

Supercritical CO₂

 Interfacial Photoreduction of Supercritical CO₂ by an Aqueous Catalyst**

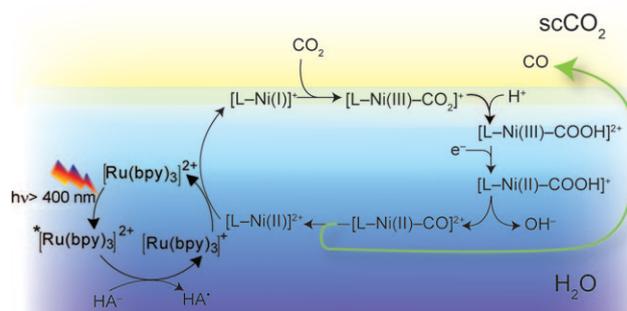
Manuel A. Méndez, Patrick Voyame, and Hubert H. Girault*

Carbon dioxide (CO₂) emissions currently represent a major concern.^[1] Accordingly, the electrochemical reduction of CO₂ is a reaction of major relevance and also of great challenges. Considering the redox potentials required for reducing CO₂, multi-electron-transfer, multiproton reactions are the most viable pathways for driving CO₂ reduction.^[2] Nonetheless, catalysts must be employed to overcome kinetic limitations of these processes. Molecular catalysts known to reduce CO₂ are usually monomeric metal complexes, such as ruthenium^[3] and rhenium carbonyl complexes,^[4] cobalt^[5] and iron porphyrins,^[6] and nickel^[7] and cobalt cyclams,^[8] but combinations of these systems into bimetallic structures have also been proposed.^[4a,9] More recently, the introduction of supercritical CO₂ (scCO₂) as a reaction medium has been investigated, as comprehensively reviewed by Fujita and co-workers.^[10] Interestingly, it has been observed that increasing the CO₂ pressure in the reaction medium usually does not provide any advantage.^[11]

Herein, water–scCO₂ binary biphasic systems are evaluated for reducing carbon dioxide using a well-known aqueous cycle with (1,4,8,11-tetraazacyclotetradecane)nickel(II) ([Ni^{II}cyclam]) as the catalytic unit, given its high affinity towards CO₂ upon reduction^[12] (see the Supporting Information, Figure S1a) and proven efficiency in aqueous media. As for the photosensitizer (PS), an aqueous soluble salt of tris(2,2'-bipyridyl)ruthenium(II) ([Ru(bpy)₃]²⁺) was chosen. This catalytic cycle was pioneered electrochemically by Sauvage and co-workers,^[13] photochemically by Calvin and co-workers,^[12a,14] and by Kimura et al.^[9a] Based on the reduction potentials of [Ni^{II}cyclam] and PS, this cycle (see the Supporting Information, Figure S1b) involves in its initial stage the absorption of light by [Ru(bpy)₃]²⁺ and subsequent reductive quenching of its excited state by ascorbate ($k_q = 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$).^[15] Subsequent reactions between the reduced photosensitizer and the catalyst in presence of CO₂ were shown to yield exclusively CO and H₂ in aqueous media.

Over the last few years, we have shown that reactions such as hydrogen evolution^[16] or oxygen reduction^[17] could be

carried out efficiently at the water–1,2-dichloroethane interface at atmospheric pressure by treating aqueous protons or oxygen with organic electron donors. Herein, we show that the interface between an aqueous solution and supercritical CO₂ can be the locus for CO₂ reduction, as depicted in Scheme 1.



Scheme 1. Catalytic cycle proposed for the photoreduction of CO₂ using [Ni^{II}cyclam] as catalyst in a water–supercritical CO₂ biphasic system.

