Fragments of Layered Manganese Oxide Are the Real Water Oxidation Catalyst after Transformation of Molecular Precursor on Clay

M. M. Najafpour,*,[‡] Atefeh N. Moghaddam,[‡] Holger Dau,[§] and Ivelina Zaharieva*,[§]

[‡]Department of Chemistry and Center of Climate Change and Global Warming, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731 Iran

[§]Freie Universität Berlin Arnimallee 14, 14195 Berlin, Germany

Ⓢ *Supporting Information*

ABSTRACT: A binuclear manganese molecular complex $[(OH_2)(terpy)Mn(\mu\text{-}O)_2Mn(terpy)(OH_2)]^{3+}$ (**1**) is the most prominent structural and functional model of the water-oxidizing Mn complex operating in plants and cyanobacteria. Supported on montmorillonite clay and using Ce(IV) as a chemical oxidant, **1** has been reported to be one of the best Mn-based molecular catalysts toward water oxidation. By X-ray absorption spectroscopy and kinetic analysis of the oxygen evolution reaction, we show that $[(OH_2)(terpy)Mn(\mu\text{-}O)_2Mn(terpy)(OH_2)]^{3+}$ is transformed into layered type Mn-oxide particles which are the actual water oxidation catalyst.

Electrolysis of water to molecular hydrogen and oxygen is performed as a simple experiment for high school students using, e.g., pencil cores as cheap graphite electrodes and a 9 V battery as the energy source.[1] In the future, this schoolbook reaction may become one of the most important reactions for mankind because it offers an opportunity to store the excess electrical energy produced from solar radiation, wind, ocean currents, and other fluctuating sources in form of molecular hydrogen or molecules obtained by CO_2 reduction.[2] Water oxidation, the anodic process in water electrolysis, clearly is a key reaction in the transition from an energy economy based on fossil fuels to one based on renewable energy sources. However, efficient water oxidation is chemically highly demanding, especially if the use of precious elements is avoided.[3]

Photosynthetic water oxidation in plants and cyanobacteria is catalyzed by the water-oxidizing complex (WOC) embedded in the Photosystem II (PSII) cofactor−protein complex. It contains one calcium and four manganese ions interconnected by bridging oxygen atoms.[4] Since the biological WOC comprises redox-active Mn ions, particular attention has been given to synthetic Mn compounds which mimic the WOC of PSII structurally and functionally.[5] Their synthesis has been directed toward understanding and mimicking the strategies used so successfully by nature. So far, however, only very few synthetic Mn molecular complexes have been reported that are able to catalyze water oxidation in the presence of nonoxotransferring oxidants.[6] As an alternative to molecular catalysts, purely inorganic Mn oxides[7] and supported Mn complexes[8] have been proposed as heterogeneous water oxidation catalysts. These two research strategies have different advantages: the opportunities for knowledge-guided design of the ligand system and fine-tuning of the electron properties of the metal sites in molecular complexes versus the higher stability and less expensive large scale synthesis of the amorphous oxides. Although the perspective for a stable and efficient molecular catalyst for water oxidation is highly attractive, it still remains unclear if such a molecule exists as evident from the results reported further below.

One of the most important molecular Mn complexes that was reported as a functional model of the WOC in Photosystem II is $[(OH_2)(terpy)Mn(\mu\text{-}O)_2Mn(terpy)\text{-}(OH_2)]^{3+}$ (**1**) (terpy = 2,2′:6,2″-terpyridine, Chart 1). First

Chart 1. Structure of Complex 1 ($[(OH_2)(terpy)Mn(\mu\text{-}O)_2Mn(terpy)(OH_2)]^{3+}$) (A) and Top View of Idealized Layered Mn Oxide (B)[a]
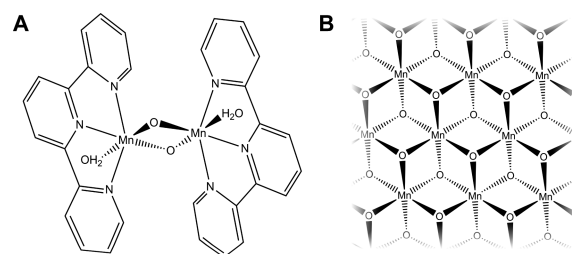
[a]We note that in the catalytically active oxides formed in this study the structure is highly disordered and most likely contains additional out-of-plane Mn ions and Mn vacancies.

