



Addressing the Reproducibility of Photocatalytic Carbon Dioxide Reduction

Maximilian Marx,^[a] Andrea Mele,^[b] Anke Spannenberg,^[a] Christoph Steinlechner,^[a] Henrik Junge,^[a] Philippe Schollhammer,^[b] and Matthias Beller^{*[a]}

Reproducibility of photocatalytic reactions, especially when conducted on small scale for improved turnover numbers with *in situ* formed catalysts can prove challenging. Herein, we showcase the problematic reproducibility on the example of attractive photocatalytic CO₂ reduction utilizing [FeFe] hydrogenase mimics. These Fe complexes, well-known for their application in proton reduction reactions, were combined with a heteroleptic Cu photosensitizer and produced CO/H₂/HCO₂H mixtures of variable constitution. However, the reactions

indicated a poor reproducibility, even when conducted with well-defined complexes. Based on our experience, we make suggestions for scientists working in the field of photocatalysis on how to address and report the reproducibility of novel photocatalytic reaction protocols. In addition, we would like to highlight the importance of studying reproducibility of novel reaction protocols, especially in the fields of photocatalytic water splitting and CO₂ reduction, where TONs are widely used as the comparable measure for catalytic activity.

Introduction

Photocatalysis is arguably one of the most active fields in nowadays catalysis research.^[1] Hence, numerous researchers all over the world investigate photocatalytic water splitting^[2] or reduction of CO₂ to potential energy carriers.^[3] In addition, photocatalysis is intensely applied for producing more value added compounds, such as fine chemicals or life science molecules.^[4] The strong interest in this technology can readily be explained by the intrinsic advantage offered by direct utilization of sunlight as an abundant and sustainable energy source. Not surprisingly, the number of publications in these fields has skyrocketed over the last decade, outlined by a more than 10-fold increase in publication numbers in the field of photocatalytic CO₂ reduction (Figure 1). With respect to the major challenges mankind has to face in the upcoming decades, which are probably the man-made climate change as a result of extensive usage of fossil fuels and an increasing demand in energy and food eventuating from the on-going demographic growth,^[5] the enhanced interest in those research

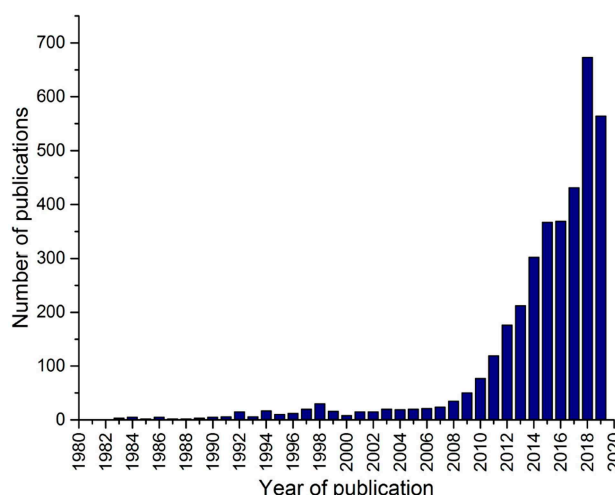


Figure 1. Number of publications in the area of photocatalytic CO₂ reduction, (compiled using SciFinder searching for "Photocatalysis CO₂ reduction" on August 12, 2019).

[a] M. Marx, Dr. A. Spannenberg, C. Steinlechner, Dr. H. Junge, Prof. M. Beller
Leibniz Institute for Catalysis at the University of Rostock
Albert-Einstein-Straße 29a
Rostock 18059 (Germany)
E-mail: Matthias.Beller@catalysis.de

[b] A. Mele, Prof. P. Schollhammer
UMR CNRS 6521 CEMCA
Faculté des Sciences et Techniques
University of Brest
6 Avenue Victor le Gorgeu
Brest 29238 (France)
E-mail: Philippe.Schollhammer@univ-brest.fr

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/cctc.201901686>

© 2019 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA.
This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

areas are justified. The ambition of scientists to compete with or even outperform previously reported methods and to aim for new record results for those transformations is certainly the foundation for future improvement. However, the stride towards better catalyst performance can just as well become ambivalent when pursued at all costs. This becomes obvious by the recent trend of lowering catalyst loadings to achieve higher turnover numbers (TONs) which are then reported as the prime measure of catalyst activity. In the case of synthetic applications, product yield and substrate conversion are direct indicators of the applicability of those lowered catalyst loadings and a reduced amount of catalyst giving similar yields is undoubtedly preferred. In contrast, photocatalytic CO₂ reduction reactions or water splitting processes are usually far from reaching full conversion under batch reaction conditions.

