

# Selective and Efficient Photocatalytic CO<sub>2</sub> Reduction to CO Using Visible Light and an Iron-Based Homogeneous Catalyst

Julien Bonin,\* Marc Robert,\* and Mathilde Routier

Université Paris Diderot, Sorbonne Paris Cité, Laboratoire d'Electrochimie Moléculaire, UMR 7591 CNRS, 15 rue Jean-Antoine de Baïf, F-75205 Paris Cedex 13, France

**S** Supporting Information

**ABSTRACT:** Converting CO<sub>2</sub> into valuable compounds using sunlight as the energy input and an earth-abundant metal complex as the catalyst is an exciting challenge related to contemporary energy issues as well as to climate change. By using an inexpensive organic photosensitizer under visible-light excitation ( $\lambda > 400$  nm) and a substituted iron(0) tetraphenylporphyrin as a homogeneous catalyst, we have been able to generate carbon monoxide from CO<sub>2</sub> selectively with high turnover numbers. Sustained catalytic activity over a long time period ( $t > 50$  h) did not lead to catalyst or sensitizer deactivation. A catalytic mechanism is proposed.

Considering CO<sub>2</sub> as a source of valuable chemicals<sup>1,2</sup> is an attractive way to deal with massive CO<sub>2</sub> release into the atmosphere. However, reduction of carbon dioxide is an energy-demanding process because of the high stability of the CO<sub>2</sub> molecule. In particular, the one-electron reduction to give its radical anion occurs at a very negative potential ( $E^0 = -1.97$  V vs NHE in DMF).<sup>3</sup> Nonetheless, a variety of multielectron reduction reactions coupled with proton transfers and having less-negative standard potentials may take place. These reactions lead to compounds such as carbon monoxide or formic acid ( $2e^-$ ,  $2H^+$ ), formaldehyde ( $4e^-$ ,  $4H^+$ ), methanol ( $6e^-$ ,  $6H^+$ ), and even methane ( $8e^-$ ,  $8H^+$ ).<sup>4</sup> The gain in potential obtained in these processes is counterbalanced by a kinetic compensation that requires the use of a catalyst to efficiently drive the reaction. Numerous studies have been dedicated to the study of metal-based molecular catalysts for either electro- and photochemical reduction of CO<sub>2</sub>.<sup>5–7</sup> Most of them are, however, based on noble metals such as rhenium<sup>8–13</sup> or ruthenium,<sup>14–17</sup> and fewer systems employ abundant and more environmentally benign catalysts such as those based on manganese,<sup>18–21</sup> cobalt,<sup>22–24</sup> or nickel.<sup>25–27</sup>

Iron tetraphenylporphyrin and derivatives have been shown to efficiently and selectively electrochemically reduce CO<sub>2</sub> into CO.<sup>28–30</sup> In particular, it has recently been demonstrated that functionalization of the macrocycle phenyl rings with hydroxyl groups (and possibly fluorine atoms) leads to enhanced performances characterized, upon addition of molar concentration of a weak Bronsted acid, by high Faradaic yields of CO (above 95%) and high turnover frequencies (TOFs) of up to  $240\text{ s}^{-1}$  at a low overpotential ( $\eta$ ) of ca.  $0.4\text{ V}$ .<sup>31–33</sup> We have recently reported that the same porphyrins can also be used as homogeneous catalysts in a photochemical process with good

