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## COMMUNICATION

# A Cobalt-NHC Complex as an Improved Catalyst for Photochemical Hydrogen Evolution from Water

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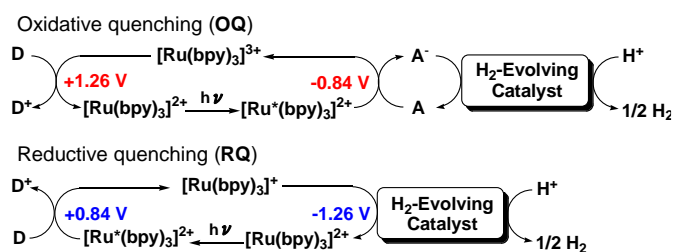
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**A macrocyclic *N*-heterocyclic carbene (NHC) cobalt complex was found to serve as an improved H<sub>2</sub>-evolving catalyst in a [Ru(bpy)<sub>3</sub>]<sup>2+</sup>-sensitized photosystem using methylviologen as a redox acceptor (MV<sup>2+</sup> + e<sup>-</sup> → MV<sup>+•</sup>, MV<sup>2+</sup> = N,N'-dimethyl-4,4'-bipyridinium), which provides only 150 meV of driving force for H<sub>2</sub> evolution at pH 5.0.**

The photochemical hydrogen evolution reaction (HER) based on molecular catalysis has been intensively studied for many years as a means of fabricating practically useful artificial photosynthetic devices.<sup>1-11</sup> Many of the molecular H<sub>2</sub>-evolving photosystems use a well-known photosensitizer (PS), i.e. [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, to drive photoinduced electron transfer (ET) events leading to H<sub>2</sub> generation. Depending on the selection of co-existing donor (D) and/or acceptor (A) reagents, two types of ET processes, oxidative and reductive quenching, are available (see Scheme 1).

For instance, it was reported that photochemical H<sub>2</sub> evolution from the AA/[Ru(bpy)<sub>3</sub>]<sup>2+</sup>/[Co(bpy)<sub>3</sub>]<sup>2+</sup> system (AA = ascorbic acid; pH 5.0) affords a reductively quenched product (i.e., [Ru(bpy)<sub>3</sub>]<sup>+</sup>, formally expressed as [Ru<sup>II</sup>(bpy)<sub>2</sub>(bpy<sup>+•</sup>)]<sup>+</sup>,<sup>4</sup> where the driving force (DF) for the HER using this reducing equivalent is estimated as 960 meV (*high DF*) based on the reported value of  $E_{1/2}([\text{Ru}(\text{bpy})_3]^{2+}/[\text{Ru}(\text{bpy})_3]^+) = -1.26 \text{ V vs. NHE}$  (see Table 1).<sup>12</sup> On the other hand, the EDTA/[Ru(bpy)<sub>3</sub>]<sup>2+</sup>/MV<sup>2+</sup>/catalyst system initially affords the oxidatively quenched product MV<sup>+•</sup>, which only has a DF of 150 meV (*low DF*) for HER at pH 5.0 ( $E_{1/2}$



**Scheme 1** Oxidative and reductive quenching of the <sup>3</sup>MLCT state, where each numerical value is an individual redox potential arising from the corresponding [Ru(bpy)<sub>3</sub>]<sup>2+</sup>-based redox process.

(MV<sup>2+</sup>/MV<sup>+•</sup>) = -0.45 V vs. NHE; see also Table 1).<sup>13</sup> Some other reported photosystems are listed in Table 1.