Hence, lower catalyst loadings, albeit feigning higher catalytic activity, diminish the applicability of these systems, since intricate upscaling of those reactions is most often not performed!

In addition, the impact of impurities on the catalyst performance becomes more pronounced at lower catalyst concentrations, potentially resulting in poor reproducibility for the described reactions.^[6] Combined with elaborate reaction setups used for photocatalytic CO₂ reduction reactions and the crucial influence of the light source (position and constant radiant flux),^[2h,7] reproduction of reported systems and further improvement of literature-known CO₂ reduction protocols can prove challenging. Interestingly, the reproducibility of photocatalytic CO₂ reduction reactions is seldom addressed and often no information on the number of reaction runs utilized for the calculation of the TONs is given.

Herein, we showcase the importance of these factors on the example of photocatalytic CO₂ reduction using [FeFe] hydrogenase mimics. Based on this example, we would like to encourage researchers in the field of photocatalysis to pay special attention to the reproducibility of novel reaction protocols.

Results and Discussion

Recently, Wang and co-workers reported the electrocatalytic CO₂ reduction to CO, hydrogen and formate utilizing [FeFe] hydrogenase mimics [Fe₂(μ-bdt)(CO)₆] (1, bdt = benzene-1,2-dithiolate) and [Fe₂(μ-edt)(CO)₆] (edt = ethane-1,2-dithiolate).^[8] In parallel to their study, we investigated the photocatalytic CO₂ reduction using complex 1 and similar hydrogenase mimics. We started our investigations based on 1 in combination with a heteroleptic copper photosensitizer (CuPS) 2 previously utilized for photocatalytic CO₂ reduction in our group.^[9] CuPS 2 can be readily formed *in situ* from [Cu(MeCN)₄](PF₆), bathocuproine and xantphos in a 1:1:3 ratio.^[9] At a wavelength of 415 nm and a radiant flux of 1.00 W, we were pleased to find simultaneous CO₂ and proton reduction with a total TON for CO, HCO₂H and H₂ of 614 (average of 7 reactions, detailed results are presented in Table S1) at a CO/H₂/HCO₂H ratio of 1.8/1.2/1 after 3 h of illumination in 5:1 *N*-methylpyrrolidinone (NMP) / triethanolamine (TEOA) using BIH (1,3-dimethyl-2-phenylbenzo[d]imidazole) as the sacrificial electron donor (Scheme 1). This correlates with the reported results for the electrocatalytic CO₂ reduction utilizing complex 1, where HCO₂H was the main product.^[8] However, we already observed a low reproducibility for the HCO₂H TONs, which we at first attributed partially to

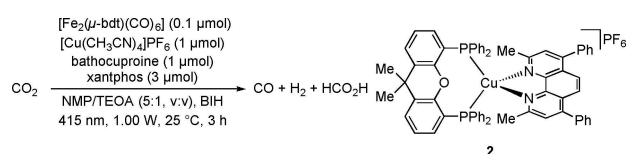
direct CO₂ reduction by BIH.^[10] Interestingly, conducting the same reaction with the isolated heteroleptic copper complex CuPS 2 instead of the *in situ* prepared photosensitizer resulted in a total TON of 865 and a CO/H₂/HCO₂H ratio of 1/7/3 (average of 2 reactions, for single experiment results see Table S1). Since previously reported systems developed in our group showed a good correlation between the utilization of isolated 2 and the *in situ* generated CuPS,^[9a, 11] this was an unexpected result. In addition, we already observed a significant difference between the TONs for H₂ formation of the single experiments (476 vs. 623).

Heteroleptic Cu complexes, such as 2, are well-known to exist in an equilibrium with the homoleptic [Cu(N[^]N)₂]⁺ complex in solution.^[11–12] This equilibrium is depending on the solvent, the illumination conditions and the amount of ancillary ligands present in the reaction mixture.^[9a, 11] Since no excess bisphosphine ligand is present in the well-defined 2, enhanced formation of the [Cu(N[^]N)₂]⁺ complex could occur in this case. Even though this might account for the decreased catalytic activity with respect to CO formation of the well-defined CuPS 2, the plain difference compared to the *in situ* CuPS could also result from a more complex equilibrium that includes the [FeFe] hydrogenase mimic itself.

