Carbon Dots

Deutsche Ausgabe: DOI: 10.1002/ange.201604355
Internationale Ausgabe: DOI: 10.1002/anie.201604355

Clean Donor Oxidation Enhances the H_2 Evolution Activity of a Carbon Quantum Dot–Molecular Catalyst Photosystem

*Benjamin C. M. Martindale, Evelyne Joliat, Cyril Bachmann, Roger Alberto, and Erwin Reisner**

Abstract: *Carbon quantum dots (CQDs) are new-generation light absorbers for photocatalytic H_2 evolution in aqueous solution, but the performance of CQD-molecular catalyst systems is currently limited by the decomposition of the molecular component. Clean oxidation of the electron donor by donor recycling prevents the formation of destructive radical species and non-innocent oxidation products. This approach allowed a CQD-molecular nickel bis(diphosphine) photocatalyst system to reach a benchmark lifetime of more than 5 days and a record turnover number of 1094 ± 61 $mol_{H2}(mol_{Ni})^{-1}$ for a defined synthetic molecular nickel catalyst in purely aqueous solution under AM1.5G solar irradiation.*

Carbon quantum dots (CQDs) have recently emerged as an exciting new allotrope of carbon because of their ability to absorb UV/Vis light and fluoresce. These properties have found use in a variety of applications, from biosensing and fluorescence probes, to chemical sensing and light-emitting devices.[1–5] More recently, CQDs have been employed as light harvesters in photocatalytic applications, such as the co-sensitization of metal oxides in solar cells, photodegradation of organic dyes, and as photosensitizers in solar fuel synthesis.[6–13]

A recent study showed that carboxylate-terminated amorphous CQDs produced by a bottom-up synthetic method could photosensitize the water soluble molecular nickel H_2-evolving catalyst **NiP** (Figure 1).[13] This unique example of a CQD-molecular catalyst hybrid system made use of a sacrificial electron donor (ethylenediaminetetraacetic acid (EDTA)) to quench the holes formed upon generation of the photoexcited state, but only achieved a final TON_{Ni} of 64 with a lifetime of 4 hours. This limited stability is assigned to the degradation of **NiP** during catalytic turnover and/or decomposition through unwanted products generated by the overall reaction scheme—in this case the oxidation products of EDTA.

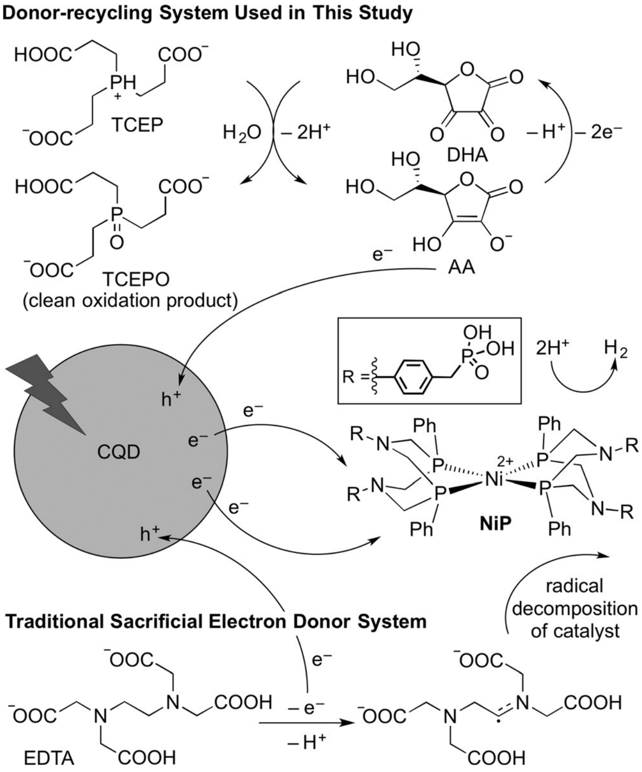

Figure 1. Representation of solar H_2 production using CQD-**NiP**. The electron-donor systems, TCEP/AA or EDTA, quench the photoinduced vacancies in the CQDs. EDTA forms radicals upon oxidation and causes decomposition of the catalyst and cessation of H_2 evolution. DHA recycling by TCEP prevents the formation of large quantities of reactive oxidation products. Two bromide anions in **NiP** are omitted for clarity.

