Water Splitting

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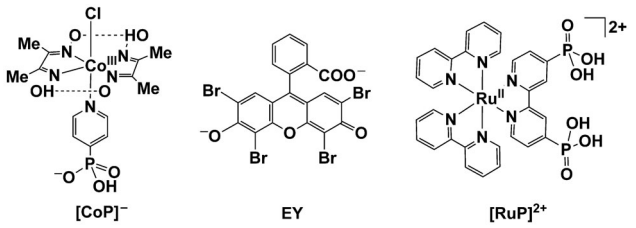
Selective Reduction of Aqueous Protons to Hydrogen with a Synthetic Cobaloxime Catalyst in the Presence of Atmospheric Oxygen**

*Fezile Lakadamyali, Masaru Kato, Nicoleta M. Muresan, and Erwin Reisner**

Sunlight provides us with a practically endless amount of carbon-neutral energy and there is currently great interest in harvesting some of this electromagnetic energy for the production of a solar fuel.[1] An attractive approach is sunlight-driven water splitting, where renewable H_2 and the by-product O_2 are released simultaneously from water during irradiation.[2] An economical H_2-evolution catalyst must not only contain inexpensive materials, but must also be active under O_2 during turnover, because a real-world device will be exposed to atmospheric O_2 and produce O_2 in situ as a result of water splitting.

Noble-metal catalysts such as platinum are excellent H_2-evolution catalysts, but they are expensive and show cross-selectivity for the reduction of O_2.[3] In biology, the [FeFe]- and [NiFe]-hydrogenases are H_2-evolution catalysts that work at high rates and small over-potentials.[4] However, isolated hydrogenases are fragile and often extremely sensitive towards O_2.[5] Many significant advances were reported recently in the development of small-molecule H_2-evolution catalysts.[6] Nevertheless, there has been very little progress in the development of homogeneous H_2-generating catalysts that operate in the presence of O_2. A noteworthy exception is an expensive rhodium catalyst that operates under O_2.[7] To the best of our knowledge, there are no reports of small-molecule 3d transition-metal catalysts that reduce protons efficiently under high levels of O_2.

Herein, we report on an inexpensive cobalt catalyst that evolves H_2 electro- and photocatalytically in pH-neutral water and in the presence of atmospheric O_2. We employ $(Et_3NH)[Co^{III}Cl(dimethylglyoximato)_2(pyridyl\text{-}4\text{-}hydrophosphonate)]$ ($(Et_3NH)[CoP]$, Scheme 1), which is a member of cobaloxime-type catalysts that currently receive much attention in electrochemical and photochemical applications.[8] The phosphonic acid group in $(Et_3NH)[CoP]$ enables the complex to dissolve in water and allows for its immobilization on metal oxide surfaces for heterogeneous applications.[8f,9]



Scheme 1. Chemical structures of the cobalt catalyst $[CoP]^-$, the organic dye eosin Y (EY), and the ruthenium dye $[RuP]^{2+}$.

First, we studied the electrocatalytic activity of the complex anion $[CoP]^-$ in a pH-neutral electrolyte solution in the absence and presence of air (21 % O_2 in N_2). Cyclic voltammetry (CV) scans were recorded in a three-electrode cell with $(Et_3NH)[CoP]$ (1 mM) on a glassy carbon working electrode in an aqueous solution of triethanolamine (TEOA) and Na_2SO_4 (0.1 M each) at pH 7 and 25 °C. A cathodic wave at $E_p = -0.13$ V versus the normal hydrogen electrode (NHE), assigned to the $Co^{III} \rightarrow Co^{II}$ reduction process, and reduction of Co^{II} with the onset of electrocatalytic proton reduction at approximately −0.55 V versus NHE was observed at a scan rate of 100 mV s^{-1} under a N_2 atmosphere (Figure 1 a, dashed