Results of comparative experiments in which the reaction time and pressure were varied while the concentration of all components were kept constant are summarized in Figure 1. A seven-fold increase in the activity of the catalyst for experiments carried out under exactly the same conditions can be observed for a fixed reaction time of 4 h (inset Figure 1). In a first attempt to rationalize this result, a higher concentration of CO₂ in water at elevated pressures can be ruled out, given that the solubility of CO₂ in water only

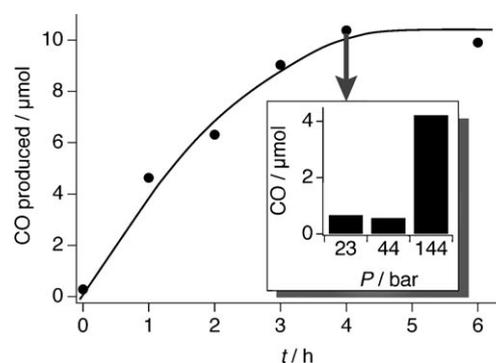


Figure 1. CO production as a function of irradiation time. [PS] = 2×10^{-3} M, [[Ni^{II}cyclam]] = 5×10^{-4} M, [Asc] = 0.5 M at 313 K and 144 bar. Inset presents comparative data after 4 h of reaction at various pressures when [PS] = 5×10^{-4} M, [[Ni^{II}cyclam]] = 2×10^{-3} M, [Asc] = 0.5 M.

[*] M. A. Méndez, P. Voyame, Prof. Dr. H. H. Girault
 Laboratoire d'Electrochimie Physique et Analytique
 Ecole Polytechnique Fédérale de Lausanne
 Station 6, 1015 Lausanne (Switzerland)
 E-mail: hubert.girault@epfl.ch
 Homepage: <http://lepa.epfl.ch>

[**] The EPFL is thanked for financial support. Valérie Devaud and Thierry Meyer are acknowledged for technical support. Thanks also to Prof. Roger Guilard, University of Bourgogne (France), for helpful discussions.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201100828>.

increases by approximately 30% when the pressure is raised from 50 to 150 bar.^[18]

This finding suggests that the complexation of CO₂ with the [Ni^Icyclam] complex could take place at the water–scCO₂ interface. Indeed, the cyclam complex is rather hydrophobic, as demonstrated by ion-transfer voltammetry at the water–1,2-dichloroethane interface (see the Supporting Information for details), and is likely to adsorb at the interface, where it is also in contact with aqueous protons. Other examples of surface-active molecules at liquid–liquid interfaces are macrocycles usually employed in solvent extraction of metallic cations,^[19] and cobalt porphyrins able to reduce oxygen at the water–1,2-dichloroethane interface.^[17b,20] Besides, protein adsorption at the water–scCO₂ interface has been reported to be a pressure-dependent process.^[21] Surface tension measurements at the air–water interface as a function of the aqueous concentration of [Ni^{II}cyclam] were conducted and analyzed according to the Gibbs adsorption equation (see the Supporting Information for details). These measurements revealed an adsorption process that follows a Langmuir type behavior (see the Supporting Information, Figure S6). A standard Gibbs energy of adsorption for [Ni^{II}cyclam] at the air–water interface of -10 kJ mol^{-1} is obtained, which is in agreement with the relatively weak adsorption of this complex. The area occupied per molecule in a monolayer of adsorbed catalyst was also calculated and found to be approximately 152 \AA^2 . The latter value clearly suggests that the adsorbed catalyst assumes a planar geometry at the interface.

A custom-built pendant drop system was used to estimate the interfacial tension at the water–scCO₂ interface. An elongation of the aqueous droplet could be observed when [Ni^{II}cyclam] was added to the aqueous phase (Figure 2).

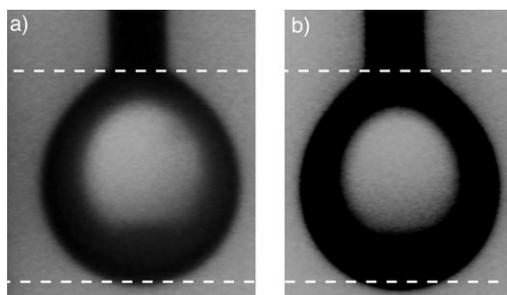


Figure 2. Photographs of a 15 µL aqueous droplet in the a) absence and b) presence of [Ni^{II}cyclam] at a concentration of 50 mM immersed in supercritical CO₂ at 140 bar and 313 K.