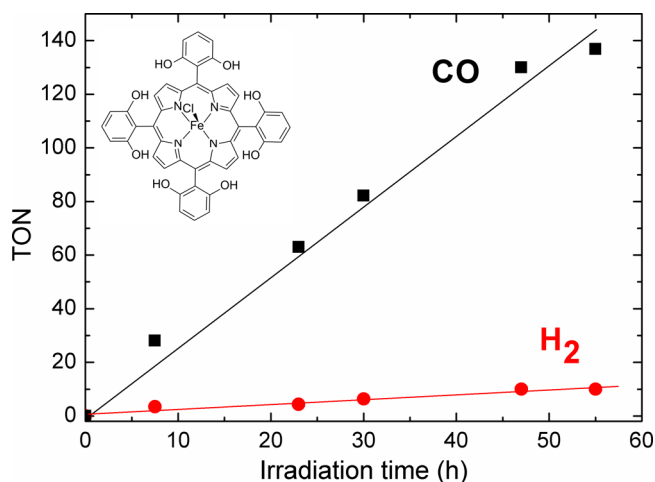
performances (turnover numbers (TONs) in CO of up to 30 and catalytic selectivities (CSs) of up to 85%).<sup>34</sup> However, we have also identified intrinsic limitations, mainly due to three factors. First, the need for near-UV irradiation of the porphyrin (around 300 nm) leads to progressive photodegradation of the catalyst. Second, the use of triethylamine (TEA) as a sacrificial electron donor furnishes a strong acid (protonated TEA) that reacts with iron(0) porphyrin to form a hydride species, thus triggering a competitive pathway for H<sub>2</sub> evolution as a byproduct. Third, the release of CO from the CO<sub>2</sub>–catalyst adduct requires the cleavage of a C–O bond. To do so, an additional electron coming from another iron(0) species, whose steady-state concentration remains very low, is needed.

To circumvent these limitations, we have developed a strategy including a photosensitizer (PS) as a coreactant in order (1) to lower the irradiation energy by shifting the absorption into the visible range, (2) to increase the efficiency of the process by boosting the final step for CO formation, i.e., the reduction of the CO<sub>2</sub>–catalyst adduct by PS<sup>•−</sup> as an electron donor, and (3) to increase the stability of the iron catalyst. The use of a PS is a common strategy to broaden and/or shift the absorption range of a system. Its role is to efficiently collect light and then to initiate the chemical process. To do so, the excited state PS\* should be efficiently quenched by a sacrificial electron donor, i.e., TEA (triethylamine) in our system (see below), thus generating the radical anion PS<sup>•−</sup>, a powerful reductant that is able to reduce the iron catalyst to its active state (CAT<sup>0</sup>). An additional role of the PS is to separate the light absorption from the catalysis itself, whereas in our initial approach the iron porphyrin plays both roles.<sup>34</sup> Typical photosensitizers used in photochemical CO<sub>2</sub> reduction systems consist of noble-metal complexes such as Ru complexes,<sup>20,35,36</sup> but ultimately, inexpensive PSs are highly desirable.

We started our investigation with *fac*-tris(2,2'-phenylpyridine)iridium(III) (Ir(ppy)<sub>3</sub>) (see the Supporting Information (SI)) as the PS, since it has recently been used for CO<sub>2</sub> reduction with a nickel complex as the catalyst.<sup>27</sup> Other iridium complexes have also been employed as visible-light photocatalysts to reduce CO<sub>2</sub> to CO.<sup>37,38</sup> As shown in Figure 1, the performance of our catalytic system with an iron porphyrin as the catalyst is remarkable. While irradiation could be set above 420 nm, only a minor amount of H<sub>2</sub> was detected by gas chromatography (a CS for CO of ca. 93% has been repeatedly measured), and a TON in CO of up to 140 after 55

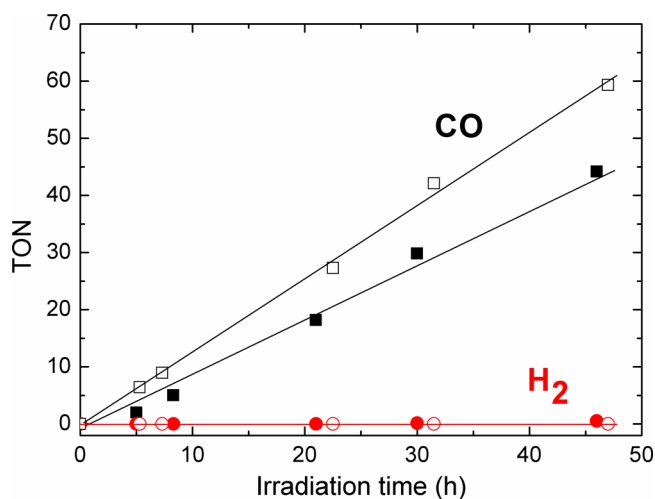
Received: October 7, 2014

Published: November 14, 2014



**Figure 1.** CO (black) and H<sub>2</sub> (red) formation with time during irradiation ( $\lambda > 420$  nm) of a CO<sub>2</sub>-saturated acetonitrile solution containing 2  $\mu$ M CAT, 0.36 M TEA, and 0.2 mM Ir(ppy)<sub>3</sub>. The inset shows the catalyst structure.