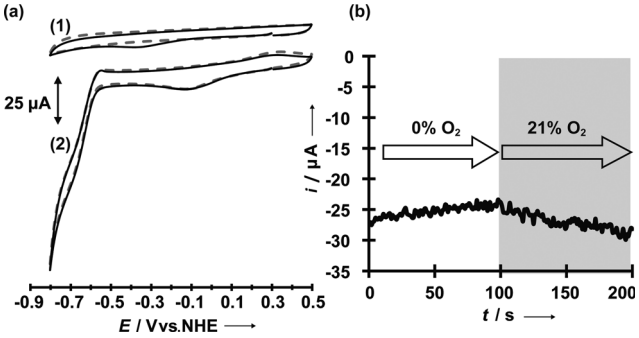


Figure 1. Electrocatalytic H_2 production in the absence and presence of atmospheric O_2. a) CV scans at a scan rate of 0.1 V s^{-1} (1) without catalyst (control experiment) and (2) in the presence of $(Et_3NH)[CoP]$ (1 mM). Dashed traces were recorded under a N_2 atmosphere and the solid traces under 21 % O_2 in N_2. b) Chronoamperometry of (Et_3NH)-[CoP] (1 mM) at −0.7 V versus NHE. The measurement was started under N_2 and the electrochemical cell was flushed with air after 100 s (gray shading). In all experiments, a glassy carbon working (3 mm diameter), a Pt counter, and a Ag/AgCl reference electrode were employed and the measurements were carried out in an aqueous solution of TEOA/Na_2SO_4 (0.1 M each, pH 7) at 25 °C.

[*] F. Lakadamyali,[+] Dr. M. Kato,[+] Dr. N. M. Muresan, 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

[+] These authors contributed equally to this work and should be considered as first authors.

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trace). This voltammetric response is consistent with previous reports of cobaloximes under an inert atmosphere.[2g,10]

CV scans of $(Et_3NH)[CoP]$ exposed to air showed a very similar voltammetric response. No additional waves were observed from the reduction of O_2, and the same potential–current curves were maintained for proton reduction (Figure 1a, solid trace). Thus, 21% O_2 has only a marginal effect on the electrocatalytic activity of $[CoP]^-$ on the short time scale of a CV experiment. Figure 1b shows the results of chronoamperometric measurements of a stirred solution of $(Et_3NH)[CoP]$ (1 mM) in a pH 7 solution of TEOA/Na_2SO_4 (0.1M) at −0.7 V versus NHE. A constant catalytic current (−27 to −25 μA) was observed under N_2. After 100 s, the headspace of the cell was flushed with air, which resulted in only a minor increase in the current from −25 to −30 μA. This experiment confirms that air has only a small effect on the catalytic activity of $[CoP]^-$.

Controlled-potential electrolysis allowed us to explore the tolerance of $[CoP]^-$ towards O_2 over a longer time scale and to determine the Faradaic yield of electrocatalytic H_2 evolution. We used a closed electrochemical cell with $(Et_3NH)[CoP]$ (0.5 mM) in a stirred aqueous solution of TEOA/Na_2SO_4 at pH 7 and applied potential of −0.7 V versus NHE on a large-area glassy carbon working electrode (ca. 2 cm^2) for two hours. A gas chromatograph was used to quantify the amount of H_2 for the determination of the Faradaic efficiency in our system. The passage of an average of 5.5 C of charge under a N_2 atmosphere resulted in 22 μmol H_2 in the headspace, whereas 6.6 C and 17 μmol H_2 were observed under atmospheric O_2. These values correspond to a respectable Faradaic efficiency of (68 ± 3)% under N_2 and (43 ± 4)% under 21% O_2 in N_2 (see Table S1 in the Supporting Information). No hydrogen was detectable after electrolysis without $[CoP]^-$. Controlled potential electrolysis, therefore, confirms that the catalyst retains its activity over a prolonged time scale (at least for 2 h), with good selectivity for proton reduction under atmospheric O_2. Previously, only the electrocatalytic reduction of O_2 and no evolution of H_2 was reported in electrochemical studies with cobaloxime-type catalysts in the presence of O_2.[11]