Image analysis using the methodology proposed by Girault et al.^[22] and comparison of the extracted profiles with the theoretical profiles calculated from numerical resolution of the Laplace equation^[23] yields a decrease in the interfacial tension of 6.7% in the presence of the catalyst. Analogously, a decrease of 5.7% in the air–water interfacial tension is obtained when the surface tensions of pure water and 50 mM aqueous [Ni^{II}cyclam] are compared (see the Supporting Information for details). These data clearly show that [Ni^{II}cyclam] adsorbs at the water–scCO₂ interface.

In consequence, it is reasonable to consider that in the present system [Ni^Icyclam] complexes also adsorb at the water–scCO₂ interface, as they are less hydrophilic than the [Ni^{II}cyclam] complexes. Both complexes probably assume a planar configuration at the interface, in accordance with the experiments described above. The latter can have a crucial impact on the reaction, since binding of CO₂ on [Ni^Icyclam] would be largely favored in a CO₂-rich environment like the water–CO₂ cluster network formed at the water–scCO₂ interface.^[24] Additionally, adsorbed CO₂–[Ni^Icyclam] complexes can be easily protonated and reduced at the interface. Considering that the reaction takes place under vigorous stirring, the contact area between the two phases is optimized.

It can also be seen from Figure 1 that the production of CO reaches a steady value after approximately 4 h of irradiation. This decrease in activity is very likely due to the degradation of the sensitizer, as previously reported.^[14]

The influence of the pH value of the aqueous phase was also examined, as it has been shown to significantly decrease in the presence of pressurized CO₂.^[25] However, depending on the composition of the aqueous phase, values up to pH 6 can be obtained (by addition of sodium bicarbonate).^[26] Here, pH spectrophotometric determinations using bromophenol blue as indicator^[27] (see the Supporting Information Figure S2) revealed a value of 3.5 for a blank binary system formed between pure water and supercritical CO₂. In the presence of 0.5 M sodium ascorbate, the aqueous pH value was measured to be approximately 5.1, as evidenced from the visible spectra of bromocresol purple^[28] (see the Supporting Information Figure S3). Therefore, sodium ascorbate has here a double purpose: To act 1) as a sacrificial electron donor and 2) as a pH buffer.

Experiments in which the pH value of the aqueous phase at 144 bar was varied (Figure 3) showed that the amount of CO produced increases above pH 3 but remains approximately constant above pH 4. At the same time, H₂ production was determined to reach a maximum at around pH 4, which is in good agreement with the results found by Grant et al.^[14] Although there is some discrepancy in the published results concerning H₂ evolution, most of the reports for this catalytic cycle in water show that H₂ is produced in approximately equal or higher amounts than CO.^[9a,14,29] In the present biphasic system, the comparison of the amounts of H₂ and CO produced indicates clearly that the reaction proceeds more

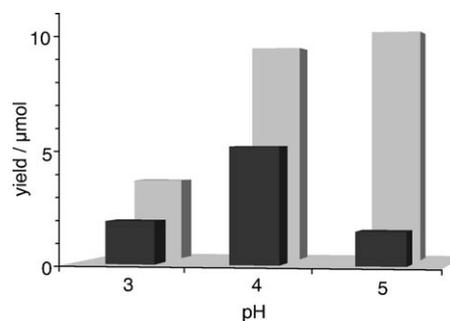


Figure 3. CO (light gray) and H₂ (dark gray) production as a function of the aqueous pH value at 144 bar and 313 K. Irradiation time = 4 h, [PS] = $2 \times 10^{-3} \text{ M}$, [[Ni^Icyclam]] = $5 \times 10^{-4} \text{ M}$.

selectively towards CO₂ reduction at all pH values tested, and optimal operation conditions are attained at pH 5. Previous reports at pH 5 estimated the CO/H₂ ratio to be 0.83,^[14] whereas this ratio is determined herein to be 7.1, representing an enhancement in the selectivity of 8.6 times.