h of irradiation was obtained, one of the highest TONs for homogeneous photocatalysis reported to date. Moreover, the evolution of TON versus time remained linear, indicating that no significant degradation process occurred. However, Ir(ppy)<sub>3</sub> is an expensive chemical, which balances the interest of using a cheap iron catalyst. We thus turned to a much cheaper organic compound, 9-cyanoanthracene (9CNA) (see the SI) to act as the PS. Despite the fact that its absorption band is mostly located in the UV, we were able to conduct photochemical reduction of CO<sub>2</sub> at irradiation wavelengths above 400 nm (Figure 2). We obtained an even better selectivity toward CO,



**Figure 2.** CO (black) and H<sub>2</sub> (red) formation during irradiation ( $\lambda > 400$  nm) of a CO<sub>2</sub>-saturated acetonitrile solution containing 2  $\mu$ M CAT, 0.36 (solid symbols) or 0.05 M (open symbols) TEA, and 0.2 mM 9CNA.

with no detectable H<sub>2</sub> formed (CS for CO of 100%). Moreover, the variation of TON versus time was linear over 45 h of irradiation, thus showing no degradation of the system. With 0.36 M TEA (solid symbols in Figure 2), the TON in CO reached ca. 40 after 45 h. When the TEA concentration was lowered to 50 mM (open symbols) in order to limit the formation of its protonated form and to decrease the global

cost of the system, the selectivity toward CO<sub>2</sub> reduction remained excellent and a TON in CO of ca. 60 was obtained.

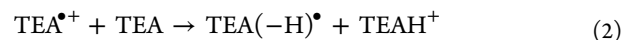
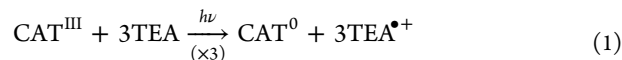
The TON and TOF values obtained in this study are comparable to or higher than the values obtained with more expensive photocatalysts. For example, Sato et al.<sup>39</sup> reported a TON in CO of up to 240 after 16 h of irradiation (TOF of up to 15 h<sup>-1</sup>) for Ru–Re dyads. They also studied mononuclear Ir<sup>III</sup> complexes and reported TON in CO of up to 50 after 5 h (TOF of up to 10 h<sup>-1</sup>).<sup>38</sup> Using Ru<sup>II</sup>–Re<sup>I</sup> binuclear complexes, Bian et al.<sup>40</sup> reported TONs in CO of 50–100 after 9 h of irradiation (TOFs of 5.5–11.1 h<sup>-1</sup>). Andrade et al.<sup>13</sup> obtained a TON in CO of 22 after 17 h (TOF of 1.3 h<sup>-1</sup>) with a Re complex containing a bodipy moiety. Takeda et al.<sup>10</sup> obtained TONs in CO of 15–30 after 25 h of UV irradiation (TOFs of 0.6–1.2 h<sup>-1</sup>). Thoi et al.<sup>27</sup> reported a TON in CO of up to 98 000 (TOF of up to 14 000 h<sup>-1</sup>) with a 2 nM Ni complex solution sensitized with Ir(ppy)<sub>3</sub>. However, at such a low concentration of catalyst, it is difficult to assess the nature of the active species (along this line, it should be noted that the concentration of CO produced slightly decreases when the catalyst concentration increases from 2 to 20 nM and then marginally increases (by a factor of 1.5) when the concentration is further increased by a factor of 10).

