# This is a JAM - Just Accepted Manuscript

#### Journal of Porphyrins and Phthalocyanines

Article Title:	First-Row Transition Metal Porphyrins for Electrocatalytic Hydrogen Evolution
Author(s):	Haitao Lei, Yabo Wang, Qingxin Zhang, Rui Cao
DOI:	10.1142/S1088424620500157

#### To be cited as:

Haitao Lei, Yabo Wang, Qingxin Zhang, Rui Cao, First-Row Transition Metal Porphyrins for Electrocatalytic Hydrogen Evolution, *Journal of Porphyrins and Phthalocyanines*, doi: 10.1142/S1088424620500157

Received: 29 January 2020 Accepted: 21 March 2020

This is the accepted and unedited version of a newly accepted manuscript after peer-review evaluation. No copyediting, typesetting or proof correction has been performed, so it is by no means the definitive final version of the manuscript. This format allows a rapid display online with a DOI, which means that the manuscript is already citable in a sustainable manner.

It has been uploaded in advance for the benefit of our customers. The manuscript will be copyedited, typeset and proofread before it is released in the final form. As a result, the published copy may differ from the unedited version. Readers should obtain the final version from the above link when it is published. The authors are responsible for the content of this Accepted Article.

When the corrected proof will be available, the manuscript will move to the Online Ready page of the website. The definitive version with page numbers will be available after publication of the issue in which it takes place.

Thanks to this free and optional opportunity, the newly accepted manuscript can be quickly shared with the scientific community.

In no case, WorldScientific can be held responsible of mistakes in the content of use of this Just Accepted Manuscript.

# First-Row Transition Metal Porphyrins for Electrocatalytic Hydrogen Evolution

Haitao Lei, Yabo Wang, Qingxin Zhang, and Rui Cao\*

Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710119, China.

E-mail: ruicao@ruc.edu.cn

#### Abstract

A series of first-row transition metal complexes of tetrakis(pentafluorophenyl)porphyrin (1), denoted as 1-M (M = Mn, Fe, Co, Ni, Cu, and Zn), were synthesized and examined as electrocatalysts for the hydrogen evolution reaction (HER). All these transition metal porphyrins were shown to be active for HER in acetonitrile using trifluoroacetic acid (TFA) as the proton source. The molecular nature and the stability of these metal porphyrins by functioning as HER catalysts were confirmed, and all catalysts gave Faradaic efficiency of >97% for H<sub>2</sub> generation during bulk electrolysis. Importantly, by using 1-Cu the most efficient one among this series of metal porphyrin catalysts. This TOF value also represents one of the highest values reported in the literature. In addition, electrochemical analysis demonstrated that catalytic HER mechanisms with these 1-M complexes are different. These results show that with the same porphyrin ligand, the change of metal ions will have significant impacts on both catalytic efficiency and mechanism. This work for the first time provides direct comparison of electrocatalytic HER features of transition metal complexes of tetrakis(pentafluorophenyl)porphyrin under identical conditions, and will be valuable for future design and development of more efficient HER electrocatalysts of this series.

Keyword: metal porphyrin, hydrogen evolution, electrocatalysis, molecular catalysis, energy conversion

### Introduction

Electrocatalytic HER is at the heart of the hydrogen-based new energy conversion and storage schemes [1,2]. With the production of hydrogen, it provides an ideal approach to convert electric energy into chemical energy [3-5]. Considering that electric energy can be generated from renewable but intermittent energy sources, such as solar, wind and hydro power, electrocatalytically produced H<sub>2</sub> can be regarded as a clean, environmentally benign, and sustainable energy source [6,7]. Hydrogenases, which are a class of nature metalloenzymes, can efficiently catalyze the reversible uptake and production of H<sub>2</sub> [8,9]. However, the difficulty in the large-scale synthesis of hydrogenases and their deactivation under O<sub>2</sub> atmosphere severely limits their practical applications [10-12]. Platinum and its alloys are very active for catalytic HER, but the very high cost and low natural abundance of this noble metal also restrict its large-scale uses [13,14]. As a consequence, developing highly efficient and robust HER electrocatalysts, which are cheap and are made of earth-abundant transition metal elements, have attracted increasing interests in the community [15].

In the past decades, tremendous efforts have resulted in the identification of a variety of molecular complexes consisting of first-row transition metals, including Mn [16,17], Fe [18-21], Co [22-24], Ni [25,26], Cu [27,28], and Zn [29,30], as active HER electrocatalysts. Among these catalysts, metal porphyrins and metal corroles have received increasing attention because of their high efficiency by functioning as HER catalysts [31-34]. In addition to their remarkable performance, choosing metal porphyrins and metal corroles as catalysts is largely based on the following reasons. First, almost all transition metal and main group elements can be incorporated into the porphyrin and corrole macrocycles through the binding with the four N atoms [3,35-37]. The resulted four-coordinated structure is rigid and stable even in the presence of acids and bases in organic and aqueous solutions without irradiation. This square-planar coordination geometry can afford two open axial sites for other ligands and substrates, which is ideal for substrate binding and activation. Second, dianionic porphyrin and trianionic corrole macrocycles are negatively charged ligands [38,39]. This feature enables them to be able to efficiently stabilize high-valent metal ions, and as a consequence, porphyrin and corrole ligands can offer low-valent metal ions with strong