The quantum yield (mole of CO produced per mole of photons absorbed) for the reaction, using a monochromatic 453 nm HeCd laser, was determined to be 1.4×10^{-3} , which is low, since there are several steps involved in the global reaction; nonetheless, it is significantly higher than the value of 6×10^{-4} reported for this system.^[12a] This finding clearly suggests that the efficiency of the system is being enhanced, but it still does not account for the sevenfold increase in the production of CO. Herein, we propose that [Ni^{II}cyclam] adsorption at the interface, probably parallel to the interface, implies that, upon reduction of the catalyst, CO₂ would be preferentially activated at the interface rather than water. Additionally, it is reasonable to expect that [Ni^Icyclam] adsorbs more strongly at the interface than [Ni^{II}cyclam] given its lower charge. Altogether, higher selectivity towards CO₂ reduction at all pH values can be expected, since the binding of CO₂ does not proceed by insertion into Ni–H bonds.^[12b] Indeed, data shown in Figure 3 is in good agreement with this hypothesis.

On the other hand, even though sodium ascorbate is an effective reductive quencher of the metal-to-ligand charge-transfer (MLCT) excited state of [Ru(bpy)₃]²⁺ in the aqueous phase, other compounds such as tertiary amines can also be used. Among them, triethanolamine (TEOA) has been widely employed.^[30] However, upon replacement of sodium ascorbate by TEOA in the present system, neither CO nor H₂ can be detected. Indeed, TEOA likely binds to the metal center, which hinders the overall CO₂ reduction process. This hindrance confirms that the CO₂ activation step is crucial. As UV/Vis spectra of [Ni^{II}cyclam] in the absence and presence of TEOA showed no significant alterations, it is likely that TEOA in excess interacts with [Ni^Icyclam].

Experimental results summarizing the aforementioned discussion are presented in Table 1. According to these data, in absence of either light, the catalyst, or a suitable sacrificial electron donor, the reaction does not proceed (Table 1,

Table 1: Summary of photoreduction experiments; the volume of the aqueous phase was 9.8 mL in all cases.

| Exp. No. | Pressure ^[a] [bar] | [[Ni ^{II} L]] [mM] | [PS] [mM] | CO produced [μmol] | H ₂ produced [μmol] |
|-------------------|-------------------------------|-----------------------------|-----------|--------------------|--------------------------------|
| 1 | 24 | 2 | 0.5 | 0.7 | 0.3 |
| 2 | 44 | 2 | 0.5 | 0.6 | 0.8 |
| 3 | 144 | 2 | 0.5 | 4.2 | N.D. ^[b] |
| 4 | 144 | 0.5 | 2 | 10.4 | 1.5 |
| 5 | 144 | 0.1 | 5 | 3.6 | 3.0 |
| 6 | 144 | 0 | 2 | N.D. | 5.5 |
| 7 ^[c] | 144 | 0.5 | 2 | N.D. | N.D. |
| 8 ^[d] | 144 | 0.5 | 2 | N.D. | N.D. |
| 9 ^[e] | 144 | 0.5 | 2 | 3.6 | 1.9 |
| 10 ^[f] | 144 | 0.5 | 2 | 9.7 | 5.2 |

[a] ± 2 bar. [b] N.D. = Not detected. [c] In the dark. [d] TEOA (0.7 M) was used instead of Asc. [e] Same as experiment 4 at pH 3. [f] Same as experiment 4 at pH 4.

