

Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

COMMUNICATION

Photocatalytic hydrogen evolution by Cu(II) complexes

Junfei Wang,^{a,b} Chao Li,^a Qianxiong Zhou,^a Weibo Wang,^a Yuanjun Hou,^{*a} Baowen Zhang,^a Xuesong Wang^{*a}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

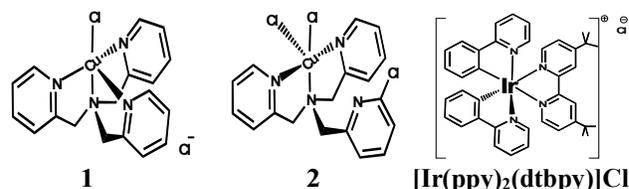
www.rsc.org/

[Cu(TMPA)Cl]Cl (1) and [Cu(Cl-TMPA)Cl₂] (2) exhibited efficient photocatalytic H₂ evolution with TON of 6108 and 10014 (6 h), respectively, in CH₃CN/H₂O solution (9:1, v/v) containing an Ir complex as photosensitizer and triethylamine as sacrificial reductant, representing the first type of photocatalytic Cu complex-based water reduction catalysts.

Hydrogen production via water splitting either electrocatalytically or photocatalytically is drawing growing attention as one of the ultimate solutions for both energy crisis and climate changes,¹ and the development of efficient, robust, and low cost water reduction catalysts (WRCs) has been the focus of research over the past decade. In this context, a lot of Fe,² Co,³ and Ni-based⁴ complexes have been scrutinized as the photocatalytic or electrocatalytic WRCs. Cu is also a kind of cheap, earth-abundant and redox-active first row transition metal, and some copper complexes have been explored as CO₂ reduction catalyst,⁵ as water oxidation catalyst,⁶ and as photosensitizer (PS) in photocatalytic H₂ generation.⁷ Surprisingly, only very recently, Wang and coworkers reported the first Cu complex-based electrocatalytic WRC,⁸ followed by Du and Cao who presented two more examples.⁹ To the best of our knowledge, Cu-based photocatalytic WRCs are still lacking up to now.

For the first row transition metal-based WRCs, metal hydride is generally believed to be a key intermediate, by which H₂ generation may be achieved via either protonolysis or bimetallic reaction.²⁻⁴ The introduction of proton relays, *e.g.* amine groups, around the metal center has proven an effective strategy to facilitate catalytic H₂ evolution, just like the case of natural [Fe–Fe]-hydrogenase enzymes.¹⁰

Experimental results and theoretical calculations revealed that the highly efficient H₂ evolution activity of the first Cu-based electrocatalytic WRC, [(bztppen)Cu(II)](BF₄)₂ (bztppen = *N*-benzyl-*N,N',N'*-tris(pyridin-2-ylmethyl)ethylenediamine), results from the dissociation and protonation of one pyridyl arm of the pentadentate bztppen ligand upon Cu(II) reduction to Cu(I), which on one hand opens a site for Cu-hydride formation, and on the other hand provides a proton relay in close proximity to the Cu center.⁸ Some polydentate ligand-based Ni and Co complexes exhibited similar behavior in catalytic H₂ generation.^{11, 3b,c,e,g} It occurs to us that a tetradentate ligand may be favorable for Cu-based WRCs since it allows for a more labile monodentate ligand, such as Cl⁻, to coordinate. Additionally, the dissociation of one pyridyl arm of a polypyridine ligand may be facilitated by anchoring an electron-withdrawing group to reduce its coordination capacity. Based on these assumptions, we herein examined for the first time the photocatalytic H₂ production behaviors of two Cu(II) complexes, [Cu(TMPA)Cl]Cl (**1**) and [Cu(Cl-TMPA)Cl₂] (**2**) (TMPA = tris(2-pyridyl)methylamine and Cl-TMPA = 1-(6-chloropyridin-2-yl)methyl-*N,N*-bis(pyridin-2ylmethyl)methanamine, Scheme 1). It was found that **2** is far efficient than **1** in photocatalytic H₂ production, as the result of a more labile Cl ligand in the first coordination sphere together with a dangling Cl-substituted pyridyl unit in the second coordination sphere. [Cu(TMPA)Cl]⁺ is a known ion,¹² however, its photocatalytic and electrocatalytic H₂ production properties have not been studied yet. Following the reported synthetic procedures,¹³ **1** and **2** were prepared and the high-resolution mass



Scheme 1. Chemical structures of **1**, **2** and [Ir(ppy)₂(dtbbpy)]Cl.