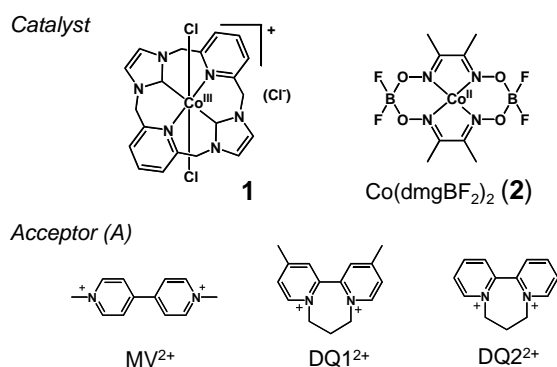
With the above background, noble-metal-based Pt(II) and Rh(II) catalysts had been the rare examples of molecular systems that can catalyze water reduction by MV<sup>+•</sup>.<sup>5,14</sup> Dark reactions of MV<sup>+•</sup> with several Pt(II) complexes were confirmed to result in thermal H<sub>2</sub> evolution from water.<sup>5d</sup> To extend the molecular catalysis of the HER driven by MV<sup>+•</sup>, we undertook efforts to develop non-noble metal molecular catalysts that effectively accelerate this reaction. Here we find that the cobalt-NHC complex **1** (see Fig. 1) effectively catalyzes the HER using MV<sup>+•</sup> as a reductant.

In the cyclic voltammogram (CV) of **1** in DMF (*N,N*-dimethylformamide), the Co(III/II) and Co(II/I) couples are observed as reversible waves at -0.11 and -1.06 V vs. NHE, respectively (Fig.

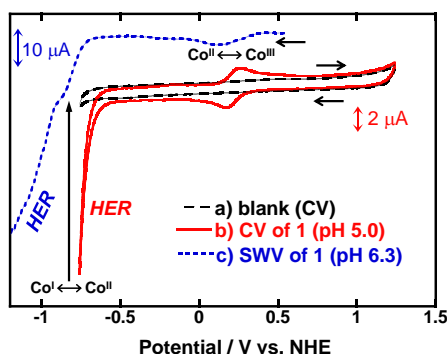
**Table 1** Some relevant photosystems for H<sub>2</sub> evolution

Quenching process	D	PS	A	Catalyst	Key potential <sup>[a]</sup>	Ref.
<b>RQ</b>	AA	[Ru(bpy) <sub>3</sub> ] <sup>2+</sup>	none	[Co(bpy) <sub>3</sub> ] <sup>2+</sup> <sup>[b]</sup>	-1.26 <sup>[c,d]</sup>	4
<b>OQ</b>	EDTA	[Ru(bpy) <sub>3</sub> ] <sup>2+</sup>	MV <sup>2+</sup>	Pt colloid, and Pt(II)/Rh(II) complexes	-0.45 <sup>[e]</sup>	2, 3, 5, 14
<b>OQ &amp; RQ<sup>[f]</sup></b>	TEOA	[Ir(ppy) <sub>2</sub> (phen)] <sup>+</sup>	none	Co(dmgbF <sub>2</sub> ) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub>	-0.64 <sup>[g]</sup> , -1.18 <sup>[c]</sup>	6
<b>OQ &amp; RQ<sup>[f]</sup></b>	TEOA	Rose Bengal	none	Co(dmgbF <sub>2</sub> ) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub>	-0.74, <sup>[c,h]</sup> -0.78 <sup>[g,h]</sup>	11a
<b>OQ</b>	TEOA	[Pt(tpy)(tolylacetylde)]Cl	none	Co(dmgbH) <sub>2</sub> (pyridine)Cl	-0.96 <sup>[g,i]</sup>	10b

[a] The redox potential of either PS/PS<sup>-</sup>, PS<sup>+/PS\*</sup>, or A/A<sup>-</sup> which is used to drive HER. [b] The precatalyst affording the active species, [Co<sup>I</sup>(bpy)<sub>2</sub>]<sup>+</sup> [c]  $E_{1/2}(\text{PS}/\text{PS}^-)$ . [d] see ref. 12 [e]  $E_{1/2}(\text{MV}^{2+}/\text{MV}^{+•})$ .<sup>13</sup> [f] Two processes were reported to compete. [g]  $E_{1/2}(\text{PS}^+/\text{PS}^*)$ . [h] see ref. 10c. [i] see ref. 10a.