reducing powers, which is favored for HER. Third, porphyrin and corrole ligands are redoxnoninnocent [40,41]. Therefore, they can participate in multielectron catalytic processes, can significantly enrich the redox chemistry of metal complexes, and can make complexes of redoxinactive metal ions, such as Ga, to be highly active for redox catalysis [31]. Fourth, metal porphyrins and metal corroles have strong and characteristic features in electronic absorption spectroscopy, which will benefit the detection and identification of reaction intermediates in homogeneous solutions for mechanistic studies [42,43]. Fifth, the systematical modification of porphyrin and corrole macrocycles is accessible at both the *meso-* and  $\beta$ -positions to introduce a variety of functional groups [44-46]. This feature makes metal porphyrins and metal corroles excellent platforms for the investigation of the structure-function relationship, and makes them readily to be assembled with other molecular architectures and/or grafted onto materials. On the basis of these considerations, we have focused on investigating the catalytic features of metal porphyrins and metal corroles for energy-related small molecule activation reactions, including hydrogen and oxygen evolution [25,28,31-33,47-57], oxygen reduction [58-64], and carbon dioxide reduction reactions [65,66].

Recently, Co porphyrin [67-69] and Ni porphyrin [25,70] complexes have been shown to be efficient and robust for HER by Nocera and by us. In order to examine the catalytic HER features of other first-row transition metal complexes of tetrakis(pentafluorophenyl)porphyrin and also to make a direct comparison of these complexes for HER under similar conditions, we herein report the synthesis and electrocatalytic HER performance of **1-M** ( $\mathbf{M} = \mathbf{Mn}$ , **Fe**, **Co**, **Ni**, **Cu**, and **Zn**). Our results show that all these transition metal porphyrins are active for HER in acetonitrile using TFA as the proton source, and their molecular nature and stability by functioning as HER catalysts are confirmed. Among these complexes, **1-Cu** is the most efficient one by achieving a remarkably high TOF of 48500 s<sup>-1</sup>. This value also represents one of the highest TOF values reported in the literature. Although thorough analysis of the catalytic performance of these **1-M** complexes is

challenging because their catalytic mechanisms are different, this work will provide new insights into the future design and development of more efficient HER electrocatalysts.

#### **Results and discussion**

#### Synthesis and characterization

In our experiment, ligand 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin was synthesized according to the literature procedure [71]. First-row transition metal porphyrins, 1-Mn [72], 1-Fe [73], 1-Co [74], 1-Ni [25], 1-Cu [27], and 1-Zn [75] were prepared by following procedures reported previously. The identity and purity of 1-Ni and 1-Zn were confirmed by using both <sup>1</sup>H nuclear magnetic resonance spectroscopy (NMR, Fig. S1 and S2, respectively) and high-resolution mass spectrometry (HRMS, Fig. S6 and S8, respectively). Due to the paramagnetism, complexes 1-Mn, 1-Fe, 1-Co, and 1-Cu were only characterized by HRMS (Fig. S3, S4. S5, and S7, respectively). Moreover, the porphyrin ligand and its corresponding metal complexes were all characterized by UV-vis absorption spectroscopy (Fig. S9-S15), showing the characteristic Soret and Q bands. All these results confirmed the successful syntheses of these metal porphyrins. Importantly, we have characterized complexes 1-Fe, 1-Co, 1-Ni, 1-Cu, and 1-Zn by using single crystal X-ray diffraction method, further confirming their structures (Fig. S16-S20). In the structure of 1-Fe, the Fe ion is at the trivalent state and has an additional axial chloride ligand to give a tetragonal pyramid geometry. For the rest metal porphyrins, 1-Co, 1-Ni, 1-Cu, and 1-Zn, their metal ions are at the divalent state and have square-planar coordination geometry as provided by the porphyrin ligand. For 1-Mn, although we were unable to get large and high-quality single crystals suitable for X-ray analysis, its structure has been reported in the literature, showing a Mn<sup>III</sup> ion with an axial chloride ligand [76]. It is worth noting that crystalline samples of these metal porphyrins were obtained and were used in all these characterizations and in the following electrochemical studies.