^a Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China. E-mail: xswang@mail.lpc.ac.cn, yuanjunhou@yahoo.com.

^b Graduate School of Chinese Academy of Sciences, Beijing 100049, P. R. China.

Electronic Supplementary Information (ESI) available: Materials, experimental methods, Synthetic; high-resolution ESI MS, ¹H NMR spectra and UV-visible absorption spectrum of **1** and **2**, Optimization of the photocatalytic H₂ production conditions, Cyclic voltammograms, Luminescence quenching, Crystal data. CCDC 1414566. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x

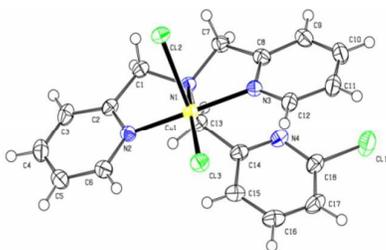


Figure 1. Crystal structure of **2** (solvent molecules are omitted for clarity and thermal ellipsoids set at 50 % probability).

spectroscopy (HR-MS), ^1H NMR and UV-visible absorption spectra, and elemental analysis data are in good agreement with the proposed composition (Figure S1-S3). The single crystals of **2** suitable for X-ray diffraction analysis were obtained by slowly diffusing Et_2O into a CH_3CN solution of **2**. It is worth noting that the coordination mode of Cl-TMPA has a dramatic change with respect to TMPA. While TMPA serves as a tetradentate ligand to support Cu(II) in a distorted trigonal-bipyramidal geometry,¹² Cl-TMPA acts as a tridentate ligand to coordinate Cu(II) with two chloride ions in a distorted square-pyramidal manner, leaving the Cl-substituted pyridyl group in the second coordination sphere (Figure 1 and Table S1 and S2). Particularly, the bond length of Cu-Cl(2) (2.5751 Å) in **2** is much longer than that of Cu-Cl(3) (2.2533 Å) in **2** and that of Cu-Cl (2.233 Å)¹² in **1**, hinting at its more labile character. ESI-MS data seem support this judgment. While a strong m/z signal at 388.0499 may be attributed to $[\text{Cu}(\text{TMPA})\text{Cl}]^+$ for **1**, only $[\text{Cu}(\text{Cl-TMPA})]^+$ and $[\text{Cu}(\text{Cl-TMPA}) + \text{COOH}]^+$ with $m/z = 387.0421$ and 432.0398 were observed for **2** (Figure S1). Such a feature of **2** might favor the Cu-hydride formation and therefore H_2 evolution.

The photocatalytic H_2 production activities of **1** and **2** were investigated in a multi-component artificial photosynthesis (AP) system, using $[\text{Ir}(\text{ppy})_2(\text{dtbpy})]\text{Cl}$ (ppy = 2-phenylpyridine, dtbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine, Scheme 1) as PS and triethylamine (TEA) as sacrificial reductant (SR). Under optimal conditions ([PS] = 0.2 mM, [**1/2**] = 1 μM , [TEA] = 0.45 M in Ar-saturated $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (9:1, v/v), Figure S4-S8), both **1** and **2** can photocatalyze H_2 production efficiently (Figure 2). Recently, Zhao, Webster and coworkers reported a highly efficient AP system, presenting a TON of 4400 at 0.5 μM of a Co-based WRC.^{3h} The absence of any component led to failure of H_2

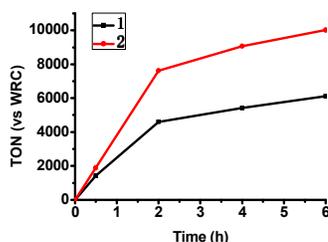


Figure 2. Photocatalytic H_2 production profiles of the AP systems containing 0.2 mM Ir-based PS, 1 μM Cu-based WRC and 0.45 M TEA in Ar-saturated $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (9:1).