Sacrificial electron donors (and acceptors) are extensively used to isolate half-reactions in photocatalytic processes because it is challenging to couple oxidative and reductive catalysts in a full photoredox cycle under the same conditions.[14] Triethanolamine (TEOA), triethylamine (TEA), and EDTA are commonly used sacrificial electron donors, but they undergo one-electron oxidation reactions that result in potentially destructive radical species. Ascorbic acid (AA) is a common proton and electron donor, but its oxidation product, dehydroascorbic acid (DHA), is known to self-inhibit the electron donor ability of AA.[15] As an effectively unlimited resource, H_2O is often considered the ideal donor molecule. However, upon oxidation it can produce intermediates such as the reactive oxygen species $OH^{\bullet}$ and H_2O_2, and even the final product O_2 can be damaging to the components of the reductive half-reaction.[16] **NiP** was shown to be irreversibly inhibited by O_2 through oxidation of

---

[*] B. C. M. Martindale, Dr. E. Reisner
Christian Doppler Laboratory for Sustainable SynGas Chemistry,
Department of Chemistry, University of Cambridge
Lensfield Road, Cambridge, CB2 1EW (UK)
E-mail: reisner@ch.cam.ac.uk
Homepage: http://www-reisner.ch.cam.ac.uk/

E. Joliat, Dr. C. Bachmann, Prof. Dr. R. Alberto
Department of Chemistry, University of Zürich
Winterthurerstrasse 190, 8057 Zürich (Switzerland)

Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201604355.

its phosphine ligands.[16–18] Furthermore, even in cases where O_2 is not detrimental to the system, it would rarely be considered a commercially useful product and requires separation from mixtures of gaseous products.

A suitable electron donor for a photocatalytic system should generate an oxidized product that is stable and innocent, causing no adverse effects on the components of the system. A donor system consisting of AA (proton/electron relay) and tris(carboxyethyl)phosphine (TCEP) was previously shown to extend the lifetime of a solar H_2 production system using molecular ruthenium and rhenium dyes, improving performance by two- to three-times by preventing electron back-transfer from the photosensitizer to DHA.[19] Herein, we employ the TCEP/AA donor system with CQDs to avoid the formation of intermediates or products that are destructive to the molecular catalyst (Figure 1). Photocatalytic H_2 generation has been studied with CQDs and TCEP/AA in combination with **NiP** and a series of molecular cobalt catalysts, and a benchmark performance for the CQD-**NiP** photosystem is reported.

Carboxylate-terminated amorphous CQDs (7 nm diameter), **NiP** (Figure 1) and the cobalt catalysts **1**–**3** (Figure 2) were synthesized according to established procedures.[13,20–24] The water-soluble DuBois-type catalyst **NiP** is active in aqueous electrocatalytic and photocatalytic systems,[17,22,25] whereas the majority of Ni-P_2N_2 complexes are active only in acidic organic solutions.[26,27] **NiP** has a low overpotential ($\eta \approx 200$ mV) for H_2 evolution, which is a significant advantage when using photosensitizers with an excited state potential closely matched to the thermodynamic potential for proton reduction. When **NiP** is used in conjunction with a molecular ruthenium dye ($E(\mathrm{RuP/RuP^-}) = -1.08$ V vs. NHE), a high initial H_2 evolution rate ($\mathrm{TOF_{Ni}}$ of 460 h^{-1}) but low stability (final $\mathrm{TON_{Ni}}$ of 723) is observed.[22]

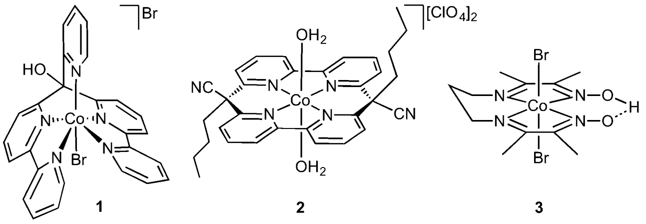

Figure 2. Chemical structures of the molecular cobalt catalysts **1**, **2**, and **3**.