described in 1999,[9] it has been extensively studied since then.[7f,10] Water oxidation activity is found in the presence of sodium hypochlorite $(NaClO)^{10a,c}$ or potassium oxone $(KHSO_5)^{.10c,11}$ Both oxidants are working as oxo-transfer reagents, and their use may be a necessary condition for water oxidation by **1**.[10h,12] Yet a reaction resembling the "real" water oxidation in PSII requires a pure electron-transfer oxidant, and mostly cerium(IV) ammonium nitrate (Ce(IV)) is used. In the presence of Ce(IV), O_2-evolution activity of **1** was not

detected, but instead there was decomposition of the complex to MnO_4^-.[10f,i,13]

In contrast to the homogeneous water oxidation catalysis by **1** where the effect of Ce(IV) is still under debate,[10q] high activity toward water oxidation in the presence of Ce(IV) has been verified for **1** adsorbed on clays.[10f,g,i,k,13] According to Narita et al.,[10f] this prevents the decomposition of **1** to MnO_4^- upon Ce(IV) treatment. However, the UV−vis diffuse reflectance and Mn K-edge XANES spectra suggested that the complex may be modified when it is adsorbed on the clay surface.[10f] It was also reported that the 16-line EPR signal typical for dimanganese(III,IV) complexes, and observed for **1** in solution,[9] was not observed for the clay (montmorillonite) hybrid.[10k] Dimerization is discussed in the literature as possible structural change as 2 equiv of oxidized **1** were suggested to cooperatively catalyze water oxidation.[14] Formation of a tetranuclear complex with a μ-oxo-bridged linear core structure upon dimerization of the oxidized **1** was observed in solution,[15] but the conclusions if the dimer can catalyze water oxidation are controversial.[10l,12,15]

Another possibility is that the strong Ce(IV) oxidant induces decomposition of the molecular complex, and purely inorganic metal oxide is formed. To our best knowledge this option has not been thoroughly investigated yet. The likely reason for that is that methods like Raman, UV−vis, FTIR, NMR, or EPR spectroscopy cannot be conclusive either because the molecular precursor and the formed oxide both contain the same $Mn(\mu\text{-O})_2Mn$ motif and cannot be clearly distinguished or due to the amorphous character of the resulting oxide which makes it invisible for many techniques (no defined spectral fingerprints).

Here we use X-ray absorption spectroscopy (XAS) to study the structure of **1** before and after deposition on clay as well as after treatment with Ce(IV). As XAS is a bulk-sensitive technique which can be used to elucidate the structure of noncrystalline materials, we could clarify a pivotal question regarding water oxidation by molecular catalysts: Does the complex stay molecular or is a water-oxidizing oxide material formed?

After its synthesis,[13] **1** was deposited on clay (montmorillonite, Mt), as described in the Supporting Information, resulting in the **1**@Mt hybrid. To investigate its structure before and after Ce(IV) treatment, we collected X-ray absorption spectra at the Mn K-edge (details are given in the Figure S2). The X-ray absorption near-edge structure (XANES, Figure 1) indicates that deposition on clay causes reduction of the Mn ions from a mean oxidation state of 3.5 of the binuclear $Mn^{III,IV}$ complex to ~2.6 in **1**@Mt, as calculated from the detected edge energies[16] (Figure S3). The treatment with Ce(IV) induces Mn reoxidation back to the original level of ~3.5. However, as judged by the shape of the XANES spectra, the **1**@Mt hybrid after Ce(IV) treatment differs clearly from the molecular complex and resembles a layered Mn oxide (Figure 1).