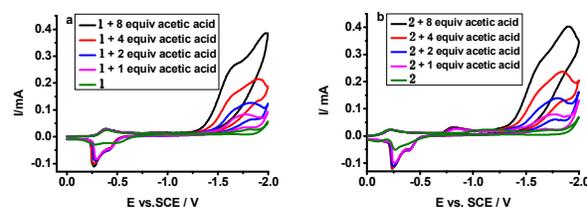


Figure 3. Cyclic voltammograms of 1 mM of **1** (a) and **2** (b) in Ar-saturated CH_3CN in the presence of varied concentrations (0, 1, 2, 4, 8 mM) of acetic acid. Conditions: 0.1 M $n\text{-Bu}_4\text{NPF}_6$, scan rate 100 mV/s.

production. Upon 6 h of irradiation, the turnover number (TON) reached 6108 for **1** and 10014 for **2**, and the photocatalytic H_2 evolution quantum yields were estimated to be 3.4% and 5.6%, for **1** and **2**, respectively. **1** and **2** represent the first class of Cu-based photocatalytic WRCs. The much higher activity of **2** with respect to **1** encouraged us to elucidate the underlying mechanism.

We at first compared the electrochemical properties of **1** and **2** in Ar-saturated CH_3CN . As shown in Figure 3, **1** experienced two irreversible redox processes at -0.40 V and -1.81 V (vs. SCE), while the former may be assigned to $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$, the later may result from either $\text{Cu}^{\text{I}}/\text{Cu}^0$ or the mixture of $\text{Cu}^{\text{I}}/\text{Cu}^0$ and $\text{TMPA}/\text{TMPA}^-$ (see Figure S9 and the corresponding discussion in ESI). Similar electrochemical processes were also found for **2** at -0.21 V and -1.72 V (Figure S9). Different to **1**, **2** displayed a broad electrochemical wave with an onset of -0.9 V between the redox potentials of $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ and $\text{Cu}^{\text{I}}/\text{Cu}^0$, assignable to the reduction of the dangling Cl-substituted pyridyl unit. This assignment is approved by the fact that 6-chloro-2-picoline has a similar redox process at the same potential window, as shown in Figure S10. Upon addition of acetic acid, a significant catalytic current was observed over the potential of $\text{Cu}^{\text{I}}/\text{Cu}^0$ in both cases, suggesting that the Cu hydride formation and then catalytic H_2 evolution happened in the Cu^0 state of **1** and **2**. Without **1** or **2**, the reduction current within the examined region may be neglected (Figures S11), confirming the origin of the electrocatalytic process. In the presence of acetic acid, the reduction wave of the Cl-substituted pyridyl unit shifted anodically to -0.82 V, as the result of the protonation and in line with the redox property of the protonated 6-chloro-2-picoline (Figure S10).

To better understand the electrochemical behaviors of **1** and **2**, we conducted cyclic voltammetry experiments within a narrow potential region (0 ~ -1.0 V) to forbid the access of the Cu^0 states. When potential scans of different rates were performed between 0 and -0.8 V, the redox processes belonging to $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ of **1** and **2** were observed as expected (Figure S12). However, the processes became electrochemically reversible in all cases, ruling out the loss of the Cl ligand from the Cu^{I} state of **1** and **2**. Once the potential scans were extended to -1.0 V where the reduction of the Cl-substituted pyridyl unit may occur, remarkable disparity emerged between **1** and **2**. At the low scan rates of 50 and 100 mV/s, **2** showed an irreversible $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ redox process (Figure 4a). Notably, this redox process became reversible at the high scan rates of 300 and 400 mV/s. This finding implies an EC process, which may be attributed to the dissociation of a Cl ligand from the Cu center following the reduction of the Cl-substituted pyridyl unit. Thus, the new oxidation peak

