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# Electrochemical proton reductions in varying acidic media by a simple synthetic hydrogenase mimic

Shang Gao<sup>\*</sup>, Qingcheng Liang, Qian Duan, Dayong Jiang, Jianxun Zhao

School of Materials Science and Engineering, Changchun University of Science and Technology, 7989 Weixing Road, Changchun 130022, PR China

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## ABSTRACT

A simple diiron dithiolate  $[(\mu-S_2C_4N_2H_2)Fe_2(CO)_6]$  (**M2**) as mimic of the active site of [FeFe] hydrogenase catalyzed the reduction of protons to dihydrogen ( $H_2$ ). The strength of the acid played an important role in controlling the mechanism of electrocatalytic proton reduction. The catalysis of weak acid (acetic acid) occurred around  $-2$  V vs.  $Fc/Fc^+$ , at which **M2** did not have a counterpart in the absence of acid. The catalyst was actually the reduced form of **M2** and an (E)ECEC mechanism was proposed. With a moderately strong acid (trifluoroacetic acid), two significant catalyses operated. Reduction of the  $2e^- + 2H^+$  intermediate ( $[M2IM-H_2]$ ) catalyzed the proton reduction at ca.  $-1.4$  V, whereas a competed catalysis at ca.  $-1.6$  V dominated when the protonation of the reduced form of  $[M2IM-H_2]$  exceeded  $H_2$  elimination at higher acid concentrations. Upon addition of a strong acid (triflic acid), one of the ring nitrogen atoms could be protonated. After two successive one-electron reductions, the formed species proceeded a catalytic cycle via a CECE process at a comparatively mild potential of  $-0.65$  V vs. NHE.

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## Introduction

The development of hydrogen as an energy resource is of significance for a competitively sustainable economy [1]. Fortunately, nature long ago figured out how to use the biocatalysts to catalyze  $H_2$  evolution [2]. Hydrogenases, which are widespread metalloenzymes in certain bacteria and algae, efficiently and reversibly catalyze the hydrogen production and oxidation [3]. The enzymes are usually classified as [NiFe], [FeFe], and [Fe] hydrogenases depending on the metals at the active sites [4,5]. Out of these distinct enzymes, [FeFe] hydrogenases have further progressed due to their high turnover frequencies under mild conditions (e.g. the [FeFe] hydrogenase from *Desulfovibrio desulfuricans* can evolve up to 9000 molecules of  $H_2$  at ca.  $-0.4$  V vs. NHE at neutral pH) [6,7]. On the basis of the

spectroscopic and crystallographic determinations [8–10] of the architecture of [FeFe] hydrogenase active center (Scheme 1), numerous bioinspired diiron compounds featuring the formula of  $[(\mu-SR)_2\{Fe(CO)_3-nL_n\}_2]$  with alkyldithiolates like edt/pdt/adt (edt = 1,2-ethanedithiolate, pdt = 1,3-propanedithiolate, adt = azadithiolate) as bridging ligands and phosphines,  $CN^-$  and *N*-heterocyclic carbenes as  $\sigma$ -donor ligands (*L*) have been designed and synthesized in an effort to structurally and functionally mimic the active site of [FeFe] hydrogenase [11–16]. A large number of the synthetic catalysts are catalytically active for electrochemical proton reduction with addition of acids of varying acidity [17–21]. However, most catalyses occur at relatively negative potentials (ca.  $-1.0$  to  $-1.2$  V vs. NHE) in the presence of strong acids [22–24].

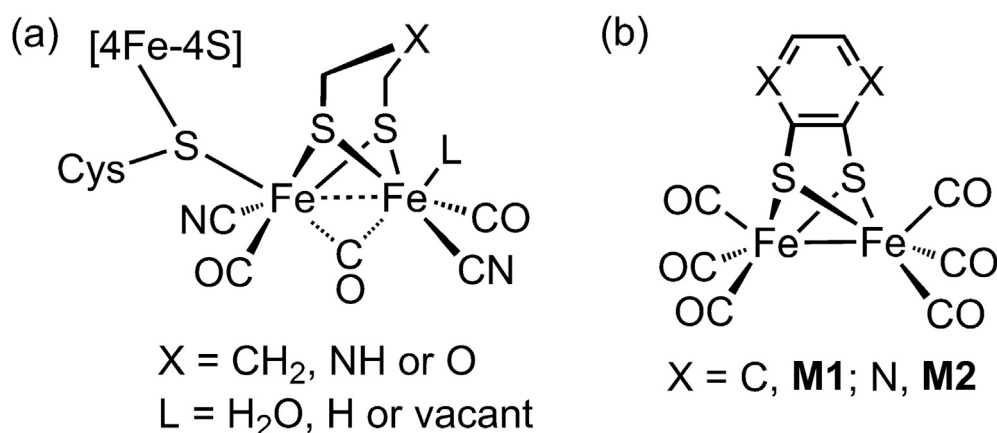
Amongst the synthetic diiron dithiolates,  $[(\mu-bdt)Fe_2(CO)_6]$  (bdt = 1,2-benzenedithiolate, compound **M1** in Scheme 1)

<sup>\*</sup> Corresponding author.

