

# An approach to water-soluble hydrogenase active site models: Synthesis and electrochemistry of diiron dithiolate complexes with 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane ligand(s)

Yong Na<sup>a</sup>, Mei Wang<sup>a,\*</sup>, Kun Jin<sup>a</sup>, Rong Zhang<sup>a</sup>, Licheng Sun<sup>a,b,\*</sup>

<sup>a</sup> State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Centre on Molecular Devices, Dalian University of Technology, Zhongshan Road 158-46, Dalian 116012, PR China

<sup>b</sup> Department of Chemistry, Royal Institute of Technology (KTH), Stockholm 10044, Sweden

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## Abstract

In order to improve the hydro- and protophilicity of the active site models of the Fe-only hydrogenases, three diiron dithiolate complexes with DAPTA ligand(s) (DAPTA = 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane), ( $\mu$ -pdt)[Fe(CO)<sub>3</sub>][Fe(CO)<sub>2</sub>(DAPTA)] (**1**, pdt = 1,3-propanedithiolato), ( $\mu$ -pdt)[Fe(CO)<sub>2</sub>(DAPTA)]<sub>2</sub> (**2**) and ( $\mu$ -pdt)[Fe(CO)<sub>2</sub>(PTA)][Fe(CO)<sub>2</sub>(DAPTA)] (**3**), were prepared and spectroscopically characterized. The water solubility of DAPTA-coordinate complexes **1–3** is better than that of the PTA-coordinate analogues. With complexes **1–3** as electrocatalysts, the overvoltage is reduced by 460–770 mV for proton reduction from acetic acid at low concentration in CH<sub>3</sub>CN. Significant decrease, up to 420 mV, in reduction potential for the Fe(I)Fe(I) to Fe(I)Fe(0) process and the curve-crossing phenomenon are observed in cyclic voltammograms of **2** and **3** in CH<sub>3</sub>CN/H<sub>2</sub>O mixtures. The introduction of the DAPTA ligand to the diiron dithiolate model complexes indeed makes the water solubility of **2** and **3** sufficient for electrochemical studies in pure water, which show that the proton reduction from acetic acid in pure water is electrochemically catalyzed by **2** and **3** at ca. –1.3 V vs. NHE.

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## 1. Introduction

Since establishment of the structure of the Fe-only hydrogenase active site by spectroscopic and high-resolution X-ray crystallographic studies of the enzymes, isolated from CpI (*Clostridium pasteurianum*) and DdH (*Desulfovibrio desulfuricans*) [1,2], the chemistry of diiron dithiolate complexes has become an attractive topic in bioinorganic and organometallic fields. In recent years, diiron dithiolate complexes with diverse non-carbonyl

ligands were prepared by CO-displacement of the well-known organometallic complex ( $\mu$ -pdt)[Fe(CO)<sub>3</sub>]<sub>2</sub> in the aim of (1) improving the redox potentials and the protophilicity of the iron centres [3–7], (2) ameliorating the water solubility [8], and (3) having an insight into the coordination ability and configuration of the non-carbonyl ligands to the diiron centres [9–14]. In addition to the biologically relevant CN<sup>–</sup> ligand, various phosphine derivatives have been used in the biomimic studies of the Fe-only hydrogenase active site.

A certain water solubility is one of the desired properties of the diiron dithiolate complexes, considering the following two aspects: (1) The active site of Fe-only hydrogenases, surrounding by an unknown number of water

\* Corresponding authors. Tel.: +86 411 88993886; fax: +86 411 83702185 (M. Wang).

E-mail address: [symbueno@dlut.edu.cn](mailto:symbueno@dlut.edu.cn) (M. Wang).

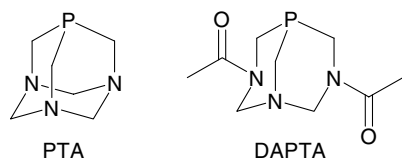


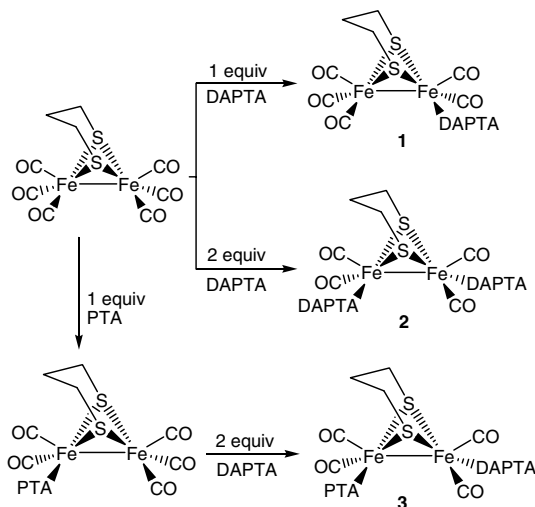
Chart 1.