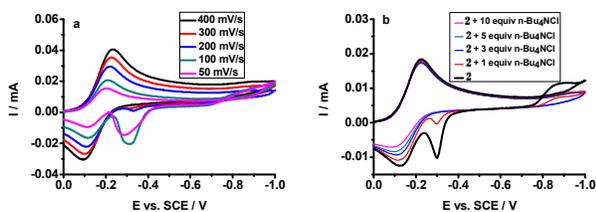


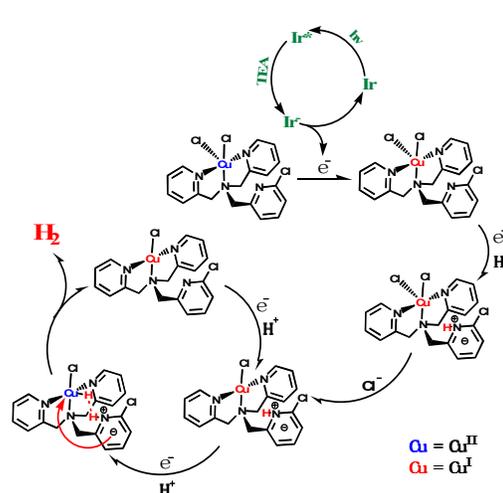
Figure 4. (a) Cyclic voltammograms of **2** (1 mM) in Ar-saturated CH₃CN (a) at different scan rates and (b) in the presence of varied concentrations of *n*-Bu₄NCl at scan rate of 100 mV/s.

centered at -0.3 V is most likely from the Cu^I species that has lost a Cl ligand. It is expected that the presence of free Cl⁻ ion in the solution may restrict the dissociation of the Cl ligand.¹⁴ Upon addition of 3 equiv of *n*-Bu₄NCl into the electrolyte, the Cu^{II}/Cu^I redox process of **2** changed from irreversible to reversible (Figure 4b) and the oxidation peak at -0.3 V disappeared, supporting our assignment. In sharp contrast, **1** displayed a reversible Cu^{II}/Cu^I redox process even at the low scan rate of 50 mV/s (Figure S13), precluding the Cl ligand dissociation in this condition. The more labile character of the Cl ligand of **2** is in good agreement with its crystal data, where one Cu-Cl bond is much longer than that of **1**, and correlates very well with its higher photocatalytic H₂ evolution activity because ligand dissociation is the prerequisite for metal hydride formation and catalytic H₂ evolution. What more interesting is that the Cl ligand dissociation is triggered by the reduction of the Cl-substituted pyridyl unit. The protonation of this dangling group shifts its reduction to a less negative potential, and therefore may promote the Cl ligand dissociation, as evidenced by the markedly intensified oxidation peak from the Cu^I species that has lost a Cl ligand (Figure S14).

It is worth noting that no oxidation peak associated with the reduction wave of the Cl-substituted pyridinium unit can be found in Figure 3b. A possible explanation is that this reduced group has taken part in catalytic H₂ evolution by delivering an electron and a proton to the Cu-hydride center (Scheme 2). Recently, ligand reduction was also found to play an important role in some electrocatalytic WRCs.¹⁵

We also carried out controlled potential electrolysis experiments at -1.8 V vs. SCE for 2 h. The Faradaic efficiencies for H₂ production catalyzed by **1** and **2** were measured to be 95% and 96%, respectively. During the electrolysis, the current densities remained unchanged in both cases, hinting at the stability of the electrocatalytic systems. After electrolysis, the solution color changed from blue to yellow, and the characteristic NIR absorption of Cu(II) species faded remarkably (Figure S15), suggesting that the complexes were mainly in the Cu(I) state.^{8a}

In photocatalytic H₂ evolution, WRC may accept electrons either directly from the excited PS or the reduced PS, depending on the quenching efficiencies of the excited PS by WRC and by SR. In our cases, **1**, **2** and TEA can quench the luminescence of [Ir(ppy)₂(dtbpy)]Cl effectively (Figure S16-18), with bimolecular quenching constants of $5.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for **1**, $5.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for **2** and $4.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ for TEA, respectively. Though the quenching rate constants of **1** and **2** are 2 orders of magnitude larger than that of TEA, the reductive quenching is predominant, because the concentration of TEA (0.45 M) is 5 orders of magnitude higher than that of **1** or **2** (1 μM).