The observed change in the mean Mn oxidation state relates to structural changes of **1**, which are visible in the extended X-ray absorption fine-structure (EXAFS, Figure 2). The EXAFS spectrum of the initial molecular complex is well compatible with the crystal structure (Table S1), proving the intactness of the starting material. The spectrum of **1**@Mt, however, indicates a structural change. The Mn−Mn distance increases from 2.72 Å in **1**, which is typical for di-μ-oxo-bridged Mn^{III}− Mn^{IV} ions,[5d] to 3.09 Å in **1**@Mt (Table S1). Increase of the
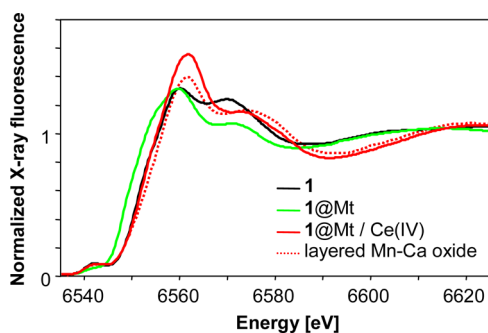

Figure 1. XANES spectra of **1** before deposition on montmorillonite (molecular complex, black line), after deposition on montmorillonite (**1**@Mt hybrid, green line), and after Ce(IV) treatment (**1**@Mt/ Ce(IV), red line). For comparison the spectrum of the Mn−Ca oxide reported in ref 7d is shown (dotted red line).
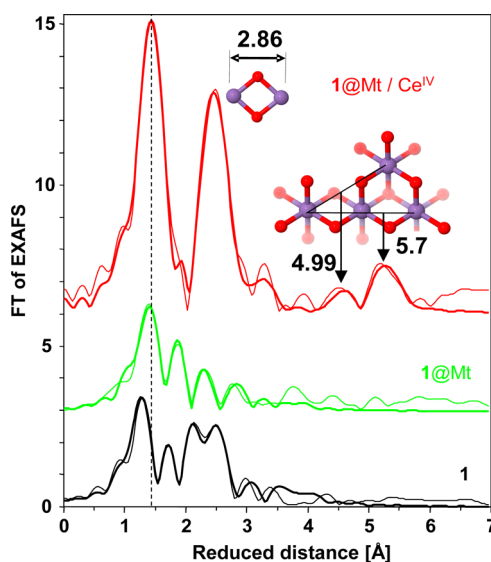

Figure 2. Fourier transformation (FT) of the EXAFS spectra of molecular complex **1** (black), **1**@Mt hybrid (green), and **1**@Mt after Ce(IV) treatment (red). The original EXAFS spectra are shown in the Figure S4. Thin lines represent the experimental spectra, and thicker lines represent the simulations with the parameters listed in Tables 1 and S1.

bond lengths is observed also for the O/N ligands in the first Mn coordination sphere and is explainable by the reduction of the Mn ions suggested by the XANES spectra. Indications for structural changes upon deposition of **1** on Mt have been found before by UV−vis absorption[13] and EPR spectroscopy.[10k] Changes in XANES and UV−vis spectra upon deposition of **1** on mica clay were reported, although Mn reduction was not observed.[10f] We may speculate that montmorillonite support can induce decomposition of the complex and partial ligand oxidation by the Mn(III,IV) ions. Incomplete decomposition of mixed Mn complexes induced by Al(III) salt was reported previously.[17] The averaged oxidation state of 2.6 together with the metal−metal distance of 3.09 Å, and the presence of carbon ligands suggests that upon deposition on montmorillonite, the structure of **1** changes, but the molecular complex does not simply degrade by formation of Mn(II) ions which are ligated by groups of the clay material and water molecules, in line with the results of a previous investigation based on EPR analysis.[10k] Such a partial decomposition where most likely the ligands are

dissociated may represent a crucial preliminary step for the formation of Mn oxide phase upon Ce(IV) treatment.

The Ce(IV) treatment not only causes Mn reoxidation (Figure 1) but also pronounced structural changes signified, *inter alia*, by appearance of a strong peak in the Fourier-transformed EXAFS spectra at a reduced distance of 2.5 Å (Figure 2), which corresponds to a real distance between Mn ions of 2.86 Å (Table 1). Distances of 2.86 Å are indicative of

Table 1. Parameters Obtained by Simulation of the k^3-Weighted EXAFS Spectra of 1 after Deposition on Clay and Treatment With Ce(IV)[a]

shell	N	R [Å]	σ [Å]
Mn−O	6.0[b]	1.87 ± 0.01	0.07 ± 0.01
Mn−Mn	3.2 ± 0.7	2.86 ± 0.01	0.05 ± 0.01
Mn−Mn	0.4 ± 0.5	3.10 ± 0.05	0.06[b]
Mn−Mn	0.8 ± 0.4	3.81 ± 0.03	0.06[b]
Mn−Mn	1.6 ± 0.8	4.99 ± 0.03	0.06[b]
Mn−Mn[c]	3.3 ± 0.6	2 × 2.86[b]	0.06[b]