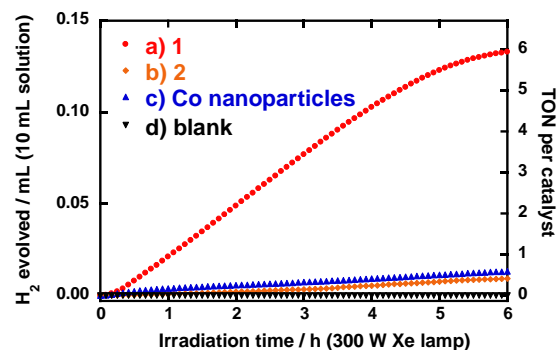
**Fig. 1** Structures of compounds



**Fig. 2** CVs in the absence (a, blank) and presence (b) of **1**·2H<sub>2</sub>O (0.1 mM) in 0.1 M aqueous acetate buffer solution (pH 5.0) containing KCl (0.1 M). Square wave voltammogram (SWV) of **1**·2H<sub>2</sub>O (0.5 mM) in 0.1 M KNO<sub>3</sub> at pH 6.3 (c). See Fig. S1 for other details.

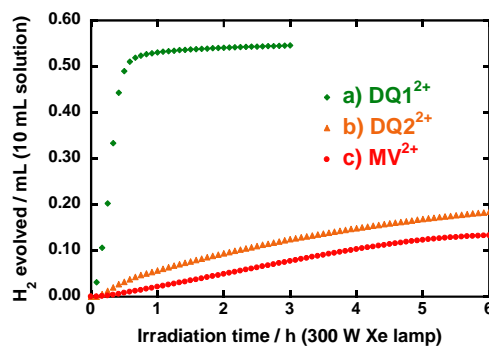
S1a). These properties are consistent with those reported for analogous cobalt-NHC complexes.<sup>15</sup> At more cathodic potential, an irreversible wave, presumably reduction at the pyridyl unit, appears at -1.75 V. On the other hand, in aqueous solution (pH 5.0), the Co(III/II) couple of **1** is observed at 0.22 V (Fig. 2b). Below this couple, a catalytic current corresponding to HER is seen with the onset potential located at ca. -0.6 V, without showing any reduction peak ascribable to the Co(II/I) couple. This is in sharp contrast to the electrochemical behaviors previously observed for the cobaloximes and related Co-based H<sub>2</sub>-evolving catalysts.<sup>7,8</sup> One of the pathways proposed for the Co-catalyzed HER follows successive one-electron reductions of a Co(III) species to afford a Co(I) species, which then undergoes oxidative addition to give a hydridocobalt(III) species as the key intermediate (i.e., Co(III)-H).<sup>7,8</sup> However, the HER catalyzed by **1** is not likely to proceed via formation of such a two-electron-reduced species, i.e., the Co(I) species. In order to clearly observe the Co(II/I) couple in aqueous media, the square wave voltammograms of **1** at higher pH values were separately recorded (Figs. 2c and S2). Actually, the Co(II/I) couple could be observed at high pH in the range pH 6.3-9.0 and the Co(II/I)-based potential was confirmed to remain constant (-0.85 V) under these pH conditions (Figs. 2c and S2). Thus, the Co(II/I) couple does not have a significant contribution to the electrocatalytic current for HER observed at pH 5.0 (Fig. 2b).

An important observation is that **1** serves as an effective H<sub>2</sub>-evolving catalyst in a photosystem consisting of EDTA (D), [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (PS) and MV<sup>2+</sup> (A) (Fig. 3a). Note that **1** was separately confirmed to be stable for at least 6 h irradiation of the

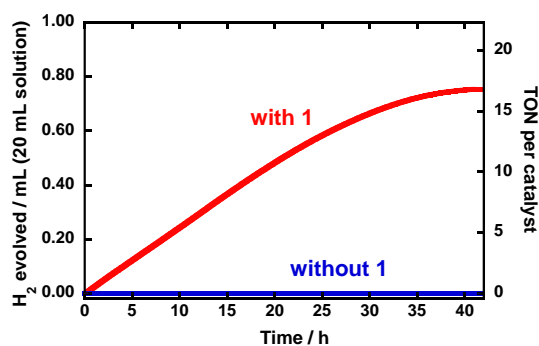


**Fig. 3** Photochemical H<sub>2</sub> production from an aqueous acetate buffer solution (0.03 M CH<sub>3</sub>COOH and 0.07 M CH<sub>3</sub>COONa; pH 5.0; 10 mL) containing EDTA (30 mM; disodium salt), [Ru(bpy)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.04 mM), and MV(NO<sub>3</sub>)<sub>2</sub> (2.0 mM) in the presence of a) **1**·2H<sub>2</sub>O (0.1 mM), b) **2**·2H<sub>2</sub>O (0.1 mM), c) cobalt nanoparticles with the average diameter of 28 nm (59 μg), or d) no catalyst, under Ar atmosphere at 20 °C.