Taking into account the fact that the reduction of CO<sub>2</sub> to CO is a two-electron process, we determined the overall quantum yield of the process ( $\Phi_{\text{CO}}$ ) using the following equation:

$$\Phi_{\text{CO}} = \frac{\text{number of CO molecules} \times 2}{\text{number of incident photons}} \times 100\%$$

We thus obtained  $\Phi_{\text{CO}} = 8 \times 10^{-4} \%$  with 9CNA as the PS and  $1.3 \times 10^{-3} \%$  with Ir(ppy)<sub>3</sub> (see the SI for details). It is not surprising that we got low  $\Phi_{\text{CO}}$  values, since each reduction step of the catalyst requires two bimolecular reactions (quenching of the PS excited state and then reduction of the iron complex by PS<sup>•-</sup>; see Scheme 1). As the catalyst active species is iron(0), three reduction steps are needed, meaning that the formation of the active catalyst is achieved after six bimolecular reactions, including three photochemical reactions.

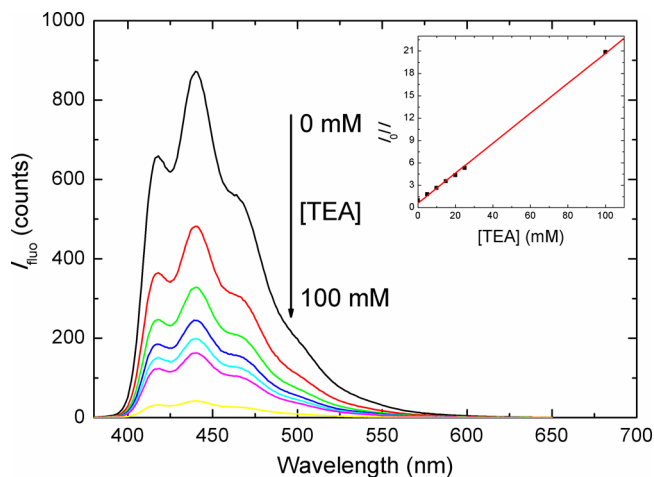
In experiments done without a PS, CAT was excited by UV light ( $\lambda > 280$  nm) and then reduced to its active state CAT<sup>0</sup> (Fe<sup>0</sup> metal center) by three successive oxidative quenching reactions with TEA (reaction 1). However, this also resulted in the formation of protonated TEA (reaction 2), a strong acid that is able to react with CAT<sup>0</sup> to form a hydride that can evolve dihydrogen as a byproduct.



In the presence of a PS, we need to determine whether the excited state PS\* is quenched by the catalyst (CAT) and/or by the sacrificial electron donor (TEA) in order to draw the mechanistic scheme. Fluorescence quenching measurements in acetonitrile solutions containing 9CNA with increasing concentrations of either TEA or CAT (using concentration ratios similar to those used under photocatalytic conditions) were analyzed through the Stern–Volmer equation:

$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q]$$

where  $I_0$  and  $I$  are the fluorescence intensities without and with quencher, respectively,  $k_q$  is the apparent quenching rate constant,  $\tau_0$  is the excited-state lifetime without quencher, and  $[Q]$  is the quencher concentration. On the basis of literature data,<sup>41–43</sup> the excited-state lifetime of 9CNA was taken as 15 ns. With TEA as the quencher (Figure 3), the evolution of the



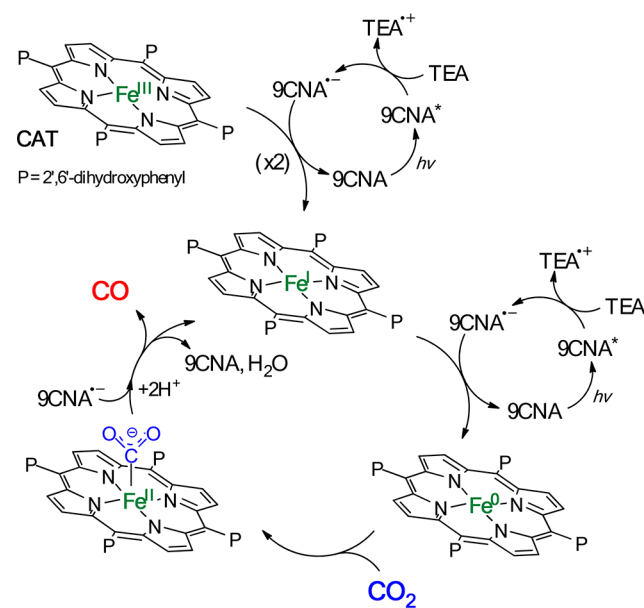
**Figure 3.** Fluorescence spectra of a 50  $\mu\text{M}$  9CNA solution in acetonitrile containing 0 (black), 5 (red), 10 (green), 15 (blue), 20 (cyan), 25 (magenta), and 100 mM (yellow) TEA. The inset shows the linear plot ( $R^2 = 0.998$ ) of the 9CNA fluorescence ratio at 438 nm versus TEA concentration according to the Stern–Volmer equation.