Exp. 6–8). When the sensitizer is in excess with respect to the catalyst, CO production turnover numbers (mole of CO produced per mole of catalyst for four hours of reaction) of 3.6 can be estimated (Table 1, Exp. 5). However, for experiments carried out using higher ratios of catalyst and sensitizer concentrations (4 and 0.25; Table 1, Exp. 3 and 4, respectively), turnover numbers of about 0.2 (Exp. 3) and 2.1 (Exp. 4) are obtained. The latter is in agreement with the very limited stability of [Ru(bpy)₃]²⁺ in aqueous media. It is then clear how changes in concentration greatly affect the turnover numbers, thus indicating that the photosensitization step might be the rate-limiting step. Finally, significant H₂ production is observed when either the concentration of the catalyst is low compared to that of PS (Table 1, Exp. 5) or the catalyst is not present at all (Table 1, Exp. 6). The latter accounts for the formation of H₂ upon irradiation of [Ru(bpy)₃]²⁺ in an ascorbate buffer solution, as reported.^[31]

In summary, the present work demonstrates that it is possible to reduce supercritical CO₂ using adsorbed [Ni(cyclam)] catalysts and that this reduction is more selective towards CO production than when the same reaction is carried out simply in water. The recycling of the catalyst and its reduction by an aqueous sensitizer occurs homogeneously, whereas the CO₂ binding process is more likely to occur at the interface, the area of which is optimized by vigorous stirring. This work clearly shows that the classical [Ni(cyclam)]–[Ru(bpy)₃]-ascorbic acid photocatalytic cycle becomes much more efficient and selective when carried out at elevated pressures, corroborating the hypothesis that the CO₂ binding step is an interfacial process. Supercritical CO₂ is an interesting reaction medium not only from a mechanistic point of view but also to develop new scenarios for CO₂ reduction where water acts as both electron and proton source.^[32]

Experimental Section

High-purity CO₂ (99.9995%) was provided by Carbagas. Tris(2,2'-bipyridyl)ruthenium(II) (99.9%, metal basis), 1,4,8,11-tetraazacyclotetradecane (cyclam), and NiCl₂ were purchased from Aldrich and used without any further purification. Sodium ascorbate was purchased from Merck. [Ni^{II}cyclam]Cl₂ and was prepared according to literature procedures.^[33] All aqueous solutions were prepared employing deionized water (Mili-Q, 18.2 MΩ cm⁻¹). All other chemical reagents were analytical grade and used as received.

The reactor employed for the photoreduction of CO₂ consisted of a 31 mL stainless steel cell equipped with one sapphire window. Temperature was controlled by circulating water through a stainless steel jacket wrapping the reactor. Pressure was monitored using a piezoelectric pressure sensor (Swagelok). The cell employed for the spectrophotometric measurements was equipped with three sapphire windows (Rayotek). The chemicals in the reactor were homogenized by magnetic stirring.

Photoinduced CO₂ reduction catalyzed by [Ni^{II}cyclam] was studied at 25 °C using a 600 Watt Xe lamp (Oriel, Model 66021) with a cutoff filter ($\lambda > 400$ nm). In a typical experiment carried out under supercritical conditions, suitable volumes of separate aqueous solutions of the photosensitizer, the catalyst, and the sacrificial electron donor were loaded into the reactor. The cell was purged with CO₂ and heated to 313 K. After reaching thermal equilibrium, CO₂ was slowly loaded into the cell by a piston pump (Teledyne Isco, model 100-DX) until a pressure of 95 bar was attained. After this step, addition of water was carried out using a second piston pump

(Teledyne Isco, model 100-DX) until the final pressure was reached. Quantum yield determination was carried out at 453 nm using a HeCd continuous laser (Omnichrome, Series 43). Light intensity for the quantum yield measurements was determined with a Gentec model TPM-310 power meter. Pendant drop experiments under supercritical conditions were always carried out at a constant pressure of 140 bar, and water injection was carried out at a constant flow of 10 $\mu\text{L min}^{-1}$ (see the Supporting Information for further details). Collection of the gas after reaction was followed by its injection into a GC-TCD instrument for H_2 determination. Quantification of CO was carried out by using a GC-FID instrument (Perkin-Elmer, Clarus 500) equipped with a methanizer (see the Supporting Information for further details). In situ spectra were recorded with a UV/Vis spectrometer (Ocean Optics, Model ChemUSB 2000)