Subsequently, we explored the photocatalytic activity of $[CoP]^-$ in homogeneous and heterogeneous systems in the presence of O_2. Our electrochemical studies demonstrated that $[CoP]^-$ was active under air, but possible quenching of the excited state of a chromophore and formation of reactive oxygen species could easily prevent a photochemical system operating in the presence of O_2. For a homogeneous system, we selected the organic dye eosin Y (EY, used as its disodium salt, Na_2EY, Scheme 1). EY had previously been employed as a photosensitizer with cobalt-based proton reduction catalysts such as $[Co^{III}Cl(dimethylglyoximato)_2(pyridine)]$[12] and $[Co^{II}(bipy)_3]Cl_2$[13] (bipy = 2,2′-bipyridine) under an inert atmosphere. The multicomponent system works as follows: photoexcitation of EY results in the formation of a triplet excited state (*EY), which can either inject electrons directly into a cobalt catalyst or be reductively quenched by an electron donor (e.g., TEOA), followed by injection of the electron into a cobalt complex.[12]

A homogeneous solution of $(Et_3NH)[CoP]$ (0.2 μmol) and Na_2EY (0.1 μmol) was exposed to visible light (solar light simulator; 100 mW cm^{-2}, $\lambda > 420$ nm) in an aqueous solution of TEOA (4.5 mL, 0.1M) at pH 7 and 25 °C. After irradiation of the mixture for one hour under N_2 (containing 2% CH_4 as internal GC standard), (12.5 ± 0.6) μmol H_2 evolved (Figure 2a; headspace volume: 4.85 mL). This result corresponds to a cobalt-based turnover frequency (TOF_{Co}) of (62 ± 3) mol H_2 per mol $[CoP]^-$ per hour and a dye-based turnover frequency (TOF_{EY}) of (125 ± 6) mol H_2 per mol EY per hour. The homogeneous system is photoactive between 1 and 2 h, whereupon a turnover number for $[CoP]^-$ (TON_{Co}) of (73 ± 4) mol H_2 per mol $[CoP]^-$ was obtained. The catalytic activity of $[CoP]^-$ in organic-solvent-free aqueous solution compares favorably to other homogeneous photocatalytic systems, where organic solvents are typically added to water and inert conditions are required. One example is $[Ni(P_2^{Ph}N_2^{Ph})_2](BF_4)_2$ ($P_2^{Ph}N_2^{Ph}$ = 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane), which shows a light-driven H_2 production TOF of 20 h^{-1} in a water/acetonitrile mixture under N_2.[14]

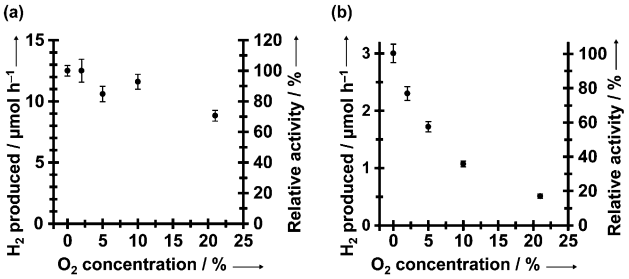

Figure 2. Photocatalytic H_2 production in the presence of various concentrations of O_2. Visible-light-driven ($\lambda > 420$ nm, 100 mW cm^{-2}) H_2 production rates versus concentration of O_2 with a) a homogeneous system consisting of $[CoP]^-$ and EY and b) a heterogeneous system with $[CoP]^-$ and $[RuP]^{2+}$ co-attached to TiO_2 nanoparticles (5 mg) at 25 °C. An aqueous solution of TEOA as a sacrificial electron donor was used (4.5 mL. 0.1 M, pH 7), and 0.2 μmol of $(Et_3NH)[CoP]$ and 0.1 μmol of the dye (EY or $[RuP]^{2+}$) were used. Relative H_2 production activity (%) to the activity under an inert atmosphere is also shown.

Exposing the homogeneous system to various concentrations of O_2 resulted only in a small decrease in the photoinduced H_2-evolution activity, and (70 ± 4)% activity remained in the presence of 21% O_2 compared to that under an inert atmosphere (Figure 2a, see also Table S2 in the Supporting Information). The homogeneous system consisting of $[CoP]^-$ and EY in an aqueous solution of TEOA is, therefore, highly robust in the presence of O_2: the catalyst $[CoP]^-$ tolerates high concentrations of O_2, and *EY (or a reductively quenched, reduced EY) can inject electrons efficiently into $[CoP]^-$ despite a potential quenching mechanism by O_2.[15]