Photocatalytic systems comprised of CQDs (10 mg) as the photosensitizer, **NiP** (10 nmol) as the catalyst, and the regenerating donor TCEP/AA, were assembled and placed under simulated solar light irradiation (100 mW cm^{-2}, AM1.5G; Figure 3). The results obtained with these components indicate that the CQD-**NiP** photocatalyst system is remarkably more stable in the presence of the TCEP/AA donor than in EDTA, which can be attributed to clean formation of the stable product tris(carboxyethyl)phosphine oxide (TCEPO); TCEPO does not act to degrade **NiP**, in contrast to the destructive radicals formed during EDTA oxidation (Supporting Information, Figure S1).[28]

The maximum catalytic rates (expressed as $\mathrm{TOF_{Ni}}$ of 41 and 53 h^{-1} for EDTA and TCEP/AA, respectively) are similar for both systems (see inset of Figure 1), but activity decreases after the first hour in EDTA, leading to a final $\mathrm{TON_{Ni}}$ of 64 ± 4. By comparison, the TCEP/AA system continues almost linearly for around 24 hours, giving rise to a $\mathrm{TON_{Ni}}$ of 1094 ± 61 (a 17-fold increase). This is a record TON for **NiP**,[13,22,25] and indeed any water-soluble DuBois-type catalyst,[29] achieved by replacing the most expensive component of the previous benchmark system, the ruthenium dye,[22] with the low-cost, scalable and photostable CQDs. This CQD-**NiP** photosystem also achieves the highest turnover with a defined synthetic molecular nickel catalyst in purely aqueous solution, and is competitive with the best-performing systems in molecular photocatalysis, which make

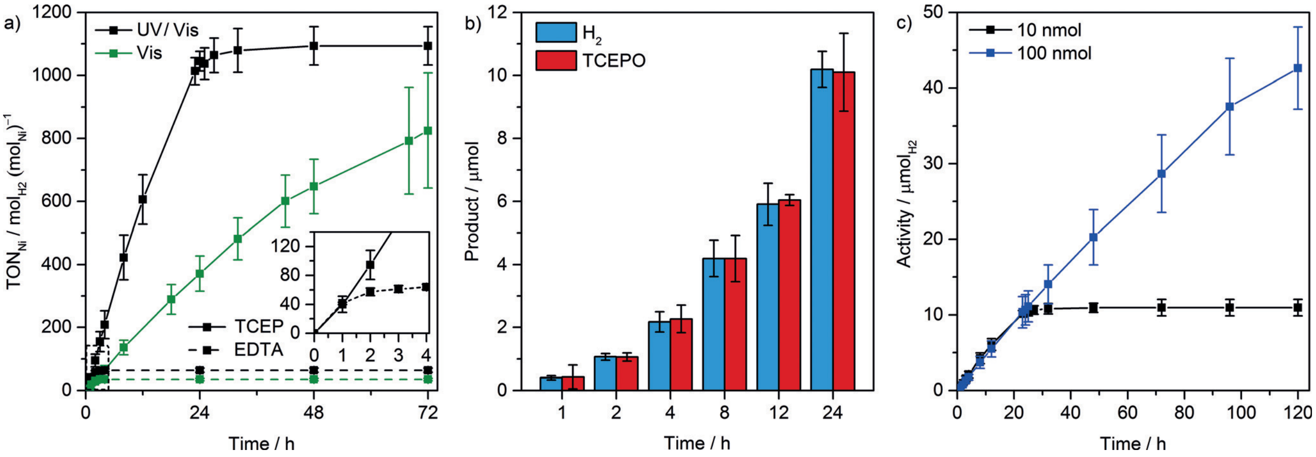

Figure 3. a) Photocatalytic H_2 generation using CQD (10 mg) and **NiP** (10 nmol) in an aqueous solution containing TCEP/AA (0.1 M each, pH 5, 3 mL, solid traces) or EDTA (0.1 M, pH 6, 3 mL, dashed traces) under 1 sun UV/Vis ($\lambda > 300$ nm, black traces) and visible-only ($\lambda > 400$ nm, green traces) irradiation. The inset shows the first 4 hours of activity. b) Time-resolved H_2 and TCEPO formation using CQD (10 mg) and **NiP** (10 nmol) with TCEP/AA and c) H_2 generation using CQD (10 mg) and **NiP** (10 and 100 nmol) with TCEP/AA (0.1 M each, pH 5, 3 mL) under 1 sun UV/Vis irradiation. All experiments thermoregulated at 25 °C, under an N_2 atmosphere (containing 2% CH_4) and irradiated with simulated solar light (100 mW cm^{-2}, AM1.5G).