same light source (300 W Xe lamp, 400-800 nm, see Fig. S3). The initial H<sub>2</sub> evolution rate and total amount of H<sub>2</sub> evolved are estimated as 4.7 × 10<sup>-4</sup> mL/min and 0.133 mL, respectively. The H<sub>2</sub> evolution rate decreases by 88% when the experiment was carried out without adding MV<sup>2+</sup> (see Fig. S4). This reveals that oxidative quenching of [Ru\*(bpy)<sub>3</sub>]<sup>2+</sup> by MV<sup>2+</sup> (see Scheme 1) is essential for the effective H<sub>2</sub> generation. It also shows that direct electron transfer from [Ru\*(bpy)<sub>3</sub>]<sup>2+</sup> to **1** can also lead to H<sub>2</sub> production. The turnover number (TON) for **1** in Fig. 3a can be estimated as 5.9 (6 h). This catalytic activity is not as high as those observed, under compatible conditions, for Pt(II)-based molecular catalysts (TON = 10-100),<sup>5b</sup> but is comparable to those reported for carboxylate-bridged dirhodium(II) catalysts (TON = 3.8-9.0).<sup>14</sup> However, we must emphasize again that this is the first Co-based molecular catalyst that can promote the HER driven with the MV<sup>2+</sup>/MV<sup>•+</sup> couple. It must be also noted that one of the well-known H<sub>2</sub>-evolving cobaloxime derivatives, **2**,<sup>8a,16</sup> does not serve as a catalyst for the HER with MV<sup>•+</sup> (Fig. 3b). In addition, cobalt nanoparticles (28 nm in diameter; purchased from Ionic Liquids Technologies) do not promote HER under our conditions, consistent with the report of Fukuzumi *et al.* in which cobalt nanoparticles were shown to exhibit low catalytic activity for HER.<sup>17</sup> This rules out contribution of such nanoparticles



**Fig. 4** Photochemical H<sub>2</sub> production from an aqueous acetate buffer solution (0.03 M CH<sub>3</sub>COOH and 0.07 M CH<sub>3</sub>COONa; pH 5.0; 10 mL) containing EDTA (30 mM; disodium salt), [Ru(bpy)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.04 mM), and **1**·2H<sub>2</sub>O (0.1 mM), in the presence of a) DQ1(NO<sub>3</sub>)<sub>2</sub> (2.0 mM), b) DQ2(NO<sub>3</sub>)<sub>2</sub> (2.0 mM), or c) MV(NO<sub>3</sub>)<sub>2</sub> (2.0 mM), under Ar atmosphere at 20 °C.



**Fig. 5** Thermal H<sub>2</sub> evolution from water based on the reduction of water by MV<sup>+•</sup> (5.0 mM) catalyzed by 1·2H<sub>2</sub>O (0.1 mM) in an aqueous acetate buffer solution containing 0.03 M CH<sub>3</sub>COOH, 0.07 M CH<sub>3</sub>COONa, and 0.08 M KNO<sub>3</sub> (pH 5.0, 20 mL) at 20 °C in the dark. A solution of MV<sup>+•</sup>, generated *in situ* by bulk electrolysis of MV<sup>2+</sup>, was mixed with a solution of **1** under N<sub>2</sub> atmosphere inside a glovebox, where sampling of gas was carried out with continuous flow of Ar (10 mL/min) bubbled through the catalysis solution.