molecules [1,15], works in a water-containing medium at relatively low reductive potentials (ca.  $-0.4$  V) [16]; (2) electrochemical and photo-induced biomimetic catalysts with water solubility, at least to a certain extent, are required for the ultimate goal of building a biomimetic  $H_2$  production system by combining the proton reduction model complexes of the Fe-only hydrogenase active site with the water splitting systems. Most previously reported organophosphine-coordinate diiron dithiolate model complexes are only soluble in organic solvent [11,14,17,18]. Some efforts were made to enhance the hydrophilicity of diiron dithiolate complexes by introducing water-soluble phosphine ligand(s) [8]. The ligand PTA (1,3,5-triaza-7-phosphaadamantane, Chart 1), with comparable donating ability to  $PMe_3$ , indeed improves the solubility of the diiron dithiolate complexes in mixtures of water and organic solvents, but the solubility of PTA-mono- and disubstituted complexes in pure water is still poor. Phosphine ligand DAPTA (3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane, Chart 1) is an acetylated derivative of PTA and proves to be one of the most water-soluble phosphine ligands [19]. Additionally, DAPTA readily dissolves in common polar organic solvents such as  $CH_2Cl_2$ ,  $CH_3COCH_3$  and alcohols, making it a suitable ligand to be used in a variety of solvents [20]. We have reported the effect of different phosphine ligands on the molecular structures and the redox potentials of diiron dithiolate complexes [14]. In continuing studies, the effect of the DAPTA ligand on the hydrophilicity and the redox properties of the diiron model complexes was explored. Herein we present the synthesis and spectroscopic characteristics of three diiron complexes with DAPTA ligand(s),  $(\mu\text{-pdt}) [Fe(CO)_3][Fe(CO)_2(DAPTA)]$  (**1**),  $(\mu\text{-pdt})[Fe(CO)_2(DAPTA)]_2$  (**2**) and  $(\mu\text{-pdt})[Fe(CO)_2(PTA)][Fe(CO)_2(DAPTA)]$  (**3**), as well as their water solubility and electrocatalytic properties in the presence of acetic acid in  $CH_3CN$ ,  $CH_3CN/H_2O$  mixtures and in pure water.

## 2. Results and discussion

### 2.1. Preparation and spectroscopic characterization of 1–3

Treatment of an equivalent of DAPTA with all-CO diiron complex  $(\mu\text{-pdt})[Fe(CO)_3]_2$  in refluxing  $CH_3CN$  gave mono-substituted complex **1** in 64% yield. DAPTA-disubstituted complex **2** was obtained as major product together with a small amount of **1** when  $(\mu\text{-pdt})[Fe(CO)_3]_2$  was refluxed with 2 equiv of DAPTA in  $CH_3CN$  for an



Scheme 1.

extended reaction time. Unsymmetrically PTA- and DAPTA-substituted complex **3** was prepared by the reaction of  $(\mu\text{-pdt})[Fe(CO)_3][Fe(CO)_2(PTA)]$  [8] with an excess of DAPTA in refluxing  $CH_3CN$  for 1 d (Scheme 1). These CO-displacement reactions of diiron dithiolate complexes with DAPTA all afforded substituted products in low yields (52% for **2** and 44% for **3**) because of the large bulk of the DAPTA ligand.

Complexes **1–3** are very soluble in polar organic solvents, such as  $CH_2Cl_2$ ,  $CH_3COCH_3$ ,  $CH_3CH_2OH$  and  $CH_3CN$ . The DAPTA-monosubstituted diiron complex **1** is scarcely soluble in water, but relatively soluble in the mixture of  $CH_3CN/H_2O$  (1:1, v/v). As expected, the water solubility of complexes **2** and **3** is much better than that of **1**. About 1.3 mg of DAPTA-disubstituted diiron complex **2** can be dissolved in 1 mL water (ca. 1.6 mM), to the best of our knowledge, which is the most water-soluble model complex of the Fe-only hydrogenase active site thus far reported. As for complex **3**, the water solubility was found to be 0.7 mg in 1 mL water (ca. 0.9 mM). The good water solubility of the DAPTA ligand makes complex **2** more hydrophilic than complexes **3** and  $(\mu\text{-pdt})[Fe(CO)_2(PTA)]_2$ . Complexes **2** and **3** are stable for at least 10 h in the solution of  $CH_3CN$ ,  $CH_3CN/H_2O$  mixtures and pure water under nitrogen atmosphere.

Complexes **1–3** were characterized by HRMS, IR,  $^1H$ ,  $^{13}C$  and  $^{31}P$  NMR spectra and elemental analysis. The results of the elemental analyses for **1–3** are in good agreement with the supposed compositions. The peak of the mono-charged species  $[M+Na]$  at  $m/z$  609.9242 (calc. 609.9233) for **1** and the peak of  $[M+H]$  at  $m/z$  788.9816 (calc. 789.0445) for **2** are observed as primary peaks in the HRMS spectra of **1** and **2**, respectively. Complex **3** shows the primary peak of  $[M+H]$  at  $m/z$  717.0241 (calc. 717.0234), and the  $[M+H]^+$  and  $[M+Na]^+$  peaks for  $(\mu\text{-pdt})[Fe(CO)_2(PTA)]_2$  (631.2, 653.2) and  $(\mu\text{-pdt})[Fe(CO)_2(DAPTA)]_2$  (789.0, 811.0) are not observed in the mass spectrum of **3**. The HRMS spectra of **1–3** give clear

evidences for the coordination of DAPTA to the iron atoms of diiron dithiolate complexes.