use of toxic, expensive, and fragile photosensitizers, as well as organic co-solvents.[30–34] Although an impressive TON_{Ni} was previously reported in a photocatalytic system using thiol-capped CdSe QDs and nickel ions, this system utilizes toxic components and does not make use of a well-defined molecular catalyst.[35]

Control experiments using either TCEP (0.1M, pH 5) or AA (0.1M, pH 5) showed much lower photoactivity (Supporting Information, Figure S2). With AA the system stability was low (4 hours), in agreement with previous reports describing re-reduction of DHA into AA by the photosensitizer, effectively creating a short circuit in the system (TOF_{Ni} 20 h^{-1}, TON_{Ni} 50). When only TCEP was used the stability was longer (> 12 hours) but the initial rate of activity was lower (TOF_{Ni} 10 h^{-1}) and a TON_{Ni} of only 143 was obtained. This observation suggests that although the direct photo-oxidation of TCEP by CQD is possible, its kinetics are slower than AA oxidation, and the primary quenching of photo-induced holes is mediated by AA, followed by subsequent irreversible reduction of DHA back to AA by TCEP (Figure 1).[19]

Proof that TCEP is the ultimate source of electrons in the photocatalytic system comes from quantitative analysis of the product TCEPO using ^{31}P NMR spectroscopy. Time-resolved measurements confirmed a 1:1 ratio of H_2:TCEPO throughout the photocatalytic reaction (Figure 3b). These results also confirmed the presence of TCEPO as the only detectable product of TCEP oxidation, in agreement with the quantitative and irreversible formation of TCEPO and the absence of radical breakdown products (Supporting Information, Figure S3). Thus, the products of reduction (H_2) and oxidation (TCEPO) can accumulate over prolonged periods of time in this closed photosystem in the gas and solution phases, respectively. The absence of apparent quenching of compensating half-reactions, and clean product separation, is remarkable and emphasizes the benefit of organic substrate oxidation rather than water oxidation in a single compartment. Classical water splitting would result in O_2 generation, which gives rise to product separation issues and interference with the reductive half-reaction.

A long lifetime of approximately 1 day is observed for this system with a low catalyst loading (10 nmol). We subsequently studied the stability of **NiP** in TCEP/AA solution by UV/Vis spectroscopy; in the dark, under visible light, and under UV/Vis solar irradiation (Supporting Information, Figure S4). The absorption spectrum of **NiP** shows two bands: a weak band at 499 nm, characteristic of square-planar complexes and a stronger charge transfer band below 350 nm.[36,37] Monitoring the peak at 499 nm reveals negligible loss of **NiP** in the dark or with visible light irradiation ($\lambda >$ 400 nm), but under UV/Vis solar irradiation ($\lambda > 300$ nm) there is a 17% reduction in the **NiP** signal after 24 hours (Supporting Information, Figure S5), which is presumably due to ligand displacement from the metal center. The ligand substituted Ni^{2+} in TCEP/AA solution is not an active catalyst, as demonstrated by control experiments using $NiCl_2$ under these conditions (Supporting Information, Figure S6). As a result of the higher **NiP** stability under visible-only irradiation the H_2-photosystem was also more stable, with linear performance for the first 2 days (TON_{Ni} 825 ± 183 after 3 days). A decreased H_2 evolution rate (TOF_{Ni}) was observed with visible-only irradiation compared to UV/Vis irradiation, which is due to decreased light absorption (Figure 3a; Supporting Information, Figure S7).