For optimizing this equilibrium, we investigated the influence of the [Cu(CH₃CN)₄](PF₆)/bathocuproine/xantphos ratio on the overall catalytic activity of the catalyst system (Table S2). The optimum composition was found to be a 1/2/5 Cu/bathocuproine/xantphos ratio with a total TON of 756 at a CO/H₂/HCO₂H ratio of 1.7/1.1/1 (average of 5 reactions). However, we witnessed a diminished reproducibility under these conditions, which became even more obvious when optimizing the illumination conditions by switching to a broader 400–500 nm irradiation at an increased radiant flux of 1.50 W (Table S3). While at first a comparably high catalytic activity of 880 TON with a CO/H₂/HCO₂H ratio of 2/1/1 (average over 3 reactions) was obtained and the reproducibility for CO was within 10% range (TON(CO): 445, 417, 466), this reproducibility dramatically decreased after repeating the same reaction six months later (all results are presented in Table S4). After changing all the employed reagents and the solvent, we were unable to identify the cause of the poor reproducibility observed for this reaction (Figure 2). Notably, a five-fold increase in the utilized catalyst amount did not facilitate complete reproducibility, with an almost 200% difference in TON(CO) for reactions conducted within a timeframe of one month (Table S5).

To evaluate, whether this poor reproducibility occurs only in the single case of [Fe₂(μ-bdt)(CO)₆] (1), we also evaluated the photocatalytic CO₂ reduction using [Fe₂(μ-pbdt)(CO)₆] (3), [Fe₂(μ-Cl-bdt)(CO)₆] (4), and simple [Fe₂(CO)₉] (5). In all cases, moderate to poor reproducibility was observed with respect to CO, HCO₂H, and H₂ formation under the previously optimized conditions, even though general trends in the product mixture composition were observable (Figure 3, for detailed results see Table S6).

As mentioned earlier, Cu complexes, such as 2, exist in an equilibrium with the homoleptic [Cu(N[^]N)₂]⁺ complex.^[11–12] Since CO replacement by bidentate N or P donor ligands is



Scheme 1. General photocatalytic CO₂ reduction utilizing [Fe₂(μ-bdt)(CO)₆] (1) and *in situ* formed CuPS 2.

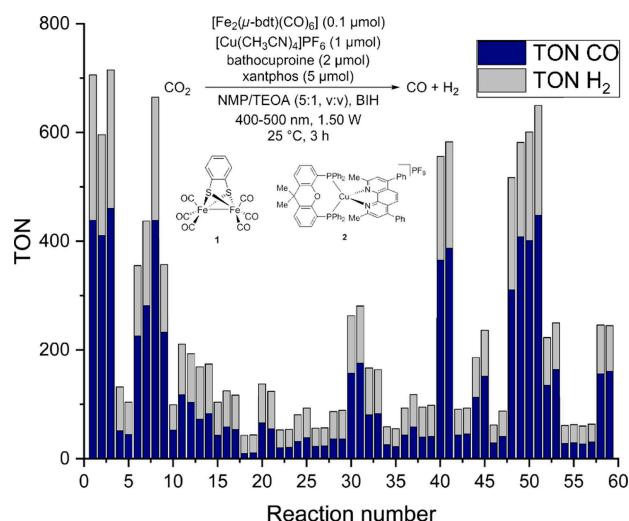


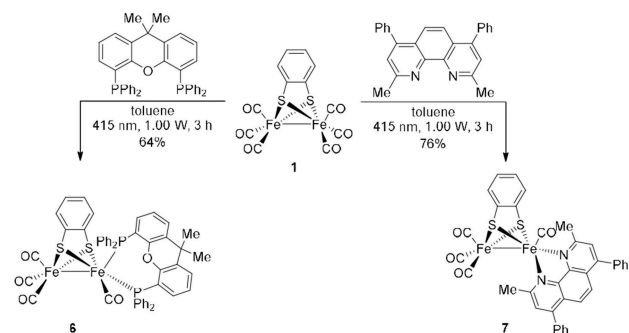
Figure 2. Single experiment results for the photocatalytic CO₂ reduction conducted with *in situ* formed CuPS 2 and Fe catalyst 1 underscoring the poor reproducibility.

well-known for [FeFe] hydrogenase mimics,^[13] we supposed that a reaction of the Fe carbonyl complexes employed as catalysts with the *in situ* CuPS might occur under our reaction conditions. This would further complicate the equilibria within the mixture and might eventually cause the poor reproducibility observed.

Thus, we reacted 1 with an equimolar amount of either bathocuproine or xantphos in toluene under illumination (415 nm, 1.00 W). To our delight, this resulted in the formation of novel diiron complexes 6 and 7 in mediocre to good yield (64% for 6; 76% for 7) (Scheme 2).