Scheme 2. A possible photocatalytic H₂ evolution mechanism of **2**.

Based on the above mentioned results and discussion, we put forth a possible photocatalytic H₂ evolution mechanism for **2**. The excited PS extracts 1e from TEA at first and donates 1e to the Cu^{II} center. Then, the protonated Cl-substituted pyridyl unit accepts 1e to initiate the dissociation of the Cl ligand at the apical position of the square-pyramid, which has a longer Cu-Cl bond length. The Cl-substituted pyridyl unit could also accept 1e at first and then undertake protonation, a more reasonable route in basic solutions. After that, the Cu^I species may accept 1e and a proton to form the Cu^I-hydride key intermediate. Finally, the reduced Cl-substituted pyridinium unit donates a proton and an electron to the Cu^I-hydride center to lead to H₂ evolution and the recovery of the Cu^I state, which may enter a new cycle of H₂ evolution. Compared to **1**, **2** has a more labile Cl ligand and a dangling Cl-substituted pyridyl unit, both contribute to its higher photocatalytic activity.

In summary, we herein present, for the first time, two Cu-based photocatalytic WRCs, **1** and **2**. Different to TMPA, Cl-TMPA coordinates Cu(II) as a tridentate ligand, making the Cl-substituted pyridyl branch dangling in the second coordination sphere to play the triple roles of monodentate ligand dissociation trigger, proton relay and electron relay. This unique feature, together with a labile Cl ligand with longer Cu-Cl bond length, renders **2** a remarkably enhanced photocatalytic activity with respect to **1**. Such a mechanism may provide guidelines for developing more efficient Cu-based WRCs.

This work was financially supported by the Ministry of Science and Technology (2013CB933801) and NSFC (21390400, 21172228, 21273259, 21571181, 21301182).

Notes and references

- (a) T. Hisatomi, J. Kubota and K. Domen, *Chem. Soc. Rev.*, 2014, **43**, 7520-7535; (b) S. Berardi, S. Drouet, L. Francàs, C. Gimbert-Suriñach, M. Guttentag, C. Richmond, T. Stoll and A. Llobet, *Chem. Soc. Rev.*, 2014, **43**, 7501-7519.