Other possible degradation pathways for **NiP** are degradation of the ligand framework during catalytic turnover, or quenching of holes in the CQD excited state by **NiP**. As described above, the latter pathway is viable because CQDs are able to oxidize the phosphine TCEP under irradiation (Supporting Information, Figure S2). We infer that the phosphine ligands of **NiP** can be oxidized in a similar way, by holes in the presence of water, albeit more slowly (Supporting Information, Figure S5). Oxidized **NiP** has also previously been formed by O_2 in solution, and was shown to be inactive as an H_2 evolving catalyst.[16–18] Nevertheless, decomposition of **NiP** by radical oxidation products in EDTA is the dominant pathway (Figure 1). Hence, the overall lifetime of the CQD-**NiP** photosystem is vastly increased when using the TCEP/AA donor system, which has a stable TCEPO oxidation product.

When using a 10-fold increased loading of **NiP** (100 nmol), the amount of H_2 produced during the first 24 hours is the same as that obtained at a lower loading, indicating that the optimal loading has been reached for the concentration of CQD and light intensity used (Figure 3c). However, an increased amount of **NiP** resulted in almost linear H_2 evolution over days, and the system was still active when the experiment was halted after 5 days. These observations clearly demonstrate the long-lived stability of CQDs as light absorbing components in such photosystems; they offer significant advantages over organic, and some precious metal based molecular dyes, which have poor photostability under solar irradiation.[22,38]

Complexes **1**, **2**, and **3** are established cobalt H_2 evolving catalysts bearing polydentate sp^2-nitrogen, pentapyridyl, pyrphyrin, and diimine–dioxime ligands, respectively (Figure 2). Previously, only molecular rhenium and ruthenium dyes with a high excited state potential were employed as photosensitizers for compounds **1** and **2** because of the large overpotential of cobalt polypyridyl complexes ($\eta \geq 800$ mV).[39] However, the increased stability of these ligand frameworks leads to long-term activity over a period of days with a final TON_{Co} of 33 300 and 21 900, respectively.[19,24] Catalyst **3** has a lower overpotential ($\eta \approx 400$ mV) than **1** and **2**,[40] but displays a lower catalytic rate.[41] Photocatalytic systems involving catalyst **3** previously showed a lower maximum TON_{Co} of 90.[15,21] These three cobalt cataysts were employed to establish CQDs more widely as a general photosensitizer for molecular catalysts other than **NiP**, and to examine the relationship between CQD and catalyst overpotential.

Analogous photocatalytic systems comprised of a CQD photosensitizer and a cobalt catalyst from the aforementioned series were tested for solar H_2 production in the TCEP/AA donor system (Figure 4). All the systems performed with a significantly lower rate of H_2 production than those using the **NiP** catalyst; the highest rate was observed using **1** (TOF_{Co} of 8 h^{-1}). Complex **2**, while slower, has greater

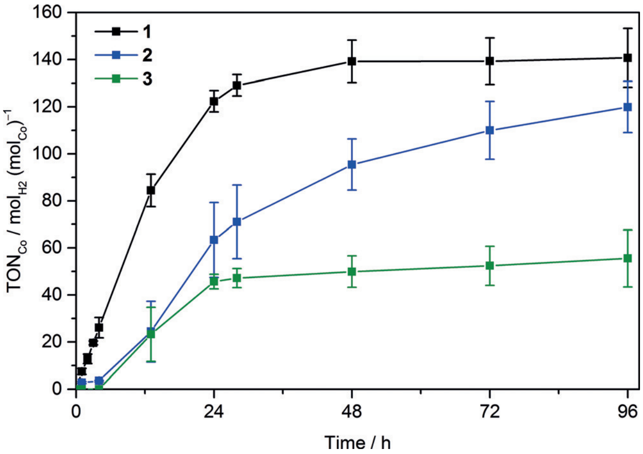

Figure 4. H_2 generation using CQD (10 mg) and various cobalt-containing molecular catalysts (10 nmol) in an aqueous solution containing TCEP/AA (0.1 M each, pH 5, 3 mL) under 1 sun UV/Vis irradiation (AM1.5G) under an N_2 atmosphere (containing 2% CH_4) at 25 °C. The structures of the catalysts **1**, **2**, and **3** are shown in Figure 2.