Complexes **1–3** each display three  $\nu(\text{CO})$  bands in IR spectra as that reported for other analogous  $\text{PR}_3$ -mono- and -disubstituted diiron complexes [11,14]. DAPTA-monosubstituted complex **1** exhibits an average red shift of  $52\text{ cm}^{-1}$  for the  $\nu(\text{CO})$  bands and DAPTA-disubstituted complex **2** manifests a further shift of  $34\text{ cm}^{-1}$  to lower frequency as compared to the parent all-CO diiron complex [21]. All disubstituted complexes, containing two DAPTA (**2**), two PTA ligands [8], or one DAPTA and one PTA ligand (**3**), display nearly identical  $\nu(\text{CO})$ -band patterns with quite similar values, indicating that the electron donor capability of the water-soluble ligand DAPTA is comparable to that of the PTA ligand.

The  $^1\text{H}$  NMR spectrum of the free DAPTA ligand shows four doublets for the  $\text{CH}_2$  hydrogen atoms of the heterobicyclic rings in the region of  $\delta$  4–6. When DAPTA coordinates to the iron centre, each hydrogen of the heterobicyclic rings displays a doublet in the region of  $\delta$  3–6 except the hydrogen atoms of the  $\text{CH}_2$  group attached to the N atom of tertiary amine, which manifest as a singlet. The  $\text{CH}_2$  group in the middle of the pdt-bridge of **1** displays two broad singlets and the  $\text{CH}_2\text{S}$  groups show two singlets, implying that **1** is a quite unsymmetric complex. DAPTA-disubstituted complex **2** exhibits a similar pattern of the  $^1\text{H}$  NMR signals with small chemical shifts to downfield as compared to that for the DAPTA ligand of mono-substituted complex **1**. In addition to the signals of the DAPTA ligand of **3**, two singlets at  $\delta$  4.51 and 4.12 are attributed to the hydrogen atoms of the PTA ligand as that reported for  $(\mu\text{-pdt})[\text{Fe}(\text{CO})_2(\text{PTA})]_2$ . The signals of the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, at  $\delta$  5.73 for **1**, 7.49 for **2** and at 7.56 and  $-16.81$  for **3**, give further supports for the coordination of DAPTA and PTA ligands to the iron atoms. The attempts to get single crystals of DAPTA-substituted diiron complexes were not successful as deep-red multi-crystals were obtained in different mixed solvents.

## 2.2. Electrochemistry of **1–3** in $\text{CH}_3\text{CN}$ and $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ mixtures

The electrochemical data recorded in  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  mixtures are summarized in Table 1. The cyclic voltammograms (CVs) of DAPTA-substituted complexes **1–3** are in the same pattern as those of PTA-coordinate analogues [8]. Complexes **1–3** display reduction events in  $\text{CH}_3\text{CN}$  at  $-1.43$ ,  $-1.66$  and  $-1.74\text{ V}$  (Table 1), respectively, assigned to the one-electron reduction process of  $\text{Fe}(\text{I})\text{Fe}(\text{I})$  to  $\text{Fe}(\text{I})\text{Fe}(\text{0})$ . The reduction potentials of **1** and **2** anodically shift by 110 and 120 mV as compared to that of their corresponding PTA-substituted diiron complexes, indicating slightly poorer donor ability of the DAPTA ligand relative to the PTA ligand.

With addition of water to the  $\text{CH}_3\text{CN}$  solution, the reduction potentials of **1–3** display apparent anodic shifts (190–420 mV). For instance, the reduction potential of **1**

Table 1  
Reduction potentials of **1–3** in  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  mixtures<sup>a</sup>

Complex	$E_{\text{pc}}$ vs. NHE ( $\text{Fe}(\text{I})\text{Fe}(\text{I})/\text{Fe}(\text{I})\text{Fe}(\text{0})$ ), V			
	$\text{CH}_3\text{CN}$	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$ , v/v		
		3:1	1:1	1:3
<b>1</b>	-1.43	-1.34	-1.28	-1.24
<b>2</b>	-1.66	-1.48	-1.47	-1.27
<b>3</b>	-1.74	-1.54	-1.51	-1.32
$(\mu\text{-pdt})[\text{Fe}(\text{CO})_3][\text{Fe}(\text{CO})_2(\text{PTA})]_2^b$	-1.54	-1.43	-1.40	-1.38
$(\mu\text{-pdt})[\text{Fe}(\text{CO})_2(\text{PTA})]_2^b$	-1.78	-1.60	-1.57	-1.53

<sup>a</sup> With 0.05 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> in pure  $\text{CH}_3\text{CN}$ , and 0.05 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> and 0.05 M KCl in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  at a scan rate of 100 mV/s.