Crystals suitable for X-ray crystallographic analysis were obtained from CH₂Cl₂/hexane and enabled indisputable elucidation of their solid state structures (Figures 4 & 5). In both cases, the dithiolate bridge remained unaltered and one molecule of the bidentate ligand is coordinated in a chelating fashion to one of the two Fe centers. This is in accordance with previously reported compounds of this type.^[13a-j]

Our result also emphasized the universality of the synthesis of chelated diiron dithiolate complexes *via* irradiation of the



Scheme 2. Synthesis of the new [FeFe] complexes 6 and 7 *via* photolytic CO replacement by xantphos and bathocuproine.

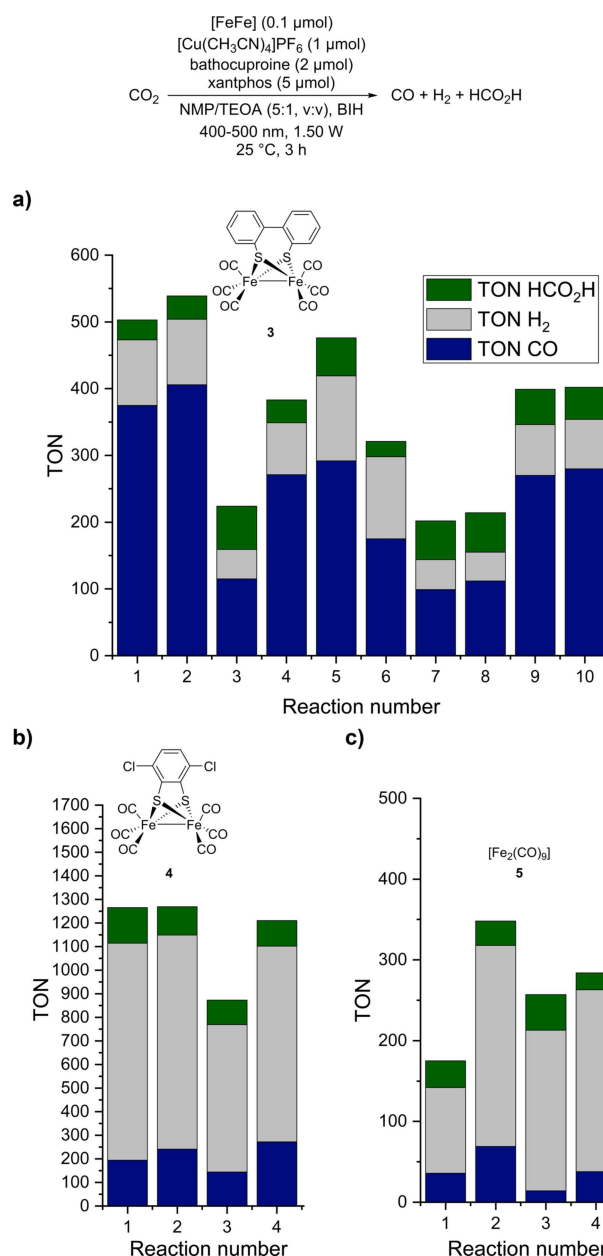


Figure 3. Reproducibility of the photocatalytic CO₂ reduction utilizing *in situ* generated CuPS 2 and various dinuclear Fe complexes. a) [Fe₂(μ-pbdt)(CO)₆] (3). b) [Fe₂(μ-Cl-bdt)(CO)₆] (4). c) [Fe₂(CO)₉] (5).

hexacarbonyl precursor and the bidentate ligand.^[13a,g,i] Interestingly, we were able to perform this reaction without the explicit utilization of UV light (maximum at 415 nm), which indicates that CO dissociation for the [Fe₂(μ-bdt)(CO)₆] can indeed be achieved using visible light i.e. our reaction conditions.^[14]

Having isolated these new complexes, we evaluated their activity in the photocatalytic CO₂ reduction. We hoped that these isolated complexes in combination with either the *in situ* or the well-defined CuPS 2 might give entirely reproducible results. Combining complex 6 with the isolated CuPS 2 gave a low TON for CO of 10, a TON of 159 for HCO₂H, and a TON for H₂ of 340 (average of two runs, Figure 6a), detailed results are

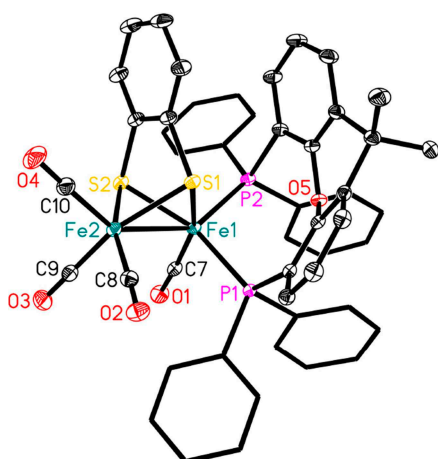


Figure 4. Molecular structure of **6**. Hydrogen atoms and solvent molecules in the crystal structure are omitted for clarity (thermal ellipsoids set to 30% probability).