stability and some activity persists even after 4 days irradiation, leading to similar final TON_{Co} values in both cases (141 ± 13 and 120 ± 11 for **1** and **2**, respectively). These systems display lower performance compared to the same catalysts using precious metal-based molecular dyes, indicating that high driving force photosensitizers are required to gain the best performance out of these high overpotential molecular cobalt catalysts. Complex **3** is shown to be an inferior catalyst with both a low initial rate and stability that only lasts about 24 hours (TON_{Co} 56 ± 12). However, this overall performance is broadly similar to that observed using high driving force rhenium dyes because of the lower overpotential requirement of this type of catalyst. The molecular catalytic mechanism of the cobalt-based catalysts was confirmed by control experiments with either $CoCl_2$ or in the absence of catalyst; negligible H_2 was evolved in both cases (Supporting Information, Figure S6).

Cyclic voltammetry of the soluble CQDs in aqueous solution showed a wave centered at around −550 mV (vs. RHE), which is assigned to the potential of the CQD/CQD^- couple (Supporting Information, Figure S8).[42] It is likely that there is a heterogeneous distribution of surface chromophores on the CQD, therefore this half-wave gives a rough estimate of the average redox potential and the thermodynamic driving force of a photoexcited electron in the CQD, which follows the expected reductive quenching of the charge separated excited state by the electron donor.[19] An excited CQD (estimated average $\eta \approx 550$ mV for proton reduction) gives ample driving force for **NiP** ($\eta \approx 200$ mV) and **3** ($\eta \approx 400$ mV) to produce H_2, but limited driving force for the stable cobalt-based catalysts **1** and **2** ($\eta > 800$ mV). Hence, catalysts with an overpotential lower than that determined for the excited CQD (such as **NiP** and catalyst **3**) display excellent performance, which matches or even exceeds that of ruthenium/rhenium dyes. On the other hand, the cobalt catalysts **1** and **2** require a higher overpotential for catalysis and the catalytic rates are therefore slow. Thus, we have established an important selection criterion for catalytic function with low-cost and scalable CQDs.

In summary, we report a photocatalyst, CQD-**NiP**, which benefits from the donor recycling system TCEP/AA. This photosystem exhibits a benchmark photostability of over 5 days and a record TON_{Ni} for photocatalytic H_2 evolution of 1094 ± 61, using a defined synthetic molecular nickel catalyst in purely aqueous solution. Several cobalt catalysts were also successfully photosensitized using CQDs, demonstrating that CQDs can be widely used in conjunction with molecular catalysts for H_2 evolution (and likely other fuel-forming reactions). This study revealed that the presented CQDs are ideally suited to sensitize low overpotential ($\eta < 500$ mV) catalysts and activities can be achieved that are comparable or even higher than those with precious metal-based molecular photosensitizers.

The use of the TCEP/AA donor system was the key to unlock this great potential. The clean two-electron oxidation of TCEP into TCEPO circumvented inhibition of the system and prevented the rapid radical-mediated decomposition of the catalyst, which is usually observed with conventional sacrificial electron donors. This concept can be extended to incorporate valuable clean synthetic transformations in place of phosphine-to-phosphine oxide conversion, which will enable coupling of solar fuel with solar chemical synthesis. Future adaptation of the photosystem into a flow system, by integration of the CQDs in a flow reactor, will lead to efficient separation of gaseous and solution phase products.

Acknowledgements

This work was financially supported by an Oppenheimer Ph.D. scholarship, the Christian Doppler Research Association (Austrian Federal Ministry of Science, Research and Economy, and the National Foundation for Research, Technology and Development), the OMV Group, the Swiss National Science Foundation Sinergia Program CRSII2-136205/1 and the University Research Priority Program (URPP) LightChEC. Georgina A. M. Hutton, Prof. Christine A. Caputo and Janina Willkomm are gratefully acknowledged for helpful discussions. The boron-doped diamond electrode was made by David W. Wakerley using facilities at the Warwick Electrochemistry and Interfaces Group.