<sup>b</sup> Ref. [8].

for the  $\text{Fe}(\text{I})\text{Fe}(\text{I})$  to  $\text{Fe}(\text{I})\text{Fe}(\text{0})$  process decreases to  $-1.24\text{ V}$  in a 1:3  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  mixture, being 160 mV lower than that of the analogous complex  $(\mu\text{-pdt})[\text{Fe}(\text{CO})_3][\text{Fe}(\text{CO})_2(\text{PTA})]_2$  [8], and the reduction potential of **2** moves to  $-1.27\text{ V}$  from  $-1.66\text{ V}$  in pure  $\text{CH}_3\text{CN}$  (Fig. 1). The shifts of 390 and 420 mV for **2** and **3**, respectively, are much larger than that of 250 mV for  $(\mu\text{-pdt})[\text{Fe}(\text{CO})_2(\text{PTA})]_2$  in the CVs measured in a 1:3  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  mixture, presumably resulting from the stronger interactions of the DAPTA ligand with water molecules. It implies that the reduction potential of the  $\text{Fe}(\text{I})\text{Fe}(\text{I})$  core in the  $\text{H}_2\text{O}$ -containing  $\text{CH}_3\text{CN}$  solvent can be considerably modulated as the hydrophilicity of the ligand is improved.

## 2.3. Electrocatalysis of proton reduction in $\text{CH}_3\text{CN}$ , $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ mixtures and in pure water

Upon addition of small amounts of acetic acid (0–4 mM) to the  $\text{CH}_3\text{CN}$  solutions of **1–3**, respectively, the current heights of the reduction events, at  $-1.43\text{ V}$  for **1**,  $-1.66\text{ V}$  for **2** and  $-1.74\text{ V}$  for **3**, apparently increase with a linear dependence on the concentration of acetic acid (Fig. 2). The control electrochemical experiment shows that

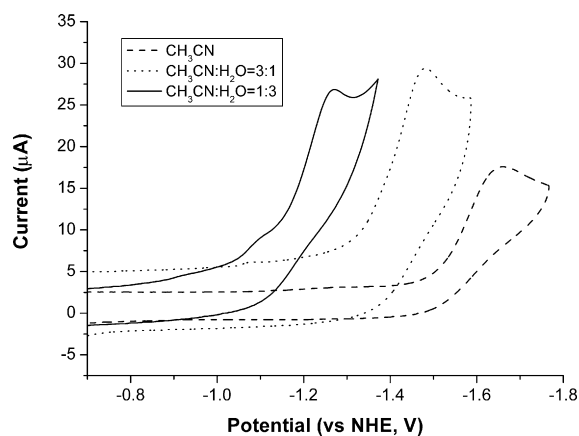


Fig. 1. Potential shifts of the reduction events of **2** in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  mixtures of various ratios. Complex **2** 1.0 mM, 0.05 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> in pure  $\text{CH}_3\text{CN}$ , 0.05 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> and 0.05 M KCl in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ , scan rate of 100 mV/s.