fluorescence ratio with  $[\text{TEA}]$  was linear (inset), and we obtained an apparent quenching rate constant of  $k_q = 1.3 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ . The reductive electron transfer between 9CNA\* and TEA is thus highly efficient, close to the diffusion limit.

With CAT as the quencher (Figure S1 in the SI), the evolution of the fluorescence ratio with  $[\text{CAT}]$  was not linear. Unlike TEA, which does not have any absorption above ca. 320 nm, CAT has non-negligible absorption at both the excitation and fluorescence wavelengths (Figure S2). The fluorescence decrease observed in this case (Figure S3) is due to the in situ absorption and emission screening of the light by CAT itself and not to a quenching process (see the SI for a detailed explanation).

On the basis of the present work and our previous results,<sup>34</sup> we propose the following mechanism (Scheme 1). 9CNA is excited and reductively quenched by TEA, whose concentration is at least 100 times higher (0.2 mM 9CNA vs 50 mM TEA at minimum). The anion radical 9CNA<sup>•-</sup> issued from the quenching then reacts with CAT along three successive steps, generating the catalytically active CAT<sup>0</sup> state. The latter species can then reduce CO<sub>2</sub> to form a CAT<sup>0</sup>–CO<sub>2</sub> adduct that is stabilized by internal hydrogen bonds.<sup>32,34</sup> Release of CO requires C–O bond breaking, necessitating an additional electron (Scheme 1).<sup>32</sup> While in the absence of a PS the only species able to give an electron is the CAT<sup>0</sup> species itself,<sup>34</sup> in the present case PS<sup>•-</sup> is a good electron donor on the basis of the highly negative standard redox potential of the 9CNA/9CNA<sup>•-</sup> couple ( $E^0 = -1.58 \text{ V vs SCE}$ ,<sup>41</sup> compared with  $-1.55 \text{ V vs SCE}$ <sup>31</sup> for the CAT<sup>1</sup>/CAT<sup>0</sup> couple). This slight thermodynamic advantage is reinforced by the larger stationary concentration of 9CNA<sup>•-</sup> compared with those of CAT<sup>0</sup>. In total, charge transfer from 9CNA<sup>•-</sup> to CAT<sup>0</sup>–CO<sub>2</sub> certainly

### Scheme 1. Proposed Mechanism for the Photosensitized Catalytic Reduction of CO<sub>2</sub> to CO



contributes significantly to the high selectivity and performance of the system.

Lowering the concentration of TEA (Figure 2) further increases the system efficiency since the TON in CO reaches ca. 60 at 0.05 M TEA instead of ca. 40 at 0.36 M TEA. As shown previously,<sup>34</sup> in situ generation of protonated TEA (reaction 2), a strong acid, partially leads to H<sub>2</sub> generation via a competitive pathway involving the formation of an intermediate hydride species. A small TEA concentration most probably minimizes this pathway since reaction 2 becomes less efficient. Finally, using visible-light excitation ( $\lambda > 400 \text{ nm}$ ) strongly reduces the photodegradation pathway in contrast to experiments without the PS,<sup>34</sup> as demonstrated by the linear increase of the TON in CO with time.