[a]The 68% confidence interval of the respective fit parameter is indicated. [b]Not varied in the least-squares fit of the EXAFS spectra. [c]Multiple scattering paths were included in the simulation.

di-μ_3-oxo bridging between high-valent Mn ions. This means that two octahedrally coordinated Mn ions share two of their oxygen ligands ('di-μ-oxo-bridging' or 'edge-sharing MnO$_6$ octahedra') and that an extended structure of edge-sharing octahedra facilitates μ_3-oxo bridging (one oxygen is bound to three Mn ions).[18] In **1**, the initial binuclear complex, the Mn−Mn distance is shorter (2.72 Å) because of di-μ_2-oxo instead of di-μ_3-oxo bridging.

Extended structures of edge-sharing octahedra result in layered Mn oxides, as found in birnesites.[18c] In perfectly ordered and infinitesimally extended layered-oxide structures as shown in Chart 1, each Mn ion would be connected by di-μ_3-oxo bridges to 6 neighboring Mn ions resulting in an EXAFS coordination number of 6 for the shortest Mn−Mn distance. In **1**@Mt/Ce(IV), the coordination number is around 3 implying a significant disorder or fragmentation of the layered oxide. Formation of a layer-type Mn oxide is further confirmed by detection of a 5.7 Å distance, which corresponds to a linear Mn^a−(μ-O)$_2$−Mn^b−(μ-O)$_2$−Mn^c motif (distance between Mn^a and Mn^c of 2 × 2.86 Å, as indicated in Figure 2). Moreover, the "diagonal" distance of a layered oxide (about 5 Å, see Figure 2) is well resolved. The atom−atom distances detected in **1**@Mt/Ce(IV) are very similar to those reported for other catalytically active, layered Mn oxides[7d] (Figure S6). However, the relatively high coordination numbers point to a comparatively better ordered structure (or larger layer fragments). Still the formed Mn oxide can not be detected by powder diffraction measurements, *inter alia* due to the strong Bragg reflections from the clay support (Figure S7). The Mn−Mn distances of 3.1 and 3.8 Å previously assigned to di-μ-oxo bridging to an out-of-plane Mn ions in a Mn$_4$(μ-O)$_4$ cubane structure and mono-μ-oxo bridging to Mn ions above layer vacancies, respectively, might be detectable in **1**@Mt/Ce(IV), but with coordination numbers close to the detection limit (Table 1).

In the EXAFS spectrum of **1**@Mt after Ce(IV) treatment, the terpyridine ligands are not detectable. Ce(IV) in the high concentrations used in water oxidation reaction can easily decompose the organic ligands.[19] Oxidation of **1** upon Ce(IV)

treatment or exposure at low pH and CO$_2$ evolution stemming from ligand decomposition was previously reported in solution.[20] We also investigated a second mixed-valent Mn(III,IV) complex, namely [(cyclam)Mn(μ-O)$_2$Mn-(cyclam)]$^{3+}$ (**2**, cyclam = 1,4,8,11-tetrazacyclotetradecane).[21] It is less prone to Ce(IV)-induced degradation possibly relating to the closed organic ligand shell without the terminal water-coordination sites present in **1** (Figure S1). The incomplete oxide conversion of **2**@Mt upon Ce(IV) treatment (Figure S5 and Table S2) correlates with a lower O$_2$-evolution activity (Figure S8). The ligand type generally may be a determinant of amount and type of Mn oxides formed from precursor complexes.[22] Interestingly the O$_2$ production rate for **1**@Mt hybrid seems to increase with time. This suggests some progressive increase in the catalytic activity of the film consistent with continuous degradation/oxide formation in the time course of Ce(IV) treatment.