### Electrochemistry

Cyclic voltammograms (CVs) of porphyrin ligand **1** and its metal complexes were carried out in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> dry acetonitrile solution using a three-compartment cell with a glassy carbon (GC) working electrode, an Ag/Ag<sup>+</sup> reference electrode, and a graphite rod auxiliary electrode. Ferrocene was used as an internal standard, and all potentials reported in this work are referenced to the ferrocenium/ferrocene couple. As shown in Fig. 1b, the CV of **1** shows two reversible 1e redox couples at  $E_{1/2} = -1.17$  and -1.61 V, which can be assigned to the first and the second reduction of the porphyrin macrocycle. Complex **1-Mn** displays two quasi-reversible redox waves and one reversible redox wave. The quasi-reversible redox waves at  $E_{1/2} = -0.36$  and -1.47 V can be assigned to the  $[1-Mn]^{0/1-}$  and  $[1-Mn]^{1-/2-}$  redox couples, respectively, while the reversible redox wave at  $E_{1/2} = -1.87$  V corresponds to the  $[1-Mn]^{2-/3-}$  couple. The quasi-reversibility is likely due to the dissociation of the axial Cl<sup>-</sup> ligand on the Mn ion. A similar CV is observed for **1-Fe**, which displays one quasi-reversible redox wave at  $E_{1/2} = -0.38$  V and two reversible redox waves at  $E_{1/2} =$ -1.25 and -1.76 V (Fig. 1b). These redox processes can be assigned to  $[1-Fe]^{0/1-}$ ,  $[1-Fe]^{1-/2-}$ , and  $[1-Fe]^{2-/3-}$  couples, respectively [18,77].

The other four metal porphyrins all exhibit two reversible 1e redox couples (Fig. 1b). For 1-Co, the  $[1-Co]^{0/1-}$  and  $[1-Co]^{1-/2-}$  couples are found at  $E_{1/2} = -1.02$  and -2.00 V; for 1-Ni, the  $[1-Ni]^{0/1-}$  and  $[1-Ni]^{1-/2-}$  couples are found at  $E_{1/2} = -1.28$  and -1.83 V; for 1-Cu, the  $[1-Cu]^{0/1-}$  and  $[1-Cu]^{1-/2-}$  couples are found at  $E_{1/2} = -1.31$  and -1.76 V. These results are all consistent with those values reported previously [25,32,33,56,69,78]. For 1-Zn, it also shows two reversible 1e redox waves at  $E_{1/2} = -1.41$  and -1.80 V for  $[1-Zn]^{0/1-}$  and  $[1-Zn]^{1-/2-}$ , respectively. Because Zn ion is considered as redox inactive, these two redox couples are thus assigned to the first and the second reduction of the porphyrin ligand [79].

### **Electrocatalytic HER studies**

The electrocatalytic HER properties of these metal porphyrins were then investigated in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile with the addition of trifluoroacetic acid (TFA,  $pK_a = 12.7$  in acetonitrile

[80]) as the proton source. As shown in Fig. 2a, the CV of 0.5 mM **1-Mn** exhibited a pronounced catalytic wave in the presence of TFA. Comparison of the CVs of **1-Mn** with and without TFA suggests that the 2e-reduced form  $[1-Mn]^{2-}$  is the catalytically active species for proton reduction. The onset potential of this catalytic wave is at -1.06 V. The catalytic peak currents increase with the first-order dependence on the concentrations of both TFA (Fig. 2a and 3a) and **1-Mn** (Fig. 4a), indicating molecular nature of this catalytic proton reduction. When the concentration of TFA reaches 50 mM (100 equivalents relevant to **1-Mn**), the catalytic HER currents with **1-Mn** reached the acid-independent region. Importantly, very small currents were observed if MnCl<sub>2</sub> and the freebase porphyrin were used as the catalyst, suggesting that the catalytic HER activity is due to **1-Mn** rather than the demetalated species. Note that the free-base porphyrin **1** is known to be active for electrocatalytic HER [70], but this activity requires the use of a stronger *p*-toluenesulfonic acid as the proton source and much more negatively applied potentials.

For 1-Fe, its second reduction wave also becomes a large catalytic wave with the addition of TFA, and the onset potential of this catalytic wave is at -1.20 V (Fig. 2b). This result suggests that the 2e-reduced form  $[1-Fe]^{2-}$  is the catalytically active species for proton reduction. Similar to 1-Mn, catalytic currents with 1-Fe also increased linearly with the concentrations of the acid (Fig. 3b) and the catalyst (Fig. 4b), and reached the acid-independent region with 40 mM TFA (80 equivalents relevant to 1-Fe, Fig. 2b). All these results demonstrated the molecular nature of this electrocatalysis.

In the case of **1-Co**, a large catalytic wave was observed with the addition of TFA (Fig. 2c). Comparison of the CVs of **1-Co** with and without TFA suggests that the 1e-reduced form  $[1-Co]^-$  is the catalytically active species for proton reduction. However, unlike **1-Mn** and **1-Fe**, the catalytic wave is well-behind the first reduction wave of **1-Co**. This result indicates that although the 1e-reduced form of **1-Co** is able to reduce TFA to form the hydride intermediate, the basicity of this metal hydride species is insufficient for the heterolytic protonolysis with TFA to evolve H<sub>2</sub>. As a consequence, further 1e reduction of this hydride species is required to give more active form for

subsequent HER. The catalytic currents with **1-Co** increased linearly with the concentrations of the acid (Fig. 3c) and the catalyst (Fig. 4c), indicating the molecular nature of this electrocatalytic HER with **1-Co**. The catalytic currents reached the acid-independent region with 70 mM TFA (140 equivalents relevant to **1-Co**, Fig. 2c).