to the H<sub>2</sub>-evolving activity of **1** in Fig. 3a. In order to further examine the effect of the DF applied, two additional acceptors, DQ1<sup>2+</sup> and DQ2<sup>2+</sup> (see Fig. 1), were used instead of MV<sup>2+</sup>. These acceptors possess shifted potentials;  $E_{1/2}(\text{DQ1}^{2+}/\text{DQ1}^{+•}) = -0.70$  V and  $E_{1/2}(\text{DQ2}^{2+}/\text{DQ2}^{+•}) = -0.55$  V.<sup>2b</sup> The DFs for the HER driven by DQ1<sup>+•</sup> and DQ2<sup>+•</sup> (pH 5.0) are estimated as 400 meV (*intermediate DF*) and 250 meV, respectively. As expected, the rate of HER is changed dramatically upon changing the DF (Fig. 4). A substantial rate enhancement is seen when DQ1<sup>2+</sup> is used, although degradation of the system is also greatly accelerated, leading to a substantial decrease in the rate of HER after around 30 min of photocatalysis (Fig. 4a). It should be noted here that almost no catalytic activity is seen for **2** even when DQ1<sup>2+</sup> is used (Fig. S5b), confirming that **1** is indeed an improved Co-based catalyst for HER. Also noteworthy is that H<sub>2</sub> evolution in the absence of catalyst with use of either MV<sup>2+</sup> or DQ2<sup>2+</sup> is negligible but is non-negligible with DQ1<sup>2+</sup> (see Fig. S5c).

We further confirmed that **1** catalyzes the thermal HER when driven with MV<sup>+•</sup> in the dark. As shown in Fig. 5, an aqueous solution of MV<sup>+•</sup>, generated *in situ* electrochemically by the published method<sup>5d</sup> with minor modifications (see ESI), was mixed with an aqueous solution of **1**, and the amount of H<sub>2</sub> evolved was measured. All these experiments were performed inside a glovebox equipped with an N<sub>2</sub> circulating system and a copper catalyst column for complete removal of O<sub>2</sub>. The conversion efficiency based on 2MV<sup>+•</sup> + 2H<sup>+</sup> → 2MV<sup>2+</sup> + H<sub>2</sub> is estimated as 65%, yielding TON = 16.8. This implies that the HER catalyzed by **1** competes with a non-H<sub>2</sub>-evolving reaction, which simply leads to the consumption of MV<sup>+•</sup>. Indeed, the visible absorption band of MV<sup>+•</sup> decays even in the absence of catalyst (see Fig. S6), under which conditions no H<sub>2</sub> evolution occurs (Fig. 5, blank).

In this work, we have demonstrated that **1** exhibits catalytic activity for HER even when driven with relatively low driving force (DF = 150 and 250 meV). Reduction of the Co(II) species into the Co(I) species cannot be driven by either MV<sup>+•</sup> or DQ2<sup>+•</sup>, and therefore the HER catalyzed by **1** is not likely to proceed via formation of a Co(I) species. This is also supported by the absence of a Co(II/I) redox wave in the CV of **1** in aqueous media under the pH condition employed for the photocatalysis. We propose that the HER catalyzed by **1** proceeds via a proton-coupled electron transfer

(PCET) process (Co(II) + H<sup>+</sup> + e<sup>-</sup> → Co(III)-H), as proposed for Pt(II)-catalyzed HER (Pt<sup>II</sup> + H<sup>+</sup> + e<sup>-</sup> → Pt<sup>III</sup>-H),<sup>5e,5f</sup> together with Rh(II)<sub>2</sub>-catalyzed HER (Rh<sup>II</sup><sub>2</sub> + H<sup>+</sup> + e<sup>-</sup> → Rh<sup>II</sup>Rh<sup>III</sup>-H).<sup>14</sup> Extended studies to clarify the detailed mechanism of the HER with **1** are now actively in progress.

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## Notes and references

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Electronic Supplementary Information (ESI) available: Experimental details and Figs. S1-S9. See DOI: 10.1039/c000000x/