Finally, we studied the photocatalytic activity in a heterogeneous system consisting of $(Et_3NH)[CoP]$ (0.2 μmol) and the tris(bipyridine)ruthenium dye $[RuP]^{2+}$ (0.1 μmol, used as the dibromide salt $[RuP]Br_2$, Scheme 1) co-attached to P25 TiO_2 nanoparticles (21 nm diameter, 5 mg).[8f,10d,16] In this

heterogeneous system, photoexcitation of $[RuP]^{2+}$ results in $[*RuP]^{2+}$ and ultrafast electron injection into the conduction band of TiO_2, followed by transfer of the TiO_2 photoelectrons to $[CoP]^-$ for H_2 evolution.[10d] Under N_2 with 2% CH_4, irradiation ($\lambda > 420$ nm) of $[RuP]^{2+}$/$[CoP]^-$-modified TiO_2 in TEOA solution (4.5 mL, 0.1M, pH 7) with visible light resulted in (3.0 ± 0.2) μmol $H_2\,h^{-1}$ and a TOF_{Co} of (15.0 ± 0.8) mol H_2 per mol $[CoP]^-$ per hour.[8f,10d,16] The heterogeneous system is photoactive for approximately 10 h with a TON_{Co} of (108 ± 9) mol H_2 per mol $[CoP]^-$.

Figure 2b shows the effect of various amounts of O_2 on the photocatalytic activity of $[RuP]^{2+}$/$[CoP]^-$-modified TiO_2 nanoparticles: increasing the amount of O_2 from zero to 21% resulted in a decrease in photoactivity from (3.0 ± 0.2) to (0.51 ± 0.04) μmol $H_2\,h^{-1}$ (see Table S3 in the Supporting Information). Therefore, approximately 17% of the H_2 production activity remained under 21% O_2 in N_2 for the colloidal system. There are several possible quenching mechanisms of $[RuP]^{2+}$-sensitized TiO_2 by O_2. Electron injection on the picosecond time scale from $[*RuP]^{2+}$ to TiO_2 makes energy transfer from $[*RuP]^{2+}$ to O_2 unlikely.[10d,17] However, a long-lived TiO_2 conduction band electron is formed during irradiation, which can either recombine with oxidized $[RuP]^{2+}$ or reduce O_2 to superoxide radicals ($O_2^{\bullet-}$). These radicals were shown to result in a significant increase in the $[RuP]^{2+}$ desorption rate from the TiO_2 surface,[18] which could decrease the H_2 production activity in our heterogeneous system.

In summary, we have described an inexpensive cobalt catalyst $[CoP]^-$ which evolves H_2 catalytically under highly desirable conditions: room temperature, pH-neutral water and atmospheric O_2. Electrochemical studies show that $[CoP]^-$ has good selectivity for the electrocatalytic reduction of protons under air. We also demonstrated that $[CoP]^-$ can be exploited in photochemical reactions under high levels of O_2. The homogeneous system consisting of EY and $[CoP]^-$ remains highly photoactive in the presence of 21% O_2, whereas the heterogeneous system with $[CoP]^-$ and $[RuP]^{2+}$ co-attached to TiO_2 nanoparticles also keeps some of the photocatalytic activity for the reduction of aqueous protons. These findings are rationalized by the high selectivity of $[CoP]^-$ for H_2 evolution and slow quenching of the excited *EY (or reduced EY) and TiO_2 photoelectrons by O_2. The low solubility of O_2 in water (0.27 mmol L^{-1} at 25°C under 1 atm of air)[19] might explain in part why our electro- and photocatalytic systems with $[CoP]^-$ operate under atmospheric O_2. Work is underway to develop a solar water splitting system, where H_2 and O_2 evolve simultaneously.

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[1] a) N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15729–15735; b) N. Armaroli, V. Balzani, *Angew. Chem.* **2007**, *119*, 52–67; *Angew. Chem. Int. Ed.* **2007**, *46*, 52–66; c) T. R. Cook, D. K. Dogutan, S. Y. Reece, Y. Surendranath, T. S. Teets, D. G. Nocera, *Chem. Rev.* **2010**, *110*, 6474–6502; d) M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.* **2010**, *110*, 6446–6473; e) R. E. Blankenship, D. M. Tiede, J. Barber, G. W. Brudvig, G. Fleming, M. Ghirardi, M. R. Gunner, W. Junge, D. M. Kramer, A. Melis, T. A. Moore, C. C. Moser, D. G. Nocera, A. J. Nozik, D. R. Ort, W. W. Parson, R. C. Prince, R. T. Sayre, *Science* **2011**, *332*, 805–809.