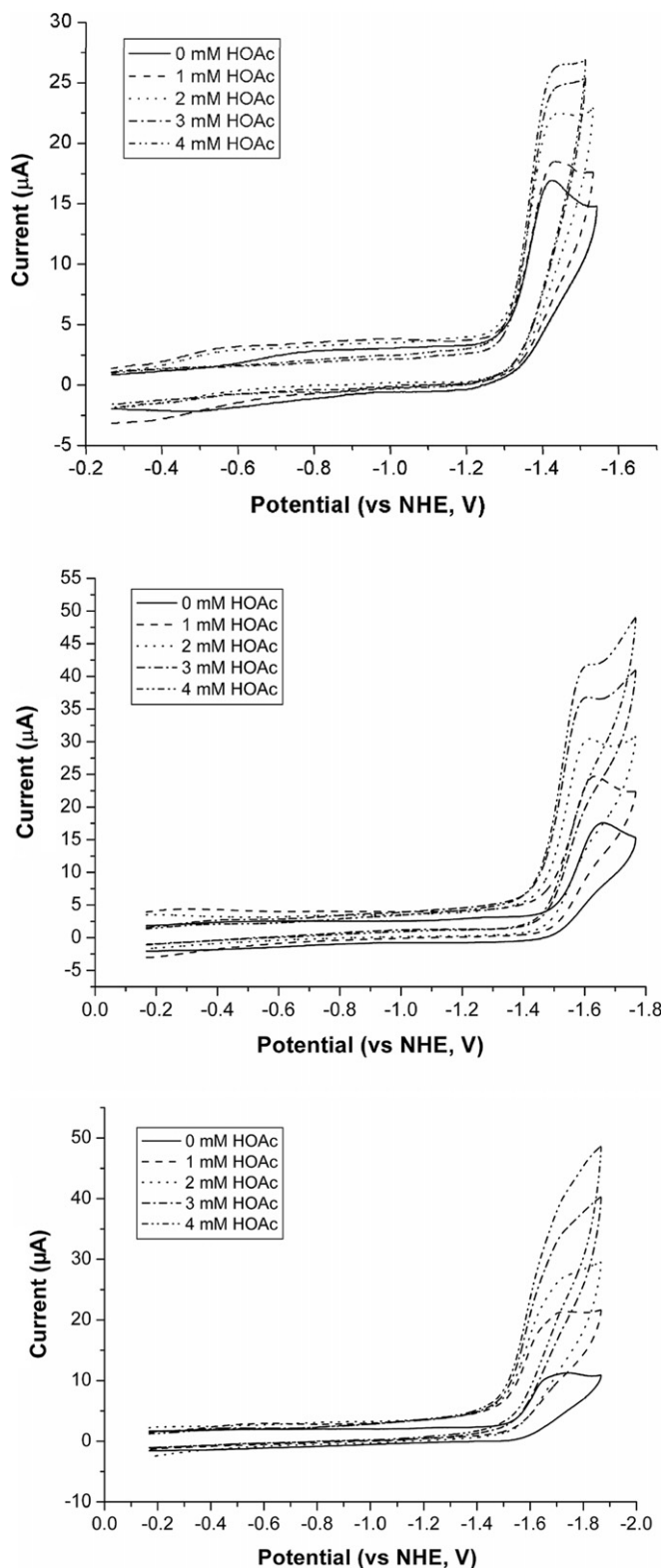


Fig. 2. Cyclic voltammograms of complexes **1** (top), **2** (middle), and **3** (bottom), 1.0 mM, with HOAc (0–4 mM) in  $\text{CH}_3\text{CN}$ , 0.05 M  $n\text{-Bu}_4\text{NPF}_6$ , scan rate 100 mV/s.

in the absence of electrocatalyst, the protons from acetic acid at 4 mM concentration are reduced to molecular hydrogen at  $-2.2$  V in  $\text{CH}_3\text{CN}$ . With DAPTA-coordinate diiron complexes **1–3** as electrocatalysts, the overvoltage

for proton reduction from acetic acid in  $\text{CH}_3\text{CN}$  is decreased by 460–770 mV.

When the cyclic voltammetry experiments of complexes **2** and **3** were carried out in the 1:1  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solvent, curve-crossing events were observed in the reverse scan following the reduction at  $-1.47$  V for **2** and  $-1.51$  V for **3** (Fig. 3) as reported in the literature [8]. The control electrochemical studies verified that such anomalies in CVs did not result from the deposition of instable complexes on the electrode. The curve-crossing phenomenon was not found when the CVs of **2** and **3** were measured in  $\text{CH}_3\text{CN}$  solution in the presence of acetic acid, while it appears immediately in the reverse scan as 1 mL  $\text{H}_2\text{O}$  was added to the solution. Upon addition of only 2 equiv of acetic acid to the solution of complex **3** in a 1:1  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  mixture, the curve-crossing events emerge in the CVs. It seems that the curve-crossing occurs with lower concentration of acetic acid as the ratio of  $\text{H}_2\text{O}$  to  $\text{CH}_3\text{CN}$  increases in the mixed solvent system. The electrochemical experiments indicate that water plays an important role for the curve-crossing event, which is proposed to be a characteristic of the ECCE (electrochemical–chemical–chemical–electrochemical) mechanism in the electrocatalytic reaction involving in a rate-limiting C step [8]. The addition of water to the electrochemical reaction system can promote the ionization of acetic acid, resulting in acceleration of the protonation of the  $\text{Fe(I)Fe(0)}$  species formed in the first electrochemical reduction step. The  $[\text{HFe(II)Fe(I)}]$  and/or  $[(\mu\text{-H}_2)\text{Fe(II)Fe(I)}]$  species generated therefrom can be reduced at a more positive potential to reproduce the  $\text{Fe(I)Fe(I)}$  species in the reverse electrochemical scan.

The introduction of the DAPTA ligand(s) to diiron dithiolate model complexes renders the water solubility of **2** and **3** sufficient for electrochemical studies in pure water with  $\text{Ag}/\text{AgCl}$  as reference electrode, providing a precedent for electrochemical study of the diiron  $\text{H}_2$ -ase model complex in pure water. The CV of **2** in pure water shows the reduction event at  $-1.52$  V (ca.  $-1.32$  V vs. NHE) [22] and the current height of the event apparently increases with small anodic shifts upon sequential addition of