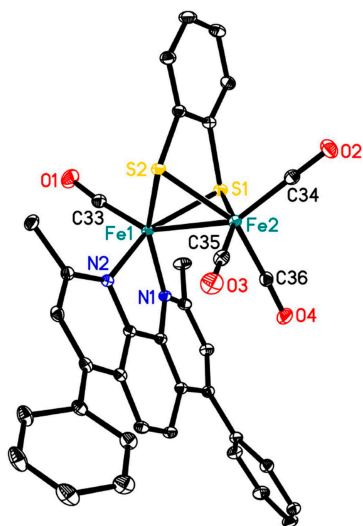


Figure 5. Molecular structure of **7**. Hydrogen atoms are omitted for clarity (thermal ellipsoids set to 30% probability).

given in Table S8 & S9), which seemed fairly reproducible. However, the combination of **6** with the *in situ* formed CuPS resulted once again in poor reproducibility (Figure 6, b)). Similar observations were made for the combination of **7** and the *in situ* generated or the isolated CuPS **2** (Figure 6c) & d)).

Again, this outlines that the observed reproducibility is not a result of the employed pre-catalyst. Interestingly, **7** appeared to yield higher TONs for CO₂ conversion compared to **6**. This might indicate a privileged role of **7** in the formation of an active CO₂ reduction catalyst, which would be similar to the effect of 2,2'-bipyridine in the photocatalytic CO₂ reduction using [Fe₃(CO)₁₂].^[15] However, the poor reproducibility prohibits a conclusive statement based exclusively on these experimental results.

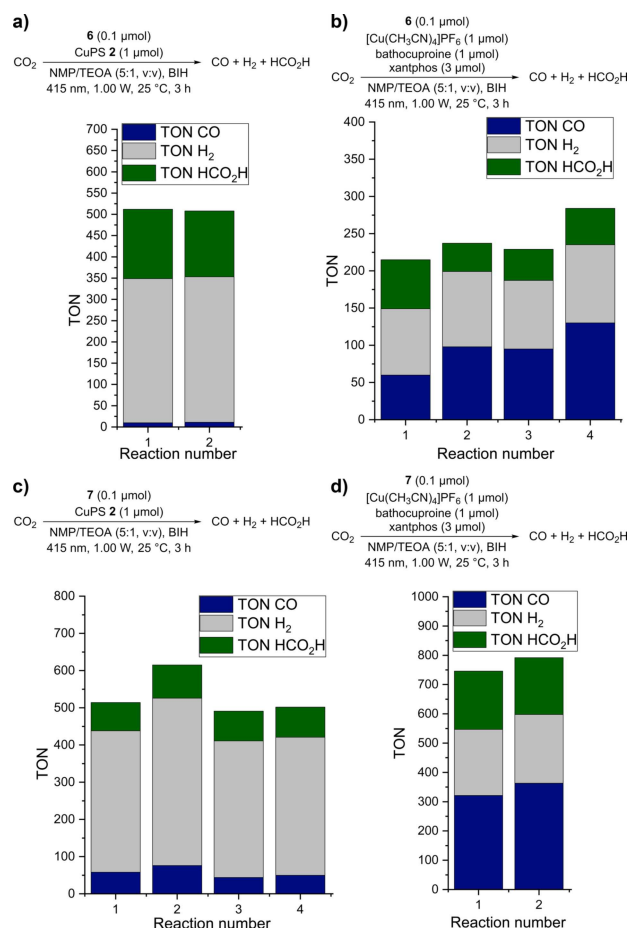


Figure 6. Photocatalytic CO₂ reduction utilizing the [FeFe] complexes **6** and **7** reported herein in combination with *in situ* formed or well-defined CuPS **2**. a) Fe complex **6** in combination with well-defined CuPS **2**. b) Complex **6** in combination with *in situ* generated CuPS **2**. c) Fe complex **7** in combination with well-defined CuPS **2**. d) *In situ* formed CuPS **2** in combination with complex **7**.