[2] a) W. Lubitz, E. J. Reijerse, J. Messinger, *Energy Environ. Sci.* **2008**, *1*, 15–31; b) T. Nann, S. K. Ibrahim, P.-M. Woi, S. Xu, J. Ziegler, C. J. Pickett, *Angew. Chem.* **2010**, *122*, 1618–1622; *Angew. Chem. Int. Ed.* **2010**, *49*, 1574–1577; c) S. D. Tilley, M. Cornuz, K. Sivula, M. Grätzel, *Angew. Chem.* **2010**, *122*, 6549–6552; *Angew. Chem. Int. Ed.* **2010**, *49*, 6405–6408; d) N. Armaroli, V. Balzani, *ChemSusChem* **2011**, *4*, 21–36; e) S. Y. Reece, J. A. Hamel, K. Sung, T. D. Jarvi, A. J. Esswein, J. J. H. Pijpers, D. G. Nocera, *Science* **2011**, *334*, 645–648; f) L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet, L. Sun, *Nat. Chem.* **2012**, *4*, 418–423; g) P. Du, R. Eisenberg, *Energy Environ. Sci.* **2012**, *5*, 6012–6021.

[3] a) J. Zhang, K. Sasaki, E. Sutter, R. R. Adzic, *Science* **2007**, *315*, 220–222; b) J. Kibsgaard, Y. Gorlin, Z. Chen, T. F. Jaramillo, *J. Am. Chem. Soc.* **2012**, *134*, 7758–7765.

[4] a) M. Hambourger, M. Gervaldo, D. Svedruzic, P. W. King, D. Gust, M. Ghirardi, A. L. Moore, T. A. Moore, *J. Am. Chem. Soc.* **2008**, *130*, 2015–2022; b) E. Reisner, D. J. Powell, C. Cavazza, J. C. Fontecilla-Camps, F. A. Armstrong, *J. Am. Chem. Soc.* **2009**, *131*, 18457–18466; c) K. A. Brown, S. Dayal, X. Ai, G. Rumbles, P. W. King, *J. Am. Chem. Soc.* **2010**, *132*, 9672–9680; d) F. A. Armstrong, J. Hirst, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 14049–14054; e) A. Abou Hamdan, S. Dementin, P.-P. Liebgott, O. Gutierrez-Sanz, P. Richaud, A. L. De Lacey, M. Roussett, P. Bertrand, L. Cournac, C. Léger, *J. Am. Chem. Soc.* **2012**, *134*, 8368–8371.

[5] a) G. Goldet, C. Brandmayr, S. T. Stripp, T. Happe, C. Cavazza, J. C. Fontecilla-Camps, F. A. Armstrong, *J. Am. Chem. Soc.* **2009**, *131*, 14979–14989; b) C. L. McIntosh, F. Germer, R. Schulz, J. Appel, A. K. Jones, *J. Am. Chem. Soc.* **2011**, *133*, 11308–11319; c) M. T. Stiebritz, M. Reiher, *Chem. Sci.* **2012**, *3*, 1739–1751.

[6] a) H. I. Karunadasa, C. J. Chang, J. R. Long, *Nature* **2010**, *464*, 1329–1333; b) T. Matsumoto, T. Nagahama, J. Cho, T. Hizume, M. Suzuki, S. Ogo, *Angew. Chem.* **2011**, *123*, 10766–10768; *Angew. Chem. Int. Ed.* **2011**, *50*, 10578–10580; c) W. Wang, T. B. Rauchfuss, L. Bertini, G. Zampella, *J. Am. Chem. Soc.* **2012**, *134*, 4525–4528; d) M. L. Helm, M. P. Stewart, R. M. Bullock, M. R. DuBois, D. L. DuBois, *Science* **2011**, *333*, 863–866; e) M. J. Rose, H. B. Gray, J. R. Winkler, *J. Am. Chem. Soc.* **2012**, *134*, 8310–8313; f) W. M. Singh, T. Baine, S. Kudo, S. Tian, X. A. N. Ma, H. Zhou, N. J. DeYonker, T. C. Pham, J. C. Bollinger, D. L. Baker, B. Yan, C. E. Webster, X. Zhao, *Angew. Chem.* **2012**, *124*, 6043–6046; *Angew. Chem. Int. Ed.* **2012**, *51*, 5941–5944.