Received: February 1, 2011
 Revised: April 6, 2011
 Published online: June 24, 2011

Keywords: adsorption · carbon dioxide · cyclam · photochemistry · supercritical fluids

- [1] C. Song, *Catal. Today* **2006**, *115*, 2–32.
- [2] a) I. Willner, R. Maida, D. Mandler, H. Durr, G. Dorr, K. Zengerle, *J. Am. Chem. Soc.* **1987**, *109*, 6080–6086; b) E. Barton Cole, P. S. Lakkaraju, D. M. Rampulla, A. J. Morris, E. Abelev, A. B. Bocarsly, *J. Am. Chem. Soc.* **2010**, *132*, 11539–11551.
- [3] J.-M. Lehn, R. Ziessel, *J. Organomet. Chem.* **1990**, *382*, 157–173.
- [4] a) H. Takeda, O. Ishitani, *Coord. Chem. Rev.* **2010**, *254*, 346–354; b) J. Hawecker, J.-M. Lehn, R. Ziessel, *J. Chem. Soc. Chem. Commun.* **1983**, 536–538.
- [5] D. Behar, T. Dhanasekaran, P. Neta, C. M. Hosten, D. Ejeh, P. Hambright, E. Fujita, *J. Phys. Chem. A* **1998**, *102*, 2870–2877.
- [6] T. Dhanasekaran, J. Grodkowski, P. Neta, P. Hambright, E. Fujita, *J. Phys. Chem. A* **1999**, *103*, 7742–7748.
- [7] M. Beley, J. P. Collin, R. Ruppert, J. P. Sauvage, *J. Am. Chem. Soc.* **1986**, *108*, 7461–7467.
- [8] S. Matsuoka, K. Yamamoto, T. Ogata, M. Kusaba, N. Nakashima, E. Fujita, S. Yanagida, *J. Am. Chem. Soc.* **1993**, *115*, 601–609.
- [9] a) E. Kimura, X. H. Bu, M. Shionoya, S. J. Wada, S. Maruyama, *Inorg. Chem.* **1992**, *31*, 4542–4546; b) J. Collin, A. Jouaiti, J. Sauvage, *Inorg. Chem.* **1988**, *27*, 1986–1990.
- [10] a) M. D. Doherty, D. C. Grills, J. T. Muckerman, D. E. Polyansky, E. Fujita, *Coord. Chem. Rev.* **2010**, *254*, 2472–2482; b) D. C. Grills, E. Fujita, *J. Phys. Chem. Lett.* **2010**, *1*, 2709–2718.
- [11] H. Hori, K. Koike, Y. Suzuki, M. Ishizuka, J. Tanaka, K. Takeuchi, Y. Sasaki, *J. Mol. Catal. A* **2002**, *179*, 1–9.
- [12] a) C. A. Craig, L. O. Spreer, J. W. Otvos, M. Calvin, *J. Phys. Chem.* **1990**, *94*, 7957–7960; b) C. A. Kelly, Q. G. Mulazzani, M. Venturi, E. L. Blinn, M. A. J. Rodgers, *J. Am. Chem. Soc.* **1995**, *117*, 4911–4919.
- [13] M. Beley, J.-P. Collin, R. Ruppert, J.-P. Sauvage, *J. Chem. Soc. Chem. Commun.* **1984**, 1315–1316.
- [14] J. L. Grant, K. Goswami, L. O. Spreer, J. W. Otvos, M. Calvin, *J. Chem. Soc. Dalton Trans.* **1987**, 2105–2109.
- [15] C. Creutz, N. Sutin, B. Brunschwig, *J. Am. Chem. Soc.* **1979**, *101*, 1297–1298.