Conclusions

In summary, we demonstrated the importance of assessing the reproducibility of a novel catalytic system for photocatalytic reduction of carbon dioxide. Here, significant reproducibility issues arose, arguably due to one of the following factors: 1. specific problems of photocatalysis (i.e. light source, transmission), 2. dynamic catalyst systems (ligand exchange), and 3. gas-liquid reaction system. If one of these or related problems exist, reproducibility issues become especially important.

The results obtained for our photocatalytic CO₂ and proton reduction system based on [FeFe] hydrogenase mimics and a CuPS clearly indicate the unreliability of single experiments. In this specific case it might be partially due to a complex equilibrium between the CuPS and the [FeFe] complexes, suggested by the isolation of two new dinuclear Fe complexes formed *via* photolytic CO dissociation. However, utilization of the isolated complexes in combination with a well-defined CuPS still resulted in low reproducibility. Therefore, an important lesson from this study is that application of isolated

complexes or well-structured nanomaterials does not guarantee reproducibility. Nevertheless, reproducibility constitutes the fundamental base for any research, especially for cutting-edge transformations, such as CO₂ reduction or water oxidation, which mostly rely on the catalytic activity reported in terms of turnover frequencies or TONs and not product yield/conversion as their quality index. In addition, the exact number of conducted reactions and the deviance of those single experiments are seldom stated for novel catalytic transformations.

Hence, we would like to make the following recommendations for scientists working in such fields as catalyst and/or method development:

1. The number of independent experiments should always be stated when reporting a novel catalytic transformation or a new catalyst system. This is especially the case for results obtained from single experiments.

2. Ideally, a minimum of two independent reactions (i.e. not the same stock solutions) on different dates should be performed.

3. Reduction of the catalyst concentration to obtain higher TONs should only be conducted when reproducibility at the reduced catalyst concentrations is still granted. This should be proven by reporting results of single experiments at those reduced concentrations. Ideally, reproducibility should be verified utilizing a minimum of two significantly different catalyst loadings.

We believe that by taking care of the crucial purity of reagents and solvents and following these simple guidelines, a higher standard for entirely reproducible catalytic systems in the fields of water splitting and CO₂ reduction can be achieved. An increased proportion of reproducible results in those fields will not only facilitate improvement of catalysis systems, but also simplify the establishment of catalytic benchmarks.

Experimental Section

Experimental procedures, chromatograms and spectra are provided free of charge in the electronic supporting information. Deposition number CCDC 1855538 (6) and CCDC 1855539 (7) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Acknowledgements

This work was supported by the European Union (H2020-MSCA-ITN-2015) as part of the NoNoMeCat (675020) and by the Danish National Research Foundation as part of the "CADIAC" project. M.M. is grateful to the Fonds der Chemischen Industrie for a Kekulé fellowship.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: CO₂ reduction · Hydrogenase · Iron · Photocatalysis · Reproducibility