For 1-Ni, its first reduction wave also becomes a pronounced catalytic wave with the addition of TFA as the proton source (Fig. 2d), suggesting that the le-reduced form [1-Ni]<sup>-</sup> is the catalytically active species for proton reduction. Careful analysis of the electrocatalytic HER wave with 1-Ni shows two plateau currents, especially in the presence of a small amount of TFA. The first plateau current is at the position of the first reduction wave of 1-Ni, while the second plateau current is well-behind the first reduction wave of 1-Ni. Recently, we demonstrated, by both experimental and theoretical studies, that the 1e-reduced form of **1-Ni** is able to reduce TFA to give a Ni-hydride intermediate [25]. Two molecules of this Ni-hydride species can undergo bimolecular homolysis to evolve H<sub>2</sub> and regenerate the [1-Ni] catalyst. On the basis of these results, we can contribute the first plateau current with 1-Ni to the homolytic HER pathway. With CV scanning to more negative potentials, this Ni-hydride intermediate can be further reduced by one electron to give more active hydride species [57], which can then undergo heterolytic protonolysis with TFA to evolve H<sub>2</sub>. This will result in the second plateau current. The molecular nature of the electrocatalytic HER with 1-Ni is also confirmed: catalytic currents with 1-Ni display first-order dependence on the concentrations of both the acid (Fig. 3d) and the catalyst (Fig. 4d). The catalytic currents reached the acid-independent region with 65 mM TFA (130 equivalents relevant to 1-Ni, Fig. 2d).

For 1-Cu, its first reduction wave becomes a large catalytic wave with the addition of TFA (Fig. 2e), suggesting that the 1e-reduced form  $[1-Cu]^-$  is the catalytically active species for proton reduction. Unlike 1-Co and 1-Ni, the catalytic plateau current is at the position of the first reduction wave of 1-Cu. The onset potential of this catalytic wave is at -1.18 V. This result suggests that [1-Cu]<sup>-</sup> can react with TFA to form a hydride intermediate, which may have sufficient basicity to

undergo heterolytic protonolysis with TFA to evolve  $H_2$ . The catalytic currents with **1-Cu** increased linearly with the concentrations of the acid (Fig. 3e) and the catalyst (Fig. 4e), confirming the molecular nature of this electrocatalytic HER. Moreover, the catalytic currents reached the acid-independent region with 70 mM TFA (140 equivalents relevant to **1-Cu**, Fig. 2e).

Similar electrocatalytic behavior is observed with **1-Zn** (Fig. 2f), showing that the first reduction wave becomes catalytic wave with the addition of TFA. The onset potential of this catalytic wave is at -1.21 V. Because Zn<sup>II</sup> ion is considered as redox inactive, this reduction is ligand centered. We propose that upon 1e reduction, **1-Zn** becomes catalytically active for proton reduction. The resulted hydride species may undergo direct heterolytic protonolysis with TFA to evolve H<sub>2</sub> or it may require one more electron reduction to evolve H<sub>2</sub>. The molecular nature of the electrocatalytic HER with **1-Zn** is confirmed: catalytic currents increase linearly with the concentrations of both the acid (Fig. 3f) and the catalyst (Fig. 4f). The catalytic currents reached the acid-independent region with 50 mM TFA (100 equivalents relevant to **1-Zn**, Fig. 2f).

We show that all metal porphyrins examined in this work are active for electrocatalytic HER. Our results clearly demonstrate that the catalytic mechanisms with these metal porphyrins are different. It is worth noting that we have recently reported the catalytic HER mechanism with **1-Ni** [25,57]. Importantly, in the reported work, we for the first time provided experimental evidence to support the involvement of bimolecular homolysis between two Ni–hydride molecules to evolve H<sub>2</sub>. Such a bimolecular homolysis has been suggested but has not been experimentally confirmed due to the high activity of hydride intermediates. Moreover, our previous results from both electrocatalytic and stopped-flow studies suggest that the oxidative protonation of [**1-Ni**]<sup>-</sup> is the rate-limiting step. This leads to kinetic studies of the first-order dependence on the concentration of the catalyst. Reaction mechanism studies of other metal porphyrin catalysts are the ongoing projects in our group.