E-mail address: [custgaoshang@126.com](mailto:custgaoshang@126.com) (S. Gao).

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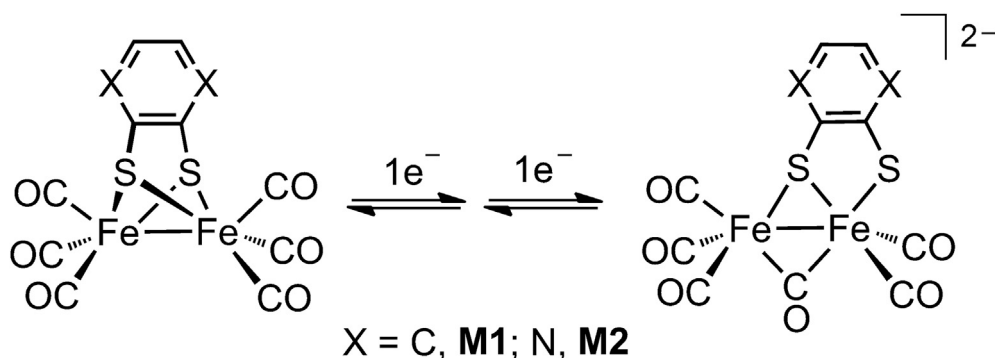
**Scheme 1** – Schematic representation of the architecture of [FeFe] hydrogenase active site (a) and the synthetic model compounds **M1**, **M2** (b).

exhibited attractive redox properties with a primary reduction at  $E_{1/2} = -1.27$  V vs.  $\text{Fc/Fc}^+$  in an acetonitrile ( $\text{CH}_3\text{CN}$ ) solution [25]. The relatively mild potential was accomplished by an interaction of the metal orbitals with a combination of the filled sulfur  $p_\pi$  orbitals and the benzene  $p_\pi$  orbitals [26]. The unsaturated bridging ligand also appeared to play a key role in stabilizing the reduced forms of the diiron core and facilitating the electron transfers. Likewise, the thiolate of an aromatic bridge could be predicted to act as substantially better leaving group, thus potentially facilitated the cleavage of Fe–S bond to open an iron coordination site [27]. Ott and co-workers had investigated the reductive changes in geometry of bdt-bridged  $\text{Fe}_2(\text{CO})_6$  compound by using UV–Vis absorption, infrared, electron paramagnetic resonance spectra, and time-resolved spectroscopy [27,28]. It was demonstrated that the delocalization of the electron density into the bdt moiety upon reduction of the diiron core resulted in large geometric changes. The primary reduction of bdt-bridged  $\text{Fe}_2(\text{CO})_6$  compound was a two-electron transfer arising from the cleavage of one Fe–S bond and the shift of a CO group from the terminal to the bridging position (Scheme 2). The large geometric changes allowed for potential inversion with the second electron transfer slightly more favorable than the first [26,29].

To further investigate these effects, we designed and prepared a chemical model compound bearing a rigid,

conjugated, and electron-withdrawing S-to-S bridge (compound **M2**, Scheme 1) [29]. The electronegative nitrogen atom decreased the nuclear electron density of the diiron core by electron-withdrawing inductive interaction through the arene carbon atom and thiolate sulfur atom. In consequence, **M2** displayed a well-behaved reversible reduction at  $E_{1/2} = -1.08$  V vs.  $\text{Fc/Fc}^+$  in  $\text{CH}_3\text{CN}$ , with ca. 0.2 V positive shift in comparison to that of  $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_6]$  (**M1**). We also investigated the electrocatalytic reaction of **M2** in the presence of a weak acid, such as acetic acid ( $\text{HOAc}$ ,  $\text{pK}_a \sim 22.3$  in  $\text{CH}_3\text{CN}$ ) [29,30]. The catalytic reduction occurred at a potential at which **M2**, in the absence of acid, did not show a reductive event. Nevertheless, a rigorous analysis of the electrochemical responses was required to determine the key metrics of the catalytic activity, such as the overpotential [31], the turnover number, and to establish the catalytic mechanism.

Aside from favoring the reductive potentials, one of the ring nitrogen atoms in **M2** molecule could be protonated in the presence of a strong acid, such as triflic acid ( $\text{HOTf}$ ,  $\text{pK}_a \sim 2.6$  in  $\text{CH}_3\text{CN}$ ) [30]. This type of protonation might compete with the formation of bridging hydride in the catalytic cycle, and provided a low energy pathway for  $\text{H}_2$  production [32,33]. The strength of the acid also had a significant influence on the intimate mechanism of the electron transfer. In this contribution, we thoughtfully benchmarked the electrochemistry of compound **M2** in  $\text{CH}_3\text{CN}$  by using a diverse range of proton



**Scheme 2** – Proposed reduction mechanism of  $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_6]$  (**M1**) and  $[(\mu\text{-S}_2\text{C}_4\text{N}_2\text{H}_2)\text{Fe}_2(\text{CO})_6]$  (**M2**) in  $\text{CH}_3\text{CN}$ .

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