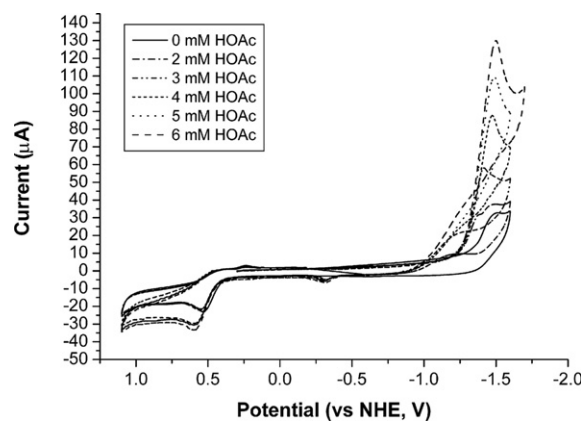


Fig. 3. Cyclic voltammograms of **3** (1.0 mM) with HOAc (0–6 mM) in  $\text{CH}_3\text{CN}$  (0.05 M  $n\text{-Bu}_4\text{NPF}_6$ )/ $\text{H}_2\text{O}$  (0.05 M  $\text{KCl}$ ) = 1:1.



1–3 equiv of acetic acid (Fig. 4 (top)). Complex **3** displays a reduction peak at  $-1.55$  V (ca.  $-1.35$  V vs. NHE) in water. A new reduction event at  $-1.43$  V (ca.  $-1.23$  V vs. NHE) was observed when 0.5 mM of acetic acid was added to the solution of **3** in water (Fig. 4 (bottom)). On raising the amount of the acid from 0.5 to 3 mM, the current height of the new event considerably enhanced accompanied with gradually disappearance of the original reduction event. The apparent anodic shift of the reduction event of **3** in the presence of acetic acid is attributed to the protonation of the PTA ligand of **3** in water, which does not appear in the CV of **2** containing two DAPTA ligands under the same measuring condition. Further evidences for this assignment are  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR data. With addition of 2 equiv of  $\text{CF}_3\text{COOH}$  to the  $\text{CD}_3\text{CN}/\text{D}_2\text{O}$  (1:1) solution of **3**, the signal of the phosphorus of the PTA ligand experiences a significant downfield shift from  $\delta -16.15$  and  $8.85$  for **3** to  $-4.96$  and  $9.33$  for  $[\text{3H}]^+$  in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra and one of the two  $^1\text{H}$  NMR signals for the  $\text{CH}_2$  hydrogen atoms in the PTA ligand of

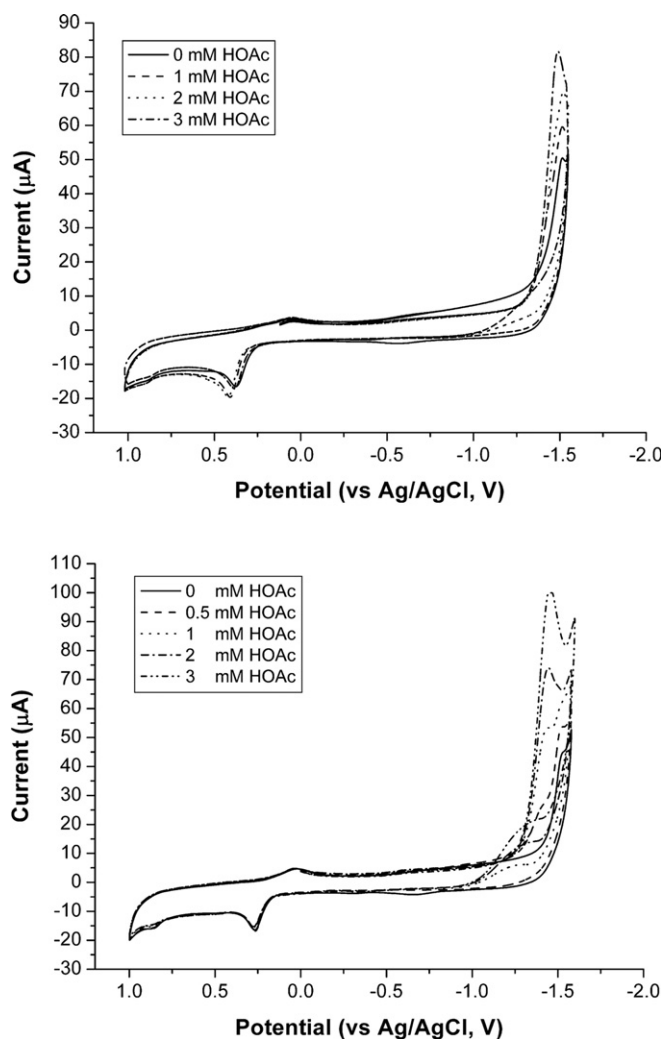


Fig. 4. Cyclic voltammograms of **2** (top) and **3** (bottom), 1.0 mM, with HOAc (0–3 mM) in pure water (KCl saturated solution) with Ag/AgCl as reference electrode at a scan rate of 100 mV/s.