Keywords: carbon quantum dots · hydrogen evolution · molecular catalysis · photocatalysis · photosensitizers

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 9402–9406
Angew. Chem. **2016**, *128*, 9548–9552

---

[1] L. Cao, X. Wang, M. J. Meziani, F. Lu, H. Wang, P. G. Luo, Y. Lin, B. A. Harruff, L. M. Veca, D. Murray, S.-Y. Xie, Y.-P. Sun, *J. Am. Chem. Soc.* **2007**, *129*, 11318–11319.
[2] C. Ding, A. Zhu, Y. Tian, *Acc. Chem. Res.* **2014**, *47*, 20–30.
[3] F. Wang, Y. Chen, C. Liu, D. Ma, *Chem. Commun.* **2011**, *47*, 3502–3504.
[4] C. Yu, X. Li, F. Zeng, F. Zheng, S. Wu, *Chem. Commun.* **2013**, *49*, 403–405.

[5] H. M. R. Gonçalves, A. J. Duarte, J. C. G. Esteves da Silva, *Biosens. Bioelectron.* **2010**, *26*, 1302 – 1306.

[6] P. Mirtchev, E. J. Henderson, N. Soheilnia, C. M. Yip, G. A. Ozin, *J. Mater. Chem.* **2012**, *22*, 1265 – 1269.

[7] J. Briscoe, A. Marinovic, M. Sevilla, S. Dunn, M. Titirici, *Angew. Chem. Int. Ed.* **2015**, *54*, 4463 – 4468; *Angew. Chem.* **2015**, *127*, 4544 – 4550.

[8] D. Tang, H. Zhang, H. Huang, R. Liu, Y. Han, Y. Liu, C. Tong, Z. Kang, *Dalton Trans.* **2013**, *42*, 6285 – 6289.

[9] H. Yu, Y. Zhao, C. Zhou, L. Shang, Y. Peng, Y. Cao, L.-Z. Wu, C.-H. Tung, T. Zhang, *J. Mater. Chem. A* **2014**, *2*, 3344 – 3351.

[10] W. Wu, L. Zhan, K. Ohkubo, Y. Yamada, M. Wu, S. Fukuzumi, *J. Photochem. Photobiol. B* **2015**, *152*, 63 – 70.

[11] L. Cao, S. Sahu, P. Anilkumar, C. E. Bunker, J. Xu, K. A. S. Fernando, P. Wang, E. A. Guliants, K. N. Tackett, Y.-P. Sun, *J. Am. Chem. Soc.* **2011**, *133*, 4754 – 4757.

[12] S. Sahu, Y. Liu, P. Wang, C. E. Bunker, K. A. S. Fernando, W. K. Lewis, E. A. Guliants, F. Yang, J. Wang, Y.-P. Sun, *Langmuir* **2014**, *30*, 8631 – 8636.

[13] B. C. M. Martindale, G. A. M. Hutton, C. A. Caputo, E. Reisner, *J. Am. Chem. Soc.* **2015**, *137*, 6018 – 6025.

[14] A. Harriman, *Philos. Trans. R. Soc. London, Ser. A* **2013**, *371*, 20110415.

[15] M. Guttentag, A. Rodenberg, R. Kopelent, B. Probst, C. Buchwalder, M. Brandstätter, P. Hamm, R. Alberto, *Eur. J. Inorg. Chem.* **2012**, 59 – 64.

[16] D. W. Wakerley, E. Reisner, *Energy Environ. Sci.* **2015**, *8*, 2283 – 2295.

[17] D. W. Wakerley, M. A. Gross, E. Reisner, *Chem. Commun.* **2014**, *50*, 15995 – 15998.

[18] J. Y. Yang, R. M. Bullock, W. G. Dougherty, W. S. Kassel, B. Twamley, D. L. DuBois, M. Rakowski DuBois, *Dalton Trans.* **2010**, *39*, 3001 – 3010.

[19] C. Bachmann, B. Probst, M. Guttentag, R. Alberto, *Chem. Commun.* **2014**, *50*, 6737 – 6739.

[20] C. X. Guo, D. Zhao, Q. Zhao, P. Wang, X. Lu, *Chem. Commun.* **2014**, *50*, 7318 – 7321.

[21] B. Probst, M. Guttentag, A. Rodenberg, P. Hamm, R. Alberto, *Inorg. Chem.* **2011**, *50*, 3404 – 3412.

[22] M. A. Gross, A. Reynal, J. R. Durrant, E. Reisner, *J. Am. Chem. Soc.* **2014**, *136*, 356 – 366.