Summarizing the above discussion, the XANES and EXAFS analyses show that upon Ce(IV) treatment, a disordered or fragmented, layered Mn oxide of the birnesite type is formed. On the contrary for **1**@Mt, Yagi et al.[10f] concluded that a dimeric form of **1** catalyzes water oxidation based on a linear increase of the turnover frequency (TOF in mol O$_2$/s·mol Mn) with increasing of concentration of the complex. However, manganese oxides@clay hybrids with similar water oxidation activity can be obtained starting not from complex **1** but from simple Mn salts, e.g., Mn(NO$_3$)$_2$@Mt.[8d] (TOF for **1**@Mt hybrid with the typical in this study loading of 0.35 mmol$_{Mn}$·gr $_{clay}^{-1}$ is ~0.06 mmol$_{O_2}$·mol$_{Mn}^{-1}$·s^{-1}) The oxides formed from Mn salts exhibit the same linear relation between TOF and Mn concentration[8d] (Figure S9), suggesting that the experiment of Yagi et al. cannot be interpreted as a clear evidence for a formation of a molecular dimer. A possible alternative explanation of the observed dependence is the need of cooperative interaction of a relatively high number of Mn ions of the oxide in order to facilitate efficient accumulation of oxidizing equivalents. Such accumulation of oxidizing equivalents before onset of O−O bond formation is known from biological water oxidation of oxygenic photosynthesis.[3,23]

For water oxidation by **1**@Mt, we determined an activation enthalpy of 60 kJ (Figure S10). This figure compares well with values recently reported for water-oxidizing Mn oxides[24] and also supports the statement that the oxide formed upon Ce(IV) treatment of **1** is the catalytically active material.

In conclusion, by Mn K-edge XAS and kinetic analyses of **1**@Mt treated with Ce(IV) we show that the active catalyst for water oxidation clearly is not a molecular complex but a layer-type Mn oxide formed on clay upon treatment with the Ce(IV) oxidant. Most likely for first-row transition metals in general, Ce(IV) is a strong promoter of formation of water-oxidizing high-valent oxides from molecular complexes or from low-valent oxide particles.[25] As Ce(IV) is very often used as a nonoxo-transferring oxidant, control experiments are generally indispensable to exclude that the putative water oxidation catalysis by a molecular complex originates from a catalytically active oxide formed upon oxidant treatment. The question remains open whether in the future a true molecular Mn-based water oxidation catalyst can be designed that offers a technological perspective.

ASSOCIATED CONTENT

S Supporting Information

Experimental details and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

mmnajafpour@iasbs.ac.ir; ivelina.zaharieva@fu-berlin.de

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) California Energy Commission, http://www.energyquest.ca.gov/projects/split_h2o.html, accessed May 6, 2014.

(2) (a) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15729. (b) Jacobson, M. Z. *Energy Environ. Sci.* **2009**, *2*, 148. (c) Barber, J. *Chem. Soc. Rev.* **2009**, *38*, 185.

(3) Dau, H.; Limberg, C.; Reier, T.; Risch, M.; Roggan, S.; Strasser, P. *ChemCatChem* **2010**, *2*, 724.

(4) (a) Umena, Y.; Kawakami, K.; Shen, J.-R.; Kamiya, N. *Nature* **2011**, *473*, 55. (b) Dau, H.; Zaharieva, I.; Haumann, M. *Curr. Opin. Chem. Biol.* **2012**, *16*, 3.

(5) (a) Wieghardt, K. *Angew. Chem., Int. Ed.* **1989**, *28*, 1153. (b) Rüttinger, W.; Dismukes, G. C. *Chem. Rev.* **1997**, *97*, 1. (c) Yagi, M.; Kaneko, M. *Chem. Rev.* **2001**, *101*, 21. (d) Mukhopadhyay, S.; Mandal, S. K.; Bhaduri, S.; Armstrong, W. H. *Chem. Rev.* **2004**, *104*, 3981. (e) Cady, C. W.; Crabtree, R. H.; Brudvig, G. W. *Coord. Chem. Rev.* **2008**, *252*, 444. (f) Mullins, C. S.; Pecoraro, V. L. *Coord. Chem. Rev.* **2008**, *252*, 416. (g) Herrero, C.; Lassalle-Kaiser, B.; Leibl, W.; Rutherford, A. W.; Aukauloo, A. *Coord. Chem. Rev.* **2008**, *252*, 456.

(6) (a) Beckmann, K.; Uchtenhagen, H.; Berggren, G.; Anderlund, M. F.; Thapper, A.; Messinger, J.; Styring, S.; Kurz, P. *Energy Environ. Sci.* **2008**, *1*, 668. (b) Shevela, D.; Koroidov, S.; Najafpour, M. M.; Messinger, J.; Kurz, P. *Chem.—Eur. J.* **2011**, *17*, 5415.