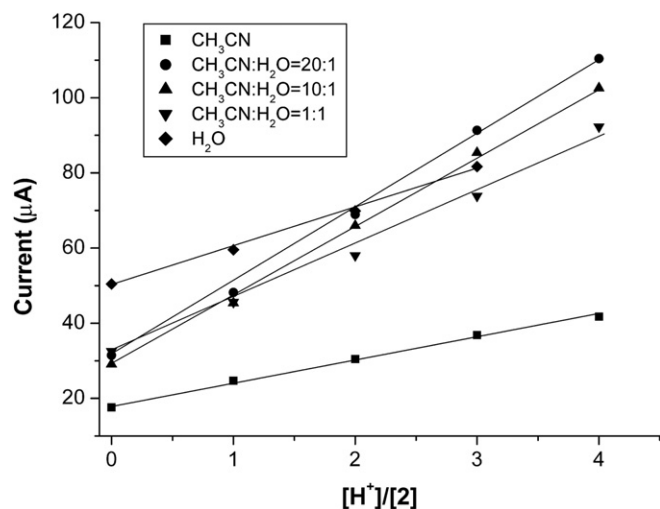


Fig. 5. Dependence of current heights of electrocatalytic events for **2** (1.0 mM) on the concentration of HOAc (0–4 mM) in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  mixtures and in pure water.

**3** moves from  $\delta$  4.85 to 5.14. The other signal for the  $\text{CH}_2$  hydrogen atoms of the PTA ligand overlaps the signal of the undeuterated  $\text{H}_2\text{O}$ . In contrast, the signals for the  $\text{CH}_2$  groups of the DAPTA ligand of **3** in the presence of  $\text{CF}_3\text{COOH}$  are almost identical to the corresponding signals appearing in the absence of acid. The protonation of the PTA ligand in the diiron complexes does not occur in the presence of acetic acid in  $\text{CH}_3\text{CN}$  as shown by the CVs of **3** (Fig. 2 (bottom)) and  $(\mu\text{-pdt})[\text{Fe}(\text{CO})_2(\text{PTA})]_2$ . The protonation of the amine nitrogen atom of the ligand is significantly facilitated in water. The CVs of **2** and **3** in pure water in the presence of acetic acid also show the curve-crossing phenomena as that in the mixture of  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ .

To evaluate the electrocatalytic activity of the DAPTA-disubstituted diiron complex **2** for proton reduction in the presence of acetic acid in different mediums, the plot of the reduction current for the  $\text{Fe}(\text{I})\text{Fe}(\text{I})$  to  $\text{Fe}(\text{I})\text{Fe}(\text{0})$  process of **2** vs. the concentration of acetic acid in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  mixtures and in pure water is drawn in Fig. 5. The reduction current of complex **2** shows a gentle slope towards the concentration of acetic acid in pure water, and the slope is less steep in pure  $\text{CH}_3\text{CN}$  than that in other mediums used. Comparatively high electrocatalytic activity of **2** is seen with a 20:1  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  mixture as solvent. Increase in the ratio of  $\text{H}_2\text{O}$  to  $\text{CH}_3\text{CN}$  up to 1:1 slightly decreases the electrochemical sensitivity of the model complex to acid concentration.

### 3. Conclusion

The coordination of the DAPTA ligand to the diiron core considerably improves the water solubility of the  $\text{H}_2\text{ase}$  model complexes in contrast to  $\text{PME}_3$ - and PTA-coordinate diiron analogues. DAPTA-Mono- and disubstituted complexes **1** and **2** display ca. 100 mV anodic shifts for the reduction potential of the  $\text{Fe}(\text{I})\text{Fe}(\text{I})$  to  $\text{Fe}(\text{I})\text{Fe}(\text{0})$

process in CH<sub>3</sub>CN as compared to that of the corresponding PTA-coordinate complexes. The catalytically active reduction event of complex **1** appears at the Fe(I)Fe(0) redox level (−1.43 V) with a low concentration of acetic acid in CH<sub>3</sub>CN, showing a 770 mV decrease in overvoltage for proton reduction. Complexes with water-soluble DAPTA ligand(s) exhibit larger anodic shifts for the Fe(I)-Fe(I)/Fe(I)Fe(0) reduction event than that displayed by complexes containing PTA ligand(s) when the water content is increased in the reaction medium. Complexes **2** and **3** possess sufficient water solubility for electrochemical studies in water, which show that they are capable of reducing protons from acetic acid electrochemically in pure water at relatively low potential (ca. −1.3 V). The CVs of **2** and **3** in CH<sub>3</sub>CN/H<sub>2</sub>O mixtures and in water all display curve-crossing phenomena, implying the formation of the possible mixed valent [HFe(II)Fe(I)] and/or [(η<sup>2</sup>-H<sub>2</sub>)Fe(II)-Fe(I)] species [8]. The electrochemical studies of **1–3** indicate that in addition to the intrinsic reduction potential of the diiron complex and the strength of the acid, the hydrophilicity of the electron-donor ligand and the content of water in the reaction medium can significantly affect the overvoltage for electrocatalytic proton reduction.