#### **Stabilities and TOF**

With the confirmation of molecular catalysis, the stability of these metal porphyrins for HER was also evaluated. Controlled potential electrolysis (CPE) of acetonitrile solution containing 0.5 mM catalysts and 0.1 M TFA was performed in a gastight three-compartment electrochemical cell. As shown in Fig. 5, catalytic currents with all examined metal porphyrins remained stable in prolonged electrolysis, suggesting their stability by functioning as HER electrocatalysts. Importantly, during electrocatalysis, a large amount of gas bubbles were observed on the surface of the GC working electrode. The evolved H<sub>2</sub> was quantitively detected by using gas chromatography, giving Faradaic efficiency of >97% for H<sub>2</sub> generation with all these metal porphyrin catalysts (Fig. 6, for details of the H<sub>2</sub> detection and the Faradaic efficiency calculation, please refer to the Supporting Information). The turnover number (TON) with respect to the total amount of catalyst in the solution in 1 h was 21 for 1-Mn, 12 for 1-Fe, 24 for 1-Co, 29 for 1-Ni, 41 for 1-Cu, and 10 for 1-Zn. In addition, the catalyst solutions after electrolysis displayed UV-vis spectra almost identical to those before electrolysis, and the GC electrodes after electrolysis showed no catalytic currents in freshly-prepared TFA solutions without catalysts. All these results confirmed the molecular nature and the stability of these metal porphyrins by functioning as HER electrocatalysts.

As mentioned above, the catalytic mechanisms with these metal porphyrins are not the same. Consequently, we only made simple and direct comparison of their catalytic efficiency using the foot-of-the-wave analysis (FOWA) [81-83]. Under pure kinetic conditions, the HER catalytic activity can be measured to afford "catalytic Tafel plots", which exhibit TOF as a function of the HER overpotential ( $\eta$ ). Taking -0.77 V as the standard electrode potential for HER using TFA as the proton source, we derived the Tafel plot from the FOWA and estimated the TOF (Fig. 7). In general, an efficient catalyst should display high TOF at low overpotentials. Therefore, our results show that **1-Cu** is the most efficient HER catalyst among these metal porphyrins by reaching a high TOF of 48500 s<sup>-1</sup> at  $\eta$  = 550 mV.

# Conclusions

In conclusion, we reported electrocatalytic HER performance of a series of first-row transition metal complexes of tetrakis(pentafluorophenyl)porphyrin **1-M** (**M** = **Mn**, **Fe**, **Co**, **Ni**, **Cu**, and **Zn**). Our results show that all six metal porphyrins are active and stable by functioning as HER electrocatalysts in acetonitrile with the use of TFA as the proton source. Although their catalytic mechanisms are different as suggested by electrochemical measurements, we can make a simple and direct activity comparison of theses metal porphyrins using FOWA. Among these complexes, **1-Cu** is the most efficient one by reaching the highest TOF 48500 s<sup>-1</sup> at  $\eta$  = 550 mV. This value represents the state-of-the-art performance for molecular HER electrocatalysts reported in the literature. This work for the first time makes a direct comparison of electrocatalytic performance of the tetrakis(pentafluorophenyl)porphyrin with different metal ions and shows that the central metal ion plays a critical role in regulating the HER performance.

### EXPERIMENTAL

### General materials and methods

Manipulations of air- and moisture-sensitive materials were performed under an atmosphere of nitrogen gas using the standard Schlenk line technique. All reagents were purchased from commercial suppliers and were used as received unless otherwise noted. Acetonitrile, dichloromethane, and chloroform were dried by distillation with calcium hydride. Porphyrin ligand 1 and its corresponding metal complexes were prepared according to the methods reported previously. Tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) was recrystallized from absolute ethanol. <sup>1</sup>H NMR spectra were acquired on a Brüker spectrometer operating at 400 MHz. Electronic absorption spectra were measured using a Hitachi U-3310 spectrophotometer. High-resolution mass spectra (HR-MS) were acquired using a Brüker MAXIS. The H<sub>2</sub> produced during controlled potential electrolysis was determined by using an SP-6890 gas chromatograph.

### **Electrochemical studies**

All electrochemical experiments were carried out using an electrochemical analyzer (CH Instruments, model CHI660E) at 20 °C, and the solution was bubbled with N<sub>2</sub> gas for at least 30 min before analysis. Cyclic voltammograms (CVs) were acquired in 5 mL of dry acetonitrile containing 0.5 mM catalyst and 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> with the use of a three-compartment cell,, which has a 0.07 cm<sup>2</sup> glassy carbon (GC) electrode as the working electrode, Ag/AgNO<sub>3</sub> as the reference electrode (BASi, 10 mM AgNO<sub>3</sub>, 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile), and a graphite rod as the auxiliary electrode. The GC electrode was polished with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> of decreasing size (1.0 µm to 50 nm) and washed with distilled water and absolute ethanol. Ferrocene was used as an internal standard, and all potentials reported in this work are referenced to the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) couple. Addition of TFA (1.0 M solution in acetonitrile) was done using a micro-syringe.

## Acknowledgments

We are grateful for support from the "Thousand Talents Program" of China, the Fok Ying-Tong Education Foundation for Outstanding Young Teachers in University, the National Natural Science Foundation of China (Grants 21101170, 21573139, 21773146, and 21902099), the China Postdoctoral Science Foundation (2018M631120), the Shaanxi Province Postdoctoral Science Foundation (2018BSHEDZZ107), the Fundamental Research Funds for the Central Universities, and the Research Funds of Shaanxi Normal University.