- 1 M. Kirch, J.-M. Lehn and J.-P. Sauvage, *Helv. Chim. Acta*, 1979, **62**, 1345.
- 2 a) P. Keller, A. Moradpour, E. Amouyal and H. B. Kagan, *Nouv. J. Chim.*, 1980, **4**, 377; b) E. Amouyal and B. Zidler, *Chem. Phys. Lett.*, 1980, **74**, 314; c) E. Amouyal, *Sol. Energ. Mat. Sol. Cells*, 1995, **38**, 249.
- 3 E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca and M. Grätzel, *J. Am. Chem. Soc.*, 1981, **103**, 6324.
- 4 C. V. Krishnan and N. Sutin, *J. Am. Chem. Soc.*, 1981, **103**, 2141.
- 5 a) K. Sakai and K. Matsumoto, *J. Coord. Chem.*, 1988, **18**, 169; b) H. Ozawa, Y. Yokoyama, M. Haga and K. Sakai, *Dalton Trans.*, 2007, 1197; c) K. Sakai and H. Ozawa, *Coord. Chem. Rev.*, 2007, **251**, 2753; d) K. Yamauchi, S. Masaoka and K. Sakai, *J. Am. Chem. Soc.*, 2009, **131**, 8404; e) M. Ogawa, G. Ajayakumar, S. Masaoka, H.-B. Kraatz and K. Sakai, *Chem. Eur. J.*, 2011, **17**, 1148; f) H. Ozawa and K. Sakai, *Chem. Commun.*, 2011, **47**, 2227.
- 6 J. I. Goldsmith, W. R. Hudson, M. S. Lowry, T. H. Anderson and S. Bernhard, *J. Am. Chem. Soc.*, 2005, **127**, 7502.
- 7 a) M. Razavet, V. Artero and M. Fontecave, *Inorg. Chem.*, 2005, **44**, 4786; b) C. Baffert, V. Artero and M. Fontecave, *Inorg. Chem.*, 2007, **46**, 1817; c) V. Artero, M. Chavarot-Kerlidou and M. Fontecave, *Angew. Chem. Int. Ed.*, 2011, **50**, 7238.
- 8 a) X. Hu, B. M. Cossairt, B. S. Brunschwig, N. S. Lewis and J. C. Peters, *Chem. Commun.*, 2005, 4723; b) X. Hu, B. S. Brunschwig and J. C. Peters, *J. Am. Chem. Soc.*, 2007, **129**, 8988.
- 9 A. J. Esswein and D. G. Nocera, *Chem. Rev.*, 2007, **107**, 4022.
- 10 a) P. Du, J. Schneider, P. Jarosz, J. Zhang, W. W. Brennessel and R. Eisenberg, *J. Phys. Chem. B*, 2007, **111**, 6887; b) P. Du, J. Schneider, G. Luo, W. W. Brennessel and R. Eisenberg, *Inorg. Chem.*, 2009, **48**, 4952; c) T. Lazarides, T. McCormick, P. Du, G. Luo, B. Lindly and R. Eisenberg, *J. Am. Chem. Soc.*, 2009, **131**, 9192.
- 11 a) P. Zhang, M. Wang, J. Dong, X. Li, F. Wang, L. Wu and L. Sun, *J. Phys. Chem. C*, 2010, **114**, 15868; b) M. Wang, L. Chen and L. Sun,

- Energy Environ. Sci.*, 2012, **5**, 6763; c) L. Chen, M. Wang, K. Han, P. Zhang, F. Gloaguen and L. Sun, *Energy Environ. Sci.*, 2014, **7**, 329.
- 12 C. R. Bock, J. A. Connor, A. R. Gutierrez, T. J. Meyer, D. G. Whitten, B. P. Sullivan and J. K. Nagle, *J. Am. Chem. Soc.*, 1979, **101**, 4815.
- 13 T. M. Bockman and J. K. Kochi, *J. Org. Chem.*, 1990, **55**, 4127.
- 14 S. Tanaka, S. Masaoka, K. Yamauchi, M. Annaka and K. Sakai, *Dalton Trans.*, 2010, **39**, 11218.
- 15 a) Z. Mo, Y. Li, H. K. Lee and L. Deng, *Organometallics*, 2011, **30**, 4687; b) S. R. Park, N. J. Findlay, J. Garnier, S. Zhou, M. D. Spicer and J. A. Murphy, *Tetrahedron*, 2009, **65**, 10756.
- 16 P. Connolly and J. H. Espenson, *Inorg. Chem.*, 1986, **25**, 2684.
- 17 Y. Yamada, T. Miyahigashi, H. Kotani, K. Ohkubo and S. Fukuzumi, *Energy Environ. Sci.*, 2012, **5**, 6111.

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