- 2 (a) T. Liu, X. Wang, C. Hoffmann, D. L. DuBois and R. M. Bullock, *Angew. Chem. Int. Ed.*, 2014, **53**, 5300-5304; (b) S. Pullen, H. Fei, A. Orthaber, S. M. Cohen and S. Ott, *J. Am. Chem. Soc.*, 2013, **135**, 16997-17003; (c) W. Wang, M. J. Nilges, T. B. Rauchfuss and M. Stein, *J. Am. Chem. Soc.*, 2013, **135**, 3633-3639; (d) J. M. Gardner, M. Beyler, M. Karnahl, S. Tschierlei, S. Ott and L. Hammarström, *J. Am. Chem. Soc.*, 2012, **134**, 19322-19325; (e) B. D. Yuhas, A. L. Smeigh, A. P. Douvalis, M. R. Wasielewski and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2012, **134**, 10353-10356; (f) M. J. Rose, H. B. Gray and J. R. Winkler, *J. Am. Chem. Soc.*, 2012, **134**, 8310-8313; (g) F. Wang, W.-G. Wang, X.-J. Wang, H.-Y. Wang, C.-H. Tung and L.-Z. Wu, *Angew. Chem. Int. Ed.*, 2011, **50**, 3193-3197.
- 3 (a) A. J. Clough, J. W. Yoo, M. H. Mecklenburg and S. C. Marinescu, *J. Am. Chem. Soc.*, 2015, **137**, 118-121; (b) D. Z. Zee, T. Chantarojsiri, J. R. Long and C. J. Chang, *Acc. Chem. Res.*, 2015, **48**, 2027-2036; (c) D. Basu, S. Mazumder, X. Shi, H. Baydoun, J. Niklas, O. Poluektov, H. B. Schlegel and C. N. Verani, *Angew. Chem. Int. Ed.*, 2015, **54**, 2105-2110; (d) C. Gimbert-Suriñach, J. Alberro, T. Stoll, J. Fortage, M.-N. Collomb, A. Deronzier, E. Palomares and A. Lobet, *J. Am. Chem. Soc.*, 2014, **136**, 7655-7661; (e) Lianpeng Tong, Ruifa Zong, and Randolph P. Thummel, *J. Am. Chem. Soc.*, 2014, **136**, 4881-4884; (f) V. Atero and M. Fontecave, *Chem. Soc. Rev.*, 2013, **42**, 2338-2356; (g) W. T. Eckenhoff and R. Eisenberg, *Dalton Trans.*, 2012, **41**, 13004-13021; (h) W. M. Singh, T. Baine, S. Kudo, S. Tian, X. A. N. Ma, H. Zhou, N. J. DeYonker, T. Pham, J. C. Bollinger, D. L. Baker, B. Yan, C. E. Webster and X. Zhao, *Angew. Chem. Int. Ed.*, 2012, **51**, 5941-5944; (i) V. Artero, M. Chavarot-Kerlidou and M. Fontecave, *Angew. Chem. Int. Ed.*, 2011, **50**, 7238-7266.
- 4 (a) B. C. M. Martindale, G. A. M. Hutton, C. A. Caputo and E. Reisner, *J. Am. Chem. Soc.*, 2015, **137**, 6018-6025; (b) L. Gan, T. L. Groy, P. Tarakeshwar, S. K. S. Mazinani, J. Shearer, V. Mujica and A. K. Jones, *J. Am. Chem. Soc.*, 2015, **137**, 1109-1115; (c) A. S. Weingarten, R. V. Kazantsev, L. C. Palmer, M. McClendon, A. R. Koltonow, A. P. S. Samuel, D. J. Kiebal, M. R. Wasielewski and S. I. Stupp, *Nature Chem.*, 2014, **6**, 964-970; (d) J. Hou, M. Fang, A. J. P. Cardenas, W. J. Shaw, M. L. Helm, R. M. Bullock, J. A. S. Roberts and M. O'Hagan, *Energy Environ. Sci.*, 2014, **7**, 4013-4017; (e) M. A. Gross, A. Reynal, J. R. Durrant and Erwin Reisner, *J. Am. Chem. Soc.*, 2014, **136**, 356-366; (f) H. Lv, W. Guo, K. Wu, Z. Chen, J. Bacsá, D. G. Musaev, Y. V. Geletii, S. M. Lauinger, T. Lian and C. L. Hill, *J. Am. Chem. Soc.*, 2014, **136**, 14015-14018; (g) D. C. Powers, B. L. Anderson and D. G. Nocera, *J. Am. Chem. Soc.*, 2013, **135**, 18876-18883; (h) Z. Han, L. Shen, W. W. Brennessel, P. L. Holland and R. Eisenberg, *J. Am. Chem. Soc.*, 2013, **135**, 14659-14669 (i) M. L. Helm, M. P. Stewart, R. M. Bullock, M. R. DuBois, D. L. DuBois, *Science*, 2011, **333**, 863-866.