[7] R. Bauer, H. A. F. Werner, *Int. J. Hydrogen Energy* **1994**, *19*, 497–499.

[8] a) X. Hu, B. S. Brunschwig, J. C. Peters, *J. Am. Chem. Soc.* **2007**, *129*, 8988–8998; b) P.-A. Jacques, V. Artero, J. Pécaut, M. Fontecave, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 20627–20632; c) S. Losse, J. G. Vos, S. Rau, *Coord. Chem. Rev.* **2010**, *254*, 2492–2504; d) J. L. Dempsey, J. R. Winkler, H. B. Gray, *J. Am. Chem. Soc.* **2010**, *132*, 16774–16776; e) V. Artero, M. Chavarot-Kerlidou, M. Fontecave, *Angew. Chem.* **2011**, *123*, 7376–7405; *Angew. Chem. Int. Ed.* **2011**, *50*, 7238–7266; f) F. Lakadamyali, E. Reisner, *Chem. Commun.* **2011**, *47*, 1695–1697; g) J. T. Muckerman, E. Fujita, *Chem. Commun.* **2011**, *47*, 12456–12458; h) L. Li, L. Duan, F. Wen, C. Li, M. Wang, A. Hagfeldt, L. Sun, *Chem. Commun.* **2012**, *48*, 988–990.

[9] C. Queffélec, M. Petit, P. Janvier, D. A. Knight, B. Bujoli, *Chem. Rev.* **2012**, *112*, 3777 – 3807.
[10] a) M. Razavet, V. Artero, M. Fontecave, *Inorg. Chem.* **2005**, *44*, 4786 – 4795; b) C. Baffert, V. Artero, M. Fontecave, *Inorg. Chem.* **2007**, *46*, 1817 – 1824; c) C. C. L. McCrory, C. Uyeda, J. C. Peters, *J. Am. Chem. Soc.* **2012**, *134*, 3164 – 3170; d) F. Lakadamyali, A. Reynal, M. Kato, J. R. Durrant, E. Reisner, *Chem. Eur. J.*, **2012**, DOI: 10.1002/chem.201202149.
[11] a) A. Salimi, M. Ghadermazi, *Anal. Sci.* **2001**, *17*, 1165 – 1170; b) M. Shamsipur, A. Salimi, H. Haddadzadeh, M. F. Mousavi, *J. Electroanal. Chem.* **2001**, *517*, 37 – 44.
[12] T. Lazarides, T. McCormick, P. Du, G. Luo, B. Lindley, R. Eisenberg, *J. Am. Chem. Soc.* **2009**, *131*, 9192 – 9194.
[13] J. Dong, M. Wang, P. Zhang, S. Yang, J. Liu, X. Li, L. Sun, *J. Phys. Chem. C* **2011**, *115*, 15089 – 15096.
[14] M. P. McLaughlin, T. M. McCormick, R. Eisenberg, P. L. Holland, *Chem. Commun.* **2011**, *47*, 7989 – 7991.
[15] R. W. Redmond, J. N. Gamlin, *Photochem. Photobiol.* **1999**, *70*, 391 – 475.
[16] F. Lakadamyali, M. Kato, E. Reisner, *Faraday Discuss.* **2012**, *155*, 191 – 205.
[17] a) S. Ardo, G. J. Meyer, *Chem. Soc. Rev.* **2009**, *38*, 115 – 164; b) M. C. DeRosa, R. J. Crutchley, *Coord. Chem. Rev.* **2002**, *233 – 234*, 351 – 371.
[18] K. Hanson, M. K. Brennaman, H. Luo, C. R. K. Glasson, J. J. Concepcion, W. Song, T. J. Meyer, *ACS Appl. Mater. Interfaces* **2012**, *4*, 1462 – 1469.
[19] *Handbook of Chemistry and Physics*, 52nd ed., Chemical Rubber Co., Cleveland, **1971**.