(7) (a) Gorlin, Y.; Jaramillo, T. F. *J. Am. Chem. Soc.* **2010**, *132*, 13612. (b) Najafpour, M. M.; Ehrenberg, T.; Wiechen, M.; Kurz, P. *Angew. Chem., Int. Ed.* **2010**, *49*, 2233. (c) Robinson, D. M.; Go, Y. B.; Greenblatt, M.; Dismukes, G. C. *J. Am. Chem. Soc.* **2010**, *132*, 11467. (d) Zaharieva, I.; Najafpour, M. M.; Wiechen, M.; Haumann, M.; Kurz, P.; Dau, H. *Energy Environ. Sci.* **2011**, *4*, 2400. (e) Takashima, T.; Hashimoto, K.; Nakamura, R. *J. Am. Chem. Soc.* **2012**, *134*, 1519. (f) Wiechen, M.; Berends, H.-M.; Kurz, P. *Dalton Trans.* **2012**, *41*, 21. (g) Zaharieva, I.; Chernev, P.; Risch, M.; Klingan, K.; Kohlhoff, M.; Fischer, A.; Dau, H. *Energy Environ. Sci.* **2012**, *5*, 7081. (h) Bergmann, A.; Zaharieva, I.; Dau, H.; Strasser, P. *Energy Environ. Sci.* **2013**, *6*, 2745.

(8) (a) Brimblecombe, R.; Swiegers, G. F.; Dismukes, G. C.; Spiccia, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 7335. (b) Jiao, F.; Frei, H. *Chem. Commun.* **2010**, *46*, 2920. (c) Hocking, R. K.; Brimblecombe, R.; Chang, L.-Y.; Singh, A.; Cheah, M. H.; Glover, C.; Casey, W. H.; Spiccia, L. *Nat. Chem.* **2011**, *3*, 461. (d) Najafpour, M. M.; Moghaddam, A. N. *New J. Chem.* **2012**, *36*, 2514.

(9) Collomb, M. N.; Deronzier, A.; Richardot, A.; Pecaut, J. *New J. Chem.* **1999**, *23*, 351.

(10) (a) Limburg, J.; Vrettos, J. S.; Liable-Sands, L. M.; Rheingold, A. L.; Crabtree, R. H.; Brudvig, G. W. *Science* **1999**, *283*, 1524. (b) Limburg, J.; Szalai, V. A.; Brudvig, G. W. *Dalton Trans.* **1999**, 1353. (c) Limburg, J.; Vrettos, J. S.; Chen, H. Y.; de Paula, J. C.; Crabtree, R. H.; Brudvig, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 423. (d) Collomb, M. N.; Richardot, A.; Baffert, C.; Deronzier, A. *J. Inorg. Biochem.* **2001**, *86*, 184. (e) Baffert, C.; Chen, H. G.; Crabtree, R. H.; Brudvig, G. W.; Collomb, M. N. *J. Electroanal. Chem.* **2001**, *506*, 99. (f) Narita, K.; Kuwabara, T.; Sone, K.; Shimizu, K. I.; Yagi, M. *J. Phys. Chem. B* **2006**, *110*, 23107. (g) Yagi, M.; Narita, K.; Maruyama, S.; Sone, K.; Kuwabara, T.; Shimizu, K. *Biochim. Biophys. Acta* **2007**, *1767*, 660. (h) Kurz, P.; Berggren, G.; Anderlund, M. F.; Styring, S. *Dalton Trans.* **2007**, 4258. (i) Kurz, P. *Dalton Trans.* **2009**, 6103. (j) Cady, C. W.; Shinopoulos, K. E.; Crabtree, R. H.; Brudvig, G. W. *Dalton Trans.* **2010**, *39*, 3985. (k) Berends, H. M.; Homburg, T.; Kunz, I.; Kurz, P. *Appl. Clay Sci.* **2011**, *53*, 174. (l) Gao, Y.; Crabtree, R. H.; Brudvig, G. W. *Inorg. Chem.* **2012**, *51*, 4043. (m) Hatakeyama, M.; Nakata, H.; Wakabayashi, M.; Yokojima, S.; Nakamura, S. *J. Phys. Chem. A* **2012**, *116*, 7089. (n) Yamazaki, H.; Igarashi, S.; Nagata, T.; Yagi, M. *Inorg. Chem.* **2012**, *51*, 1530. (o) Yamazaki, H.; Ueno, T.; Aiso, K.; Hirahara, M.; Aoki, T.; Nagata, T.; Igarashi, S.; Yagi, M. *Polyhedron* **2013**, *52*, 455. (p) Rumberger, E. M. W.; Ahn, H. S.; Bell, A. T.; Tilley, T. D. *Dalton Trans.* **2013**, *42*, 12238. (q) Hirahara, M.; Shoji, A.; Yagi, M. *Eur. J. Inorg. Chem.* **2014**, *2014*, 595.

