu, Q. Tang, Z. Shi, S. Ouyang, J. Ye, *J. Am. Chem. Soc.* **2012**, *134*, 19716. b) Z. Zhang, Q. Lin, D. Kurunthu, T. Wu, F. Zuo, S.-T. Zheng, C. J. Bardeen, X. Bu, P. Feng, *J. Am. Chem. Soc.* **2011**, *133*, 6934. c) T. Yamase, X. Cao, S. Yazaki, *J. Mol. Catal. A: Chem.* **2007**, *262*, 119. d) T. Yamase, R. Watanabe, *J. Chem. Soc., Dalton Trans.* **1986**, 1669. e) A. Ioannidis, E. Papaconstantinou, *Inorg. Chem.* **1985**, *24*, 439.
- 7 a) Z. Zhang, Q. Lin, S.-T. Zheng, X. Bu, P. Feng, *Chem. Commun.* **2011**, *47*, 3918. b) Z.-L. Wang, H.-Q. Tan, W.-L. Chen, Y.-G. Li, E.-B. Wang, *Dalton Trans.* **2012**, *41*, 9882. c) B. Matt, J. Fize, J. Moussa, H. Amouri, A. Pereira, V. Artero, G. Izzet, A. Proust, *Energy Environ. Sci.* **2013**, *6*, 1504. d) X. Liu, Y. Li, S. Peng, G. Lu, S. Li, *Int. J. Hydrogen Energy* **2012**, *37*, 12150. e) H. Lv, J. Song, H. Zhu, Y. V. Geletii, J. Bacsá, C. Zhao, T. Lian, D. G. Musaev, C. L. Hill, *J. Catal.* **2013**, *307*, 48.
- 8 K. Suzuki, F. Tang, Y. Kikukawa, K. Yamaguchi, N. Mizuno, *Angew. Chem., Int. Ed.* **2014**, *53*, 5356.
- 9 We have recently reported the syntheses of multinuclear metal-containing POMs in organic solvents: a) Y. Kikukawa, K. Yamaguchi, N. Mizuno, *Angew. Chem., Int. Ed.* **2010**, *49*, 6096. b) K. Suzuki, Y. Kikukawa, S. Uchida, H. Tokoro, K. Imoto, S.-i. Ohkoshi, N. Mizuno, *Angew. Chem., Int. Ed.* **2012**, *51*, 1597. c) Y. Kikukawa, K. Suzuki, M. Sugawa, T. Hirano, K. Kamata, K. Yamaguchi, N. Mizuno, *Angew. Chem., Int. Ed.* **2012**, *51*, 3686. d) K. Suzuki, M. Sugawa, Y. Kikukawa, K. Kamata, K. Yamaguchi, N. Mizuno, *Inorg. Chem.* **2012**, *51*, 6953. e) R. Sato, K. Suzuki, M. Sugawa, N. Mizuno, *Chem.—Eur. J.* **2013**, *19*, 12982. f) K. Suzuki, R. Sato, N. Mizuno, *Chem. Sci.* **2013**, *4*, 596.
- 10 Visible-light-induced metal-to-POM(W⁶⁺) charge transfers have recently been reported: a) T. Takashima, R. Nakamura, K. Hashimoto, *J. Phys. Chem. C* **2009**, *113*, 17247. b) T. Takashima, A. Yamaguchi, K. Hashimoto, R. Nakamura, *Chem. Commun.* **2012**, *48*, 2964. c) C. Zhao, Z. Huang, W. Rodríguez-Córdoba, C. S. Kambara, K. P. O'Halloran, K. I. Harcastle, D. G. Musaev, T. Lian, C. L. Hill, *J. Am. Chem. Soc.* **2011**, *133*, 20134. d) E. N. Glass, J. Fielden, A. L. Kaledin, D. G. Musaev, T. Lian, C. L. Hill, *Chem.—Eur. J.* **2014**, *20*, 4297.
- 11 The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **I** predominantly consisted of Ce³⁺- and POM(W⁶⁺)-based orbitals, respectively. Additionally, Ce³⁺-based HOMO existed between the POM-(W⁶⁺)-based LUMO and oxygen-based orbitals (HOMO-1). These results suggest that the Ce³⁺-to-POM(W⁶⁺) charge transfer occurs by irradiation of visible light.⁸
- 12 Typical procedure for photocatalytic hydrogen evolution: Into a Pyrex reaction vessel (volume: 55 mL) were successively placed **I** (1 μmol), H₂[PtCl₆] (0.5 μmol), *N,N*-dimethylacetamide (5 mL), and 4-methoxybenzyl alcohol (50 mmol). A Teflon-coated magnetic stir bar was added, and the atmosphere of the reaction vessel was replaced by Ar. The reaction was initiated by irradiation of visible light ($\lambda > 400$ nm) with a 300 W Xe lamp equipped with a 400 nm cut off filter. Hydrogen evolution was confirmed and monitored by GC (TCD) analysis. Products in the liquid phase were confirmed by comparison of their GC (FID) retention times and GC-MS spectra with those of authentic data. Every 10 h, the reaction system was replaced by Ar to remove the evolved hydrogen. After the reaction, the catalyst was retrieved by precipitation method by addition of excess diethyl ether to the reaction solution. The retrieved **I** was washed with *n*-hexane and then air-dried prior to being used for the reuse experiment. The IR and CSI-MS spectra of the retrieved catalyst showed that the structure of **I** was preserved after the hydrogen evolution (Figures S3 and S4).
- 13 Without H₂[PtCl₆] (Pt cocatalyst), no hydrogen was evolved (Table 1, Entry 7). The Pt cocatalyst likely acted as a proton reduction site in the present photocatalytic system.
- 14 W⁶⁺/W⁵⁺ redox potential (reduction ability) of **I** shifted to more negative reduction potential with an increase in the acceptor number of solvents (Table S2).
- 15 The quantum efficiency for photocatalytic hydrogen evolution of the present system at 440 nm (using band-pass filter) was 0.35%.