- 5 R. Angamuthu, P. Byers, M. Lutz, A. L. Spek and E. Bouwman, *Science*, 2010, **327**, 313-315.
- 6 (a) T. Zhang, C. Wang, S. Liu, J. Wang and W. Lin, *J. Am. Chem. Soc.*, 2014, **136**, 273-281; (b) M. Zhang, Z. Chen, P. Kang and T. J. Meyer, *J. Am. Chem. Soc.*, 2013, **135**, 2048-2051; (c) Z. Chen and T. J. Meyer, *Angew. Chem. Int. Ed.*, 2013, **52**, 700-703; *Angew. Chem.*, 2013, **125**, 728-731; (d) S. M. Barnett, K. I. Goldberg and J. M. Mayer, *Nat. Chem.*, 2012, **4**, 498-502.
- 7 E. Mejía, S.-P. Luo, M. Karnahl, A. Friedrich, S. Tschierlei, A.-E. Surkus, H. Junge, S. Gladiali, S. Lochbrunner and M. Beller, *Chem. Eur. J.*, 2013, **19**, 15972-15978.
- 8 (a) P. Zhang, M. Wang, Y. Yang, T. Yao and L. Sun, *Angew. Chem. Int. Ed.*, 2014, **53**, 13803-13807; (b) R. Liao, M. Wang, L. Sun and E. M. Siegbahn, *Dalton Trans.*, 2015, **44**, 9736-9739.
- 9 (a) X. Liu, S. Cui, Z. Sun and P. Du, *Chem. Commun.*, 2015, **51**, 12954-12957; (b) H. Lei, H. Fang, Y. Han, W. Lai, X. Fu, and R. Cao, *ACS Catal.*, 2015, **5**, 5145-5153.
- 10 (a) V. Artero and M. Fontecave, *Coord. Chem. Rev.*, 2005, **249**, 1518-1535; (b) J. C. Fontecilla-Camps, A. Volbeda, C. Cavazza and Y. Nicolet, *Chem. Rev.*, 2007, **107**, 4273-4303; (c) A. Volbeda, M.-H. Charon, C. Piras, E. C. Hatchikian, M. Frey and J. C. Fontecilla-Camps, *Nature*, 1995, **373**, 580-587; (d) F. A. Armstrong and J. C. Fontecilla-Camps, *Science*, 2008, **321**, 498-499.
- 11 (a) J.-F. Wang, C. Li, Q.-X. Zhou, W.-B. Wang, Y.-J. Hou, B.-W. Zhang and X.-S. Wang, *Dalton Trans.*, 2015, **44**, 17704-17711; (b) P. Zhang, M. Wang, Y. Yang, D. Zheng, K. Han and L. Sun, *Chem. Commun.*, 2014, **50**, 14153-14156; (c) J.-F. Xie, Q.-X. Zhou, C. Li, W.-B. Wang, Y.-J. Hou, B.-W. Zhang and X.-S. Wang, *Chem. Commun.*, 2014, **50**, 6520-6522; (d) V. Sara Thoi and C. J. Chang, *Chem. Commun.*, 2011, **47**, 6578-6580; (e) Y. Sun, J. Sun, J. R. Long, P. Yang and C. J. Chang, *Chem. Sci.*, 2013, **4**, 118-124.
- 12 K. D. Karlin, J. C. Hayes, S. Juen, J. P. Hutchinson and J. Zubieta, *Inorg. Chem.*, 1982, **21**, 4106-4108.
- 13 (a) S. Kim, C. Saracini, M. A. Siegler, N. Drichko and K. D. Karlin, *Inorg. Chem.*, 2012, **51**, 12603-12605; (b) D. Maiti, A. A. N. Sarjeant and K. D. Karlin, *J. Am. Chem. Soc.*, 2007, **129**, 6720-6721.
- 14 M. Elvington, J. Brown, S. M. Arachchige and K. J. Brewer, *J. Am. Chem. Soc.*, 2007, **129**, 10644-10645.
- 15 (a) G. F. Manbeck, T. Canterbury, R. Zhou, S. King, G. Nam and K. J. Brewer, *Inorg. Chem.*, 2015, **54**, 8148-8157; (b) J. W. Jurs, R. S. Khnayzer, J. A. Panetier, K. A. El Roz, E. M. Nichols, M. Head-Gordon, J. R. Long, F. N. Castellano and C. J. Chang, *Chem. Sci.*, 2015, **6**, 4954-4972; (c) D. Z. Zee, T. Chantarojsiri, J. R. Long and C. J. Chang, *Acc. Chem. Res.*, 2015, **48**, 2027-2036; (d) A. Z. Haddad, D. Kumar, K. O. Sampson, A. M. Matzner, M. S. Mashuta and C. A. Grapperhaus, *J. Am. Chem. Soc.*, 2015, **137**, 9238-9241.