- [1] a) M. A. Fox, M. T. Dulay, *Chem. Rev.* **1993**, *93*, 341–357; b) D. Ravelli, D. Dondi, M. Fagnoni, A. Albini, *Chem. Soc. Rev.* **2009**, *38*, 1999–2011.
- [2] a) C. Acar, I. Dincer, G. F. Naterer, *Int. J. Energy Res.* **2016**, *40*, 1449–1473; b) E. S. Andreiadis, M. Chavarot-Kerlidou, M. Fontecave, V. Artero, *Photochem. Photobiol.* **2011**, *87*, 946–964; c) T. Hisatomi, J. Kubota, K. Domen, *Chem. Soc. Rev.* **2014**, *43*, 7520–7535; d) A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2009**, *38*, 253–278; e) K. Maeda, K. Domen, *J. Phys. Chem. Lett.* **2010**, *1*, 2655–2661; f) F. E. Osterloh, *Chem. Soc. Rev.* **2013**, *42*, 2294–2320; g) Z. Wang, C. Li, K. Domen, *Chem. Soc. Rev.* **2019**, *48*, 2109–2125; h) Q. Wang, K. Domen, *Chem. Rev.* **2019**, DOI: 10.1021/acs.chemrev.9b00201.
- [3] a) X. Li, J. Yu, M. Jaroniec, X. Chen, *Chem. Rev.* **2019**, *119*, 3962–4179; b) A. J. Morris, G. J. Meyer, E. Fujita, *Acc. Chem. Res.* **2009**, *42*, 1983–1994; c) B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum, C. P. Kubiak, *Ann. Rev. Phys. Chem.* **2012**, *63*, 541–569; d) S. Berardi, S. Drouet, L. Francas, C. Gimbert-Surinach, M. Guttentag, C. Richmond, T. Stoll, A. Llobet, *Chem. Soc. Rev.* **2014**, *43*, 7501–7519; e) Y. Amao, *Sustain. Energy Fuels* **2018**, *2*, 1928–1950; f) K. C. Christoforidis, P. Fornasiero, *ChemCatChem* **2019**, *11*, 368–382; g) A. Harriman, *Phil. Trans. R. Soc. A* **2013**, *371*, 20110415; h) P. D. Tran, L. H. Wong, J. Barber, J. S. C. Loo, *Energy Environ. Sci.* **2012**, *5*, 5902–5918; i) C. D. Windle, R. N. Perutz, *Coord. Chem. Rev.* **2012**, *256*, 2562–2570; j) Y. Yamazaki, H. Takeda, O. Ishitani, *J. Photochem. Photobiol. C* **2015**, *25*, 106–137.
- [4] a) M. Fagnoni, D. Dondi, D. Ravelli, A. Albini, *Chem. Rev.* **2007**, *107*, 2725–2756; b) A. Maldotti, A. Molinari, R. Amadelli, *Chem. Rev.* **2002**, *102*, 3811–3836; c) N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075–10166; d) M. Oelgemöller, *Chem. Rev.* **2016**, *116*, 9664–9682; e) K. L. Skubi, T. R. Blum, T. P. Yoon, *Chem. Rev.* **2016**, *116*, 10035–10074; f) M. Reckenthäler, A. G. Griesbeck, *Adv. Synth. Catal.* **2013**, *355*, 2727–2744; g) D. M. Schultz, T. P. Yoon, *Science* **2014**, *343*, 1239176; h) C. Huang, X.-B. Li, C.-H. Tung, L.-Z. Wu, *Chem. Eur. J.* **2018**, *24*, 11530–11534.
- [5] a) IPCC, *Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, IPCC, Geneva, Switzerland, **2014**; b) T. Wheeler, J. von Braun, *Science* **2013**, *341*, 508–513; c) S. I. Seneviratne, J. Rogelj, R. Séférian, R. Wartenburger, M. R. Allen, M. Cain, R. J. Millar, K. L. Ebi, N. Ellis, O. Hoegh-Guldberg, A. J. Payne, C.-F. Schleussner, P. Tschakert, R. F. Warren, *Nature* **2018**, *558*, 41–49; d) C. J. Vörösmarty, P. Green, J. Salisbury, R. B. Lammers, *Science* **2000**, *289*, 284–288; e) D. Tilman, C. Balzer, J. Hill, B. L. Befort, *Proc. Natl. Acad. Sci.* **2011**, *108*, 20260–20264; f) C. J. A. Bradshaw, B. W. Brook, *Proc. Natl. Acad. Sci.* **2014**, 201410465.
- [6] C. Lübke, A. Dumrath, H. Neumann, M. Schäffer, R. Zimmermann, M. Beller, R. Kadyrov, *ChemCatChem* **2014**, *6*, 684–688.
- [7] M. Martín-Sómer, C. Pablos, R. van Grieken, J. Marugán, *Appl. Catal. B* **2017**, *215*, 1–7.
- [8] M. Cheng, Y. Yu, X. Zhou, Y. Luo, M. Wang, *ACS Catal.* **2019**, *9*, 768–774.
- [9] a) A. Rosas-Hernandez, C. Steinlechner, H. Junge, M. Beller, *Green Chem.* **2017**, *19*, 2356–2360; b) C. Steinlechner, A. F. Roesel, E. Oberem, A. Pöpcke, N. Rockstroh, F. Gloaguen, S. Lochbrunner, R. Ludwig, A. Spannenberg, H. Junge, R. Francke, M. Beller, *ACS Catal.* **2019**, *9*, 2091–2100.
- [10] C.-H. Lim, S. Ilic, A. Alherz, B. T. Worrell, S. S. Bacon, J. T. Hynes, K. D. Glusac, C. B. Musgrave, *J. Am. Chem. Soc.* **2019**, *141*, 272–280.
- [11] A. J. J. Lennox, S. Fischer, M. Jurrat, S.-P. Luo, N. Rockstroh, H. Junge, R. Ludwig, M. Beller, *Chem. Eur. J.* **2016**, *22*, 1233–1238.
- [12] a) A. Kaeser, M. Mohankumar, J. Mohanraj, F. Monti, M. Holler, J.-J. Cid, O. Moudam, I. Nierengarten, L. Karmazin-Brelot, C. Duhayon, B. Delavaux-Nicot, N. Armaroli, J.-F. Nierengarten, *Inorg. Chem.* **2013**, *52*, 12140–12151; b) S. Fischer, D. Hollmann, S. Tschierlei, M. Karnahl, N. Rockstroh, E. Barsch, P. Schwarzbach, S.-P. Luo, H. Junge, M. Beller, S. Lochbrunner, R. Ludwig, A. Brückner, *ACS Catal.* **2014**, *4*, 1845–1849; c) S.-M. Kuang, D. G. Cuttill, D. R. McMillin, P. E. Fanwick, R. A. Walton, *Inorg. Chem.* **2002**, *41*, 3313–3322; d) H. Junge, N. Rockstroh, S. Fischer, A. Brückner, R. Ludwig, S. Lochbrunner, O. Kühn, M. Beller, *Inorganics* **2017**, *5*, 14.
- [13] For selected examples of [FeFe] hydrogenase mimics bearing bidentate donor ligands, see: a) P.-H. Zhao, Z.-Y. Ma, M.-Y. Hu, J. He, Y.-Z. Wang, X.-B. Jing, H.-Y. Chen, Z. Wang, Y.-L. Li, *Organometallics* **2018**, *37*, 1280–