# REFERENCES

- 1. McKone JR, Marinescu SC, Brunschwig BS, Winkler JR and Gray HB. Chem. Sci. 2014; 5: 865-878.
- 2. Zhang W, Lai W and Cao R. Chem. Rev. 2017; 117: 3717-3797.
- 3. Lei H, Li X, Meng J, Zheng H, Zhang W and Cao R. ACS Catal. 2019; 9: 4320-4344.
- 4. Chu S, Cui Y and Liu N. Nat. Mater. 2017; 16: 16-22.
- 5. Choi S, Davenport TC and Haile SM. Energ. Environ. Sci. 2019; 12: 206-215.
- 6. Chen L, Chen G, Leung C-F, Yiu S-M, Ko C-C, Anxolabéhère-Mallart E, Robert M and Lau T-C. *ACS Catal.* 2015; **5**: 356-364.
- 7. Morales-Guio CG, Tilley SD, Vrubel H, Grätzel M and Hu X. Nat. Commun. 2014; 5: 3059.
- 8. Lubitz W, Ogata H, Rüdiger O and Reijerse E. Chem. Rev. 2014; 114: 4081-4148.
- 9. Fontecilla-Camps JC, Volbeda A, Cavazza C and Nicolet Y. Chem. Rev. 2007; 107: 4273-4303.
- 10. Tard C and Pickett CJ. Chem. Rev. 2009; 109: 2245-2274,
- 11. Plumeré N, Rüdiger O, Oughli AA, Williams R, Vivekananthan J, Pöller S, Schuhmann W and Lubitz W. *Nat. Chem.* 2014; **6**: 822-827.
- 12. Dey S, Rana A, Crouthers D, Mondal B, Das PK, Darensbourg MY and Dey A. J. Am. Chem. Soc. 2014; **136**: 8847-8850.
- 13. Dempsey JL, Brunschwig BS, Winkler JR and Gray HB. Acc. Chem. Res. 2009; 42: 1995-2004.
- 14. Hunt ST, Milina M, Alba-Rubio AC, Hendon CH, Dumesic JA and Román-Leshkov Y. *Science* 2016; **352**: 974.
- 15. Guo Y, Park T, Yi JW, Henzie J, Kim J, Wang Z, Jiang B, Bando Y, Sugahara Y, Tang J and Yamauchi Y. *Adv. Mater.* 2019; **31**: 1807134.
- 16. Sampson MD and Kubiak CP. Inorg. Chem. 2015; 54: 6674-6676.
- 17. Mukhopadhyay TK, MacLean NL, Flores M, Groy TL and Trovitch RJ. *Inorg. Chem.* 2018; **57**: 6065-6075.
- 18. Rana A, Mondal B, Sen P, Dey S and Dey A. Inorg. Chem. 2017; 56: 1783-1793.
- 19. Ahmed ME, Chattopadhyay S, Wang L, Brazzolotto D, Pramanik D, Aldakov D, Fize J, Morozan A, Gennari M, Duboc C, Dey A and Artero V. *Angew. Chem. Int. Ed.* 2018; **57**: 16001-16004.
- 20. Ahmed ME, Dey S, Darensbourg MY and Dey A. J. Am. Chem. Soc. 2018; 140: 12457-12468.
- 21. Rana A, Mondal B, Sen P, Dey S and Dey A. Inorg. Chem. 2017; 56: 1783-1793.
- 22. Mondal B, Sengupta K, Rana A, Mahammed A, Botoshansky M, Dey SG, Gross Z and Dey A. *Inorg. Chem.* 2013; **52**: 3381-3387.
- 23. Mahammed A, Mondal B, Rana A, Dey A and Gross Z. Chem. Commun. 2014; 50: 2725-2727.
- 24. Lee CH, Dogutan DK and Nocera DG. J. Am. Chem. Soc. 2011; 133: 8775-8777.
- 25. Han Y, Fang H, Jing H, Sun H, Lei H, Lai W and Cao R. Angew. Chem. Int. Ed. 2016; 55: 5457-5462.
- 26. Bediako DK, Solis BH, Dogutan DK, Roubelakis MM, Maher AG, Lee CH, Chambers MB, Hammes-Schiffer S and Nocera DG. *Proc. Natl. Acad. Sci. U. S. A.* 2014; **111**: 15001-15006.
- 27. Khusnutdinova D, Wadsworth BL, Flores M, Beiler AM, Reyes Cruz EA, Zenkov Y and Moore GF. ACS Catal. 2018; 8: 9888-9898.
- 28. Lei HT, Fang HY, Han YZ, Lai WZ, Fu XF and Cao R. ACS Catal. 2015; 5: 5145-5153.
- 29. Seo S, Lee K, Min M, Cho Y, Kim M and Lee H. Nanoscale 2017; 9: 3969-3979.
- 30. Haddad AZ, Garabato BD, Kozlowski PM, Buchanan RM and Grapperhaus CA. J. Am. Chem. Soc. 2016; **138**: 7844-7847.
- 31. Wang N, Lei H, Zhang Z, Li J, Zhang W and Cao R. Chem. Sci. 2019; 10: 2308-2314.
- 32. Xu G, Lei H, Zhou G, Zhang C, Xie L, Zhang W and Cao R. Chem. Commun. 2019; 55: 12647-12650.
- 33. Li H, Li X, Lei H, Zhou G, Zhang W and Cao R. ChemSusChem 2019; 12: 801-806.