In conclusion, we have performed photocatalytic reduction of CO<sub>2</sub> to CO using a iron-based homogeneous catalyst and a photosensitizer irradiated in the visible range ( $\lambda > 400 \text{ nm}$ ). Production of CO over 50 h occurs with high selectivity (no or a negligible amount of H<sub>2</sub> was formed) and increases linearly, indicating that no degradation of the system occurs. TONs of ca. 140 and 60 and CSs for CO of 93 and 100% were obtained with Ir(ppy)<sub>3</sub> and 9CNA as photosensitizers, respectively. These results are remarkable for a system that combines an abundant metal (iron)-based catalyst, a cheap organic sensitizer (9CNA), and visible photons.

### ■ ASSOCIATED CONTENT

#### Supporting Information

Structures of CAT, Ir(ppy)<sub>3</sub>, and 9CNA; experimental details and additional absorption and fluorescence data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

### ■ AUTHOR INFORMATION

#### Corresponding Authors

julien.bonin@univ-paris-diderot.fr

robert@univ-paris-diderot.fr

#### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was partially supported by the Agence Nationale de la Recherche (ANR 2010 BLANC 0808). We thank Prof. Dario Bassani (ISM, Univ. Bordeaux 1) for highly stimulating discussions.

## ■ REFERENCES

- (1) Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M. *Chem. Soc. Rev.* **2009**, *38*, 89.
- (2) Aresta, M.; Dibenedetto, A.; Angelini, A. *Chem. Rev.* **2014**, *114*, 1709.
- (3) Fujita, E. *Coord. Chem. Rev.* **1999**, *185–186*, 373.
- (4) Kumar, B.; Llorente, M.; Froehlich, J.; Dang, T.; Sathrum, A.; Kubiak, C. P. *Annu. Rev. Phys. Chem.* **2012**, *63*, 541.
- (5) Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; DuBois, D. L.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, P. J. A.; Kerfeld, C. A.; Morris, R. H.; Peden, C. H. F.; Portis, A. R.; Ragsdale, S. W.; Rauchfuss, T. B.; Reek, J. N. H.; Seefeldt, L. C.; Thauer, R. K.; Waldrop, G. L. *Chem. Rev.* **2013**, *113*, 6621.
- (6) Costentin, C.; Robert, M.; Savéant, J.-M. *Chem. Soc. Rev.* **2013**, *42*, 2423.
- (7) Qiao, J.; Liu, Y.; Hong, F.; Zhang, J. *Chem. Soc. Rev.* **2014**, *43*, 631.
- (8) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1983**, 536.
- (9) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1984**, 328.
- (10) Takeda, H.; Koike, K.; Inoue, H.; Ishitani, O. *J. Am. Chem. Soc.* **2008**, *130*, 2023.
- (11) Takeda, H.; Ishitani, O. *Coord. Chem. Rev.* **2010**, *254*, 346.
- (12) Agarwal, J.; Fujita, E.; Schaefer, H. F., III; Muckerman, J. T. *J. Am. Chem. Soc.* **2012**, *134*, 5180.
- (13) Andrade, G. A.; Pistner, A. J.; Yap, G. P. A.; Lutterman, D. A.; Rosenthal, J. *ACS Catal.* **2013**, *3*, 1685.
- (14) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1985**, 56.
- (15) Chen, Z.; Concepcion, J. J.; Brennaman, M. K.; Kang, P.; Norris, M. R.; Hoertz, P. G.; Meyer, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 15606.
- (16) Tamaki, Y.; Morimoto, T.; Koike, K.; Ishitani, O. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 15673.