[23] C. Bachmann, M. Guttentag, B. Spingler, R. Alberto, *Inorg. Chem.* **2013**, *52*, 6055 – 6061.

[24] E. Joliat, S. Schnidrig, B. Probst, C. Bachmann, B. Spingler, K. K. Baldridge, F. von Rohr, A. Schilling, R. Alberto, *Dalton Trans.* **2016**, *45*, 1737 – 1745.

[25] C. A. Caputo, M. A. Gross, V. W. Lau, C. Cavazza, B. V. Lotsch, E. Reisner, *Angew. Chem. Int. Ed.* **2014**, *53*, 11538 – 11542; *Angew. Chem.* **2014**, *126*, 11722 – 11726.

[26] A. D. Wilson, R. H. Newell, M. J. McNevin, J. T. Muckerman, M. Rakowski DuBois, D. L. DuBois, *J. Am. Chem. Soc.* **2006**, *128*, 358 – 366.

[27] U. J. Kilgore, M. P. Stewart, M. L. Helm, W. G. Dougherty, W. S. Kassel, M. Rakowski DuBois, D. L. DuBois, R. M. Bullock, *Inorg. Chem.* **2011**, *50*, 10908 – 10918.

[28] H.-S. Chang, G. V. Korshin, J. F. Ferguson, *Environ. Sci. Technol.* **2006**, *40*, 5089 – 5094.

[29] A. S. Weingarten, R. V. Kazantsev, L. C. Palmer, M. McClendon, A. R. Koltonow, A. P. S. Samuel, D. J. Kiebala, M. R. Wasielewski, S. I. Stupp, *Nat. Chem.* **2014**, *6*, 964 – 970.

[30] H. Rao, Z.-Y. Wang, H.-Q. Zheng, X.-B. Wang, C.-M. Pan, Y.-T. Fan, H.-W. Hou, *Catal. Sci. Technol.* **2015**, *5*, 2332 – 2339.

[31] M. P. McLaughlin, T. M. McCormick, R. Eisenberg, P. L. Holland, *Chem. Commun.* **2011**, *47*, 7989 – 7991.

[32] Z. Han, W. R. McNamara, M.-S. Eum, P. L. Holland, R. Eisenberg, *Angew. Chem. Int. Ed.* **2012**, *51*, 1667 – 1670; *Angew. Chem.* **2012**, *124*, 1699 – 1702.

[33] L. Chen, G. Chen, C.-F. Leung, S.-M. Yiu, C.-C. Ko, E. Anxolabéhère-Mallart, M. Robert, T.-C. Lau, *ACS Catal.* **2015**, *5*, 356 – 364.

[34] Y. Xu, X. Yin, Y. Huang, P. Du, B. Zhang, *Chem. Eur. J.* **2015**, *21*, 4571 – 4575.

[35] Z. Han, F. Qiu, R. Eisenberg, P. L. Holland, T. D. Krauss, *Science* **2012**, *338*, 1321 – 1324.

[36] D. Nakane, S. Kuwasako, M. Tsuge, M. Kubo, Y. Funahashi, T. Ozawa, T. Ogura, H. Masuda, *Chem. Commun.* **2010**, *46*, 2142 – 2144.

[37] G. J. Leigh, D. M. P. Mingos, *J. Chem. Soc. A* **1970**, 587 – 589.

[38] M. Yin, S. Ma, C. Wu, Y. Fan, *RSC Adv.* **2015**, *5*, 1852 – 1858.

[39] N. Queyriaux, R. T. Jane, J. Massin, V. Artero, M. Chavarot-Kerlidou, *Coord. Chem. Rev.* **2015**, *304 – 305*, 3 – 19.

[40] P.-A. Jacques, V. Artero, J. Pécaut, M. Fontecave, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 20627 – 20632.

[41] V. Artero, J.-M. Saveant, *Energy Environ. Sci.* **2014**, *7*, 3808 – 3814.

[42] L. Hutton, M. E. Newton, P. R. Unwin, J. V. Macpherson, *Anal. Chem.* **2009**, *81*, 1023 – 1032.

Received: May 4, 2016
Revised: May 20, 2016