- 34. Fang Y, Ou Z and Kadish KM. Chem. Rev. 2017; 117: 3377-3419.
- 35. Omagari T, Suzuki A, Akita M and Yoshizawa M. J. Am. Chem. Soc. 2016; 138: 499-502.
- 36. Wang N, Zheng H, Zhang W and Cao R. Chin. J. Catal. 2018; 39: 228-244.
- 37. Oldacre AN, Friedman AE and Cook TR. J. Am. Chem. Soc. 2017; 139: 1424-1427.
- 38. Aviv I and Gross Z. Chem. Commun. 2007: 1987-1999.
- 39. Zion N, Friedman A, Levy N and Elbaz L. Adv. Mater. 2018; 30: 1800406.
- 40. Dogutan DK, Bediako DK, Graham DJ, Lemon CM and Nocera DG. J. Porphyrins Phthalocyanines 2015; **19**: 1-8.
- 41. Mahammed A and Gross Z. Coord. Chem. Rev. 2019; 379: 121-132.
- 42. Ghosh A. Chem. Rev. 2017; 117: 3798-3881.
- 43. Ladomenou K, Natali M, Iengo E, Charalampidis G, Scandola F and Coutsolelos AG. *Coord. Chem. Rev.* 2015; **304-305**: 38-54.
- 44. Fukui N, Yorimitsu H and Osuka A. Angew. Chem. Int. Ed. 2015; 54: 6311-6314.
- 45. Barata JFB, Neves MGPMS, Faustino MAF, Tomé AC and Cavaleiro JAS. *Chem. Rev.* 2017; **117**: 3192-3253.
- 46. Rosenthal J, Young ER and Nocera DG. Inorg. Chem. 2007; 46: 8668-8675.
- 47. Han A, Jia H, Ma H, Ye S, Wu H, Lei H, Han Y, Cao R and Du P. *Phys. Chem. Chem. Phys.* 2014; **16**: 11224-11232.
- 48. Lei HT, Han AL, Li FW, Zhang MN, Han YZ, Du PW, Lai WZ and Cao R. *Phys. Chem. Chem. Phys.* 2014; **16**: 1883-1893.
- 49. Liu Y, Han Y, Zhang Z, Zhang W, Lai W, Wang Y and Cao R. Chem. Sci. 2019; 10: 2613-2622.
- 50. Sun HL, Han YZ, Lei HT, Chen MX and Cao R. Chem. Commun. 2017; 53: 6195-6198.
- 51. Xu L, Lei HT, Zhang ZY, Yao Z, Li JF, Yu ZY and Cao R. *Phys. Chem. Chem. Phys.* 2017; **19**: 9755-9761.
- 52. Chen F, Wang N, Lei H, Guo D, Liu H, Zhang Z, Zhang W, Lai W and Cao R. *Inorg. Chem.* 2017; **56**: 13368-13375.
- 53. Li XL, Lei HT, Guo XJ, Zhao XL, Ding SP, Gao XQ, Zhang W and Cao R. *ChemSusChem* 2017; **10**: 4632-4641.
- 54. Han Y, Wu Y, Lai W and Cao R. Inorg. Chem. 2015; 54: 5604-5613.
- 55. Lai W, Cao R, Dong G, Shaik S, Yao J and Chen H. J. Phys. Chem. Lett. 2012; 3: 2315-2319.
- 56. Li X, Lei H, Liu J, Zhao X, Ding S, Zhang Z, Tao X, Zhang W, Wang W, Zheng X and Cao R. *Angew. Chem. Int. Ed.* 2018; **57**: 15070-15075.
- 57. Guo X, Wang N, Li X, Zhang Z, Zhao J, Ren W, Ding S, Xu G, Li J, Apfel UP, Zhang W and Cao R. *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.202002311.
- 58. Lei HT, Liu CY, Wang ZJ, Zhang ZY, Zhang MN, Chang XM, Zhang W and Cao R. ACS Catal. 2016; 6: 6429-6437.
- 59. Liu Y, Zhou G, Zhang Z, Lei H, Yao Z, Li J, Lin J and Cao R. Chem. Sci. 2020; 11: 87-96.
- 60. Xie L, Li X, Wang B, Meng J, Lei H, Zhang W and Cao R. Angew. Chem. Int. Ed. 2019; 58: 18883-18887.
- 61. Wang ZJ, Lei HT, Cao R and Zhang MN. Electrochim. Acta 2015; 171: 81-88.
- 62. Liu C, Lei H, Zhang Z, Chen F and Cao R. Chem. Commun. 2017; 53: 3189-3192.
- 63. Guo X, Li X, Liu XC, Li P, Yao Z, Li J, Zhang W, Zhang JP, Xue D and Cao R. *Chem. Commun.* 2018; **54**: 845-848.
- 64. Meng J, Lei H, Li X, Qi J, Zhang W and Cao R. ACS Catal. 2019; 9: 4551-4560.
- 65. Guo K, Li X, Lei H, Zhang W and Cao R. ChemCatChem DOI: 10.1002/cctc.201902034R1.
- 66. Zhao B, Lei H, Wang N, Xu G, Zhang W and Cao R. Chem.-Eur. J. DOI: 10.1002/chem.201903064.
- 67. Solis BH, Maher AG, Honda T, Powers DC, Nocera DG and Hammes-Schiffer S. *ACS Catal.* 2014; **4**: 4516-4526.
- 68. Maher AG, Passard G, Dogutan DK, Halbach RL, Anderson BL, Gagliardi CJ, Taniguchi M, Lindsey JS and Nocera DG. *ACS Catal.* 2017; **7**: 3597-3606.