(11) (a) Chen, H. Y.; Tagore, R.; Das, S.; Incarvito, C.; Faller, J. W.; Crabtree, R. H.; Brudvig, G. W. *Inorg. Chem.* **2005**, *44*, 7661. (b) Wei, Z.; Cady, C. W.; Brudvig, G. W.; Hou, H. J. M. *J. Photochem. Photobiol. B* **2011**, *104*, 118. (c) Zhang, F.; Cady, C. W.; Brudvig, G. W.; Hou, H. J. M. *Inorg. Chim. Acta* **2011**, *366*, 128.

(12) Baffert, C.; Romain, S.; Richardot, A.; Lepretre, J. C.; Lefebvre, B.; Deronzier, A.; Collomb, M. N. *J. Am. Chem. Soc.* **2005**, *127*, 13694.

(13) Yagi, M.; Narita, K. *J. Am. Chem. Soc.* **2004**, *126*, 8084.

(14) Yagi, M.; Toda, M.; Yamada, S.; Yamazaki, H. *Chem. Commun.* **2010**, *46*, 8594.

(15) Chen, H.; Faller, J. W.; Crabtree, R. H.; Brudvig, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 7345.

(16) Dau, H.; Liebisch, P.; Haumann, M. *Anal. Bioanal. Chem.* **2003**, *376*, 562.

(17) Stathopoulos, V. N.; Petrakis, D. E.; Hudson, M.; Falaras, P.; Neofytides, S. G.; Pomonis, P. J. In *Studies in Surface Science and Catalysis*; Unger, K.K., G. K, Baselt, J. P., Eds.; Elsevier: Amsterdam, 2000; Vol. 128, pp 593−602.

(18) (a) Gaillot, A.-C.; Flot, D.; Drits, V. A.; Manceau, A.; Burghammer, M.; Lanson, B. *Chem. Mater.* **2003**, *15*, 4666. (b) Saratovsky, I.; Wightman, P. G.; Pasten, P. A.; Gaillard, J.-F.; Poeppelmeier, K. R. *J. Am. Chem. Soc.* **2006**, *128*, 11188. (c) Spiro, T. G.; Bargar, J. R.; Sposito, G.; Tebo, B. M. *Acc. Chem. Res.* **2010**, *43*, 2.

(19) Nair, V.; Deepthi, A. *Chem. Rev.* **2007**, *107*, 1862.

(20) Tagore, R.; Chen, H.; Zhang, H.; Crabtree, R. H.; Brudvig, G. W. *Inorg. Chim. Acta* **2007**, *360*, 2983.

(21) Brewer, K. J.; Calvin, M.; Lumpkin, R. S.; Otvos, J. W.; Spreer, L. O. *Inorg. Chem.* **1989**, *28*, 4446.

(22) Singh, A.; Hocking, R. K.; Chang, S. L. Y.; George, B. M.; Fehr, M.; Lips, K.; Schnegg, A.; Spiccia, L. *Chem. Mater.* **2013**, *25*, 1098.

(23) Dau, H.; Haumann, M. *Coord. Chem. Rev.* **2008**, *252*, 273.

(24) Najafpour, M. M.; Sedigh, D. J.; Pashaei, B.; Nayeri, S. *New J. Chem.* **2013**, *37*, 2448.

(25) Indra, A.; Menezes, P. W.; Zaharieva, I.; Baktash, E.; Pfrommer, J.; Schwarze, M.; Dau, H.; Driess, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 13206.