- (17) White, T. A.; Maji, S.; Ott, S. *Dalton Trans.* **2014**, *43*, 15028.
- (18) Bourrez, M.; Molton, F.; Chardon-Noblat, S.; Deronzier, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 9903.
- (19) Smieja, J. M.; Sampson, M. D.; Grice, K. A.; Benson, E. E.; Froehlich, J. D.; Kubiak, C. P. *Inorg. Chem.* **2013**, *52*, 2484.
- (20) Takeda, H.; Koizumi, H.; Okamoto, K.; Ishitani, O. *Chem. Commun.* **2014**, *50*, 1491.
- (21) Bourrez, M.; Orio, M.; Molton, F.; Vezin, H.; Duboc, C.; Deronzier, A.; Chardon-Noblat, S. *Angew. Chem., Int. Ed.* **2014**, *53*, 240.
- (22) Jeletic, M. S.; Mock, M. T.; Appel, A. M.; Linehan, J. C. *J. Am. Chem. Soc.* **2013**, *135*, 11533.
- (23) Jin, T.; Liu, C.; Li, G. *Chem. Commun.* **2014**, *50*, 6221.
- (24) Lacy, D. C.; McCrory, C. C. L.; Peters, J. C. *Inorg. Chem.* **2014**, *53*, 4980.
- (25) Froehlich, J. D.; Kubiak, C. P. *Inorg. Chem.* **2012**, *51*, 3932.
- (26) Schneider, J.; Jia, H.; Kobiros, K.; Cabelli, D. E.; Muckerman, J. T.; Fujita, E. *Energy Environ. Sci.* **2012**, *5*, 9502.
- (27) Thoi, V. S.; Kornienko, N.; Margarit, C. G.; Yang, P.; Chang, C. *J. J. Am. Chem. Soc.* **2013**, *135*, 14413.
- (28) Bhugun, I.; Lexa, D.; Savéant, J.-M. *J. Am. Chem. Soc.* **1994**, *116*, 5015.
- (29) Bhugun, I.; Lexa, D.; Savéant, J.-M. *J. Phys. Chem.* **1996**, *100*, 19981.
- (30) Bhugun, I.; Lexa, D.; Savéant, J.-M. *J. Am. Chem. Soc.* **1996**, *118*, 1769.
- (31) Costentin, C.; Drouet, S.; Robert, M.; Savéant, J.-M. *Science* **2012**, *338*, 90.
- (32) Costentin, C.; Passard, G.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2014**, *136*, 11821.
- (33) Costentin, C.; Passard, G.; Robert, M.; Savéant, J.-M. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111*, 14990.
- (34) Bonin, J.; Chaussemier, M.; Robert, M.; Routier, M. *ChemCatChem* **2014**, *6*, 3200.
- (35) Herrero, C.; Quaranta, A.; El Ghachtouli, S.; Vauzeilles, B.; Leibl, W.; Aukauloo, A. *Phys. Chem. Chem. Phys.* **2014**, *16*, 12067.
- (36) Voyame, P.; Toghiani, K. E.; Mendez, M. A.; Girault, H. H. *Inorg. Chem.* **2013**, *52*, 10949.
- (37) Yuan, Y.-J.; Yu, Z.-T.; Chen, X.-Y.; Zhang, J.-Y.; Zou, Z.-G. *Chem.—Eur. J.* **2011**, *17*, 12891.
- (38) Sato, S.; Morikawa, T.; Kajino, T.; Ishitani, O. *Angew. Chem., Int. Ed.* **2013**, *52*, 988.
- (39) Sato, S.; Koike, K.; Inoue, H.; Ishitani, O. *Photochem. Photobiol. Sci.* **2007**, *6*, 454.
- (40) Bian, Z.-Y.; Chi, S.-M.; Li, L.; Fu, W. *Dalton Trans.* **2010**, *39*, 7884.
- (41) Eriksen, J.; Foote, C. S. *J. Phys. Chem.* **1978**, *82*, 2659.
- (42) Boens, N.; Qin, W.; Basarić, N.; Hofkens, J.; Ameloot, M.; Pouget, J.; Lefèvre, J.-P.; Valeur, B.; Gratton, E.; vandeVen, M.; Silva, N. D., Jr.; Engelborghs, Y.; Willaert, K.; Sillen, A.; Rumbles, G.; Phillips, D.; Visser, A. J. W. G.; van Hoek, A.; Lakowicz, J. R.; Malak, H.; Gryczynski, I.; Szabo, A. G.; Krajcarski, D. T.; Tamai, N.; Miura, A. *Anal. Chem.* **2007**, *79*, 2137.
- (43) Mandal, P.; Tiwari, S. K.; Ganguly, T.; Sinha, S. *J. Lumin.* **2009**, *129*, 958.