## 4. Experimental

### 4.1. Reagents and instruments

All reactions were carried out under dry N<sub>2</sub> atmosphere with standard Schlenk techniques. Solvents were dried and distilled prior to use according to the standard methods. Ligands PTA (1,3,5-triaza-7-phosphaadamantane) [23], DAPTA (3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane) [19,20] and complexes (μ-pdt)[Fe(CO)<sub>3</sub>]<sub>2</sub> [21], (μ-pdt)[Fe(CO)<sub>3</sub>][Fe(CO)<sub>2</sub>(PTA)] [8] were prepared according to the literature procedures.

IR spectra were recorded in CHCl<sub>3</sub> on a JASCO FT/IR 430 spectrophotometer. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded with a Varian INOVA 400NMR instrument. Elemental analyses were performed on a Thermoquest-Flash EA 1112 elemental analyzer.

### 4.2. Synthesis of (μ-pdt)[Fe(CO)<sub>3</sub>][Fe(CO)<sub>2</sub>(DAPTA)]

The DAPTA (0.23 g, 1.0 mmol) in MeOH (6 mL) was added to the solution of (μ-pdt)[Fe(CO)<sub>3</sub>]<sub>2</sub> (0.39 g, 1.0 mmol) in CH<sub>3</sub>CN (40 mL) and the mixture was refluxed for 12 h. After solvent was removed on a rotary evaporator, the crude product was purified by column chromatography on silica gel first with hexane/CH<sub>2</sub>Cl<sub>2</sub> (4:1, v/v) and then with CH<sub>2</sub>Cl<sub>2</sub>/C<sub>2</sub>H<sub>5</sub>OH (10:1, v/v) as eluents. The product was obtained in a yield of 0.37 g (64%). IR (CHCl<sub>3</sub>): ν(CO) 2042, 1981, 1925, 1648 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.82 (d, 1H, J<sub>HH</sub> = 14.0 Hz, PCH<sub>2</sub>NC(O)), 5.54 (d, 1H, J<sub>HH</sub> = 12.8 Hz, NCH<sub>2</sub>N), 4.97 (d, 1H, J<sub>HH</sub> = 14.0 Hz, NCH<sub>2</sub>N), 4.54 (d, 1H, J<sub>HH</sub> = 14.0 Hz, NCH<sub>2</sub>N), 4.48 (d, 1H, J<sub>HH</sub> = 14.4 Hz, PCH<sub>2</sub>NC(O)), 3.96

(d, 1H, J<sub>HH</sub> = 14.0 Hz, PCH<sub>2</sub>NC(O)), 3.89 (d, 1H, J<sub>HH</sub> = 14.4 Hz, PCH<sub>2</sub>NC(O)), 3.67 (s, 2H, PCH<sub>2</sub>N), 3.38 (d, 1H, J<sub>HH</sub> = 12.8 Hz, NCH<sub>2</sub>N), 2.19 (s, 2H, SCH<sub>2</sub>), 2.10 (s, 6H, CH<sub>3</sub>), 2.05 (s, 2H, SCH<sub>2</sub>), 1.88 (s, 1H, CCH<sub>2</sub>C), 1.77 (s, 1H, CCH<sub>2</sub>C). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 211.87, 209.92, 170.03, 169.43, 67.19, 61.91, 52.00, 47.76, 42.87, 30.53, 23.90, 21.55. <sup>31</sup>P{<sup>1</sup>H} NMR: δ 5.73. Anal. Calc. for C<sub>17</sub>H<sub>22</sub>Fe<sub>2</sub>N<sub>3</sub>O<sub>7</sub>PS<sub>2</sub>: C, 34.77; H, 3.78; N, 7.16. Found: C, 34.73; H, 3.86; N, 7.30%. TOF-ESI-MS: *m/z* calc. (found) for [M+Na]<sup>+</sup>, 609.9233 (609.9242).

### 4.3. Synthesis of (μ-pdt)[Fe(CO)<sub>2</sub>(DAPTA)]<sub>2</sub>

A similar procedure as above described was followed with ca. 20 h reflux. As solvent was evaporated in vacuo, the product was purified by column chromatography on silica gel. Methylene chloride was used to remove the unreacted all-CO diiron complex and CH<sub>2</sub>Cl<sub>2</sub>/C<sub>2</sub>H<sub>5</sub>OH (6:1, v/v) was used to elute the DAPTA-disubstituted product. Yield: 0.41 g (52%). IR (CHCl<sub>3</sub>): ν(CO) 1988, 1951, 1908, 1637 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.81 (s br, 2H, PCH<sub>2</sub>NC(O)), 5.52 (s br, 2H, NCH<sub>2</sub>N), 4.97 (s br, 2H, NCH<sub>2</sub>N), 4.54 (s br, 4H, NCH<sub>2</sub>N and PCH<sub>2</sub>NC(O)), 3.97 (s br, 4H PCH<sub>2</sub>NC(O)), 3.70