1290; b) M. Cheng, M. Wang, D. Zheng, L. Sun, *Dalton Trans.* **2016**, 45, 17687–17696; c) M. Karnahl, S. Tschierlei, O. F. Erdem, S. Pullen, M.-P. Santoni, E. J. Reijerse, W. Lubitz, S. Ott, *Dalton Trans.* **2012**, 41, 12468–12477; d) S. Roy, T. L. Groy, A. K. Jones, *Dalton Trans.* **2013**, 42, 3843–3853; e) S. Roy, J. A. Laureanti, T. L. Groy, A. K. Jones, *Eur. J. Inorg. Chem.* **2017**, 2017, 2942–2950; f) P.-Y. Orain, J.-F. Capon, N. Kervarec, F. Gloaguen, F. Pétillon, R. Pichon, P. Schollhammer, J. Talarmin, *Dalton Trans.* **2007**, 3754–3756; g) W. Wang, T. B. Rauchfuss, C. E. Moore, A. L. Rheingold, L. De Gioia, G. Zampella, *Chem. Eur. J.* **2013**, 19, 15476–15479; h) L.-C. Song, W. Gao, X. Luo, Z.-X. Wang, X.-J. Sun, H.-B. Song, *Organometallics* **2012**, 31, 3324–3332; i) S. Ezzaher, J.-F. Capon, F. Gloaguen, F. Y. Pétillon, P. Schollhammer, J. Talarmin, *Inorg. Chem.* **2007**, 46, 9863–9872; j) S. Ezzaher, J.-F. Capon, F. Gloaguen, F. Y. Pétillon, P. Schollhammer, J. Talarmin, R. Pichon, N. Kervarec, *Inorg. Chem.* **2007**, 46, 3426–3428; k) S. Munery, J.-F. Capon, L. De Gioia, C. Elleouet, C. Greco, F. Y. Pétillon, P. Schollhammer, J. Talarmin, G. Zampella, *Chem. Eur. J.* **2013**, 19, 15458–15461; l) M. E. Carroll, B. E.

Barton, T. B. Rauchfuss, P. J. Carroll, *J. Am. Chem. Soc.* **2012**, 134, 18843–18852.

- [14] a) J. L. Bingaman, C. L. Kohnhorst, G. A. Van Meter, B. A. McElroy, E. A. Rakowski, B. W. Caplins, T. A. Gutowski, C. J. Stromberg, C. E. Webster, E. J. Heilweil, *J. Phys. Chem. A* **2012**, 116, 7261–7271; b) B. W. Caplins, J. P. Lomont, S. C. Nguyen, C. B. Harris, *J. Phys. Chem. A* **2014**, 118, 11529–11540.
- [15] P. G. Alsabeh, A. Rosas-Hernández, E. Barsch, H. Junge, R. Ludwig, M. Beller, *Catal. Sci. Technol.* **2016**, 6, 3623–3630.

Manuscript received: September 5, 2019

Revised manuscript received: October 25, 2019

Accepted manuscript online: October 28, 2019

Version of record online: December 12, 2019