- [16] I. Hatay, B. Su, F. Li, R. Partovi-Nia, H. Vrabel, X. Hu, M. Ersoz, H. H. Girault, *Angew. Chem.* **2009**, *121*, 5241–5244; *Angew. Chem. Int. Ed.* **2009**, *48*, 5139–5142.
- [17] a) A. Trojáněk, J. Langmaier, B. Su, H. H. Girault, Z. Samec, *Electrochem. Commun.* **2009**, *11*, 1940–1943; b) B. Su, I. Hatay, A. Trojáněk, Z. Samec, T. Khoury, C. P. Gros, J.-M. Barbe, A. Daina, P.-A. Carrupt, H. H. Girault, *J. Am. Chem. Soc.* **2010**, *132*, 2655–2662; c) I. Hatay, B. Su, M. A. Mendez, C. Corminboeuf, T. Khoury, C. P. Gros, M. Bourdillon, M. Meyer, J.-M. Barbe, M. Ersoz, S. Zalis, Z. Samec, H. H. Girault, *J. Am. Chem. Soc.* **2010**, *132*, 13733–13741.
- [18] Z. Duan, R. Sun, *Chem. Geol.* **2003**, *193*, 257–271.
- [19] T. G. Traylor, S. Tsuchiya, Y. S. Byun, C. Kim, *J. Am. Chem. Soc.* **1993**, *115*, 2775–2781.
- [20] R. Partovi-Nia, B. Su, F. Li, C. P. Gros, J.-M. Barbe, Z. Samec, H. H. Girault, *Chem.-Eur. J.* **2009**, *15*, 2335–2340.
- [21] F. Tewes, F. Boury, *J. Phys. Chem. B* **2005**, *109*, 1874–1881.
- [22] H. H. Girault, D. J. Schiffrin, B. D. V. Smith, *J. Electroanal. Chem.* **1982**, *137*, 207–217.
- [23] J. M. Andreas, E. A. Hauser, W. B. Tucker, *J. Phys. Chem.* **1938**, *42*, 1001–1019.
- [24] F. Tewes, F. Boury, *J. Phys. Chem. B* **2005**, *109*, 3990–3997.
- [25] a) K. L. Toews, R. M. Shroll, C. M. Wai, N. G. Smart, *Anal. Chem.* **1995**, *67*, 4040–4043; b) J. P. Hanrahan, K. J. Ziegler, J. D. Glennon, D. C. Steytler, J. Eastoe, A. Dupont, J. D. Holmes, *Langmuir* **2003**, *19*, 3145–3150.
- [26] C. Roosen, M. Ansorge-Schumacher, T. Mang, W. Leitner, L. Greiner, *Green Chem.* **2007**, *9*, 455–458.
- [27] F. Reymond, D. Fermín, H. J. Lee, H. H. Girault, *Electrochim. Acta* **2000**, *45*, 2647–2662.
- [28] D. R. MacFarlane, J. M. Pringle, K. M. Johansson, S. A. Forsyth, M. Forsyth, *Chem. Commun.* **2006**, 1905–1917.
- [29] E. Kimura, S. Wada, M. Shionoya, Y. Okazaki, *Inorg. Chem.* **1994**, *33*, 770–778.
- [30] K. Kalyanasundaram, *Coord. Chem. Rev.* **1982**, *46*, 159–244.
- [31] C. V. Krishnan, N. Sutin, *J. Am. Chem. Soc.* **1981**, *103*, 2141–2142.
- [32] A. J. Morris, G. J. Meyer, E. Fujita, *Acc. Chem. Res.* **2009**, *42*, 1983–1994.
- [33] B. Bosnich, M. L. Tobe, G. A. Webb, *Inorg. Chem.* **1965**, *4*, 1109–1112.