- 69. Lee CH, Dogutan DK and Nocera DG. J. Am. Chem. Soc. 2011; 133: 8775-8777.
- 70. Maher AG, Liu M and Nocera DG. Inorg. Chem. 2019; 58: 7958-7968.
- Costa JIT, Tomé AC, Neves MGPMS and Cavaleiro JAS. J. Porphyrins Phthalocyanines 2011; 15: 1116-1133.
- 72. Hyun MY, Jo YD, Lee JH, Lee HG, Park HM, Hwang IH, Kim KB, Lee SJ and Kim C. *Chem.–Eur. J.* 2013; **19**: 1810-1818.
- 73. Azcarate I, Costentin C, Robert M and Savéant J-M. J. Am. Chem. Soc. 2016; 138: 16639-16644.
- 74. Olsson S, Dahlstrand C and Gogoll A. Dalton Trans. 2018; 47: 11572-11585.
- 75. Kashiwagi Y, Imahori H, Araki Y, Ito O, Yamada K, Sakata Y and Fukuzumi S. J. Phys. Chem. A 2003; 107: 5515-5522.
- 76. Jannuzzi SAV, de Arruda EGR, Lima FA, Ribeiro MA, Brinatti C and Formiga ALB. *ChemistrySelect* 2016; 1: 2235-2243.
- 77. Moore KT, Fletcher JT and Therien MJ. J. Am. Chem. Soc. 1999; 121: 5196-5209.
- 78. Zhang X, Wu Z, Zhang X, Li L, Li Y, Xu H, Li X, Yu X, Zhang Z, Liang Y and Wang H. *Nat. Commun.* 2017; **8**: 14675.
- 79. García M, Aguirre MJ, Canzi G, Kubiak CP, Ohlbaum M and Isaacs M. *Electrochim. Acta* 2014; **115**: 146-154.
- 80. Hu X, Cossairt BM, Brunschwig BS, Lewis NS and Peters JC. Chem. Commun. 2005: 4723-4725.
- 81. Artero V and Saveant J-M. Energ. Environ. Sci. 2014; 7: 3808-3814.
- 82. Costentin C and Savéant J-M. J. Am. Chem. Soc. 2017; 139: 8245-8250.
- 83. Costentin C, Drouet S, Robert M and Savéant J-M. Science 2012; 338: 90.



Fig. 1. (a) Molecular structures of the six metal porphyrins 1-M examined in this work. (b) CVs of 0.5 mM 1 and 1-M in acetonitrile under N2. Conditions: 0.1 M Bu4NPF6, GC working electrode, 100 mV s<sup>-1</sup> scan rate, and 20 °C.



Fig. 2. CVs of 0.5 mM 1-M in acetonitrile with increasing TFA. Conditions: 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>, GC working electrode, 100 mV s<sup>-1</sup> scan rate, and 20 °C.



**Fig. 3.** The plot of catalytic peak current *versus* TFA concentration for 0.5 mM **1-M** in acetonitrile, showing a first-order dependence of the catalytic peak current on the concentration of TFA.





**Fig. 4.** The plot of catalytic peak current *versus* the concentration of **1-M** in acetonitrile, showing a first-order dependence of the catalytic peak current on the concentration of metal porphyrin. The concentration of TFA is at the acid-independent region.





**Fig. 5.** Catalytic currents during constant potential electrolysis with **1-M** in acetonitrile at –1.50 V. Conditions: 0.5 mM **1-M**, 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>, 100 mM TFA, GC working electrode.





**Fig. 6.** Gas chromatography detection of evolved H<sub>2</sub> during electrolysis with **1-M** (black) and the theoretical amount of H<sub>2</sub> produced (red). Electrolysis conditions: 0.5 mM **1-M**, 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>, 100 mM TFA, GC working electrode.

a 60



**Fig. 7** Catalytic Tafel plots for **1-M**. Conditions: 0.5 mM **1-M**, 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>, GC working electrode, TFA concentration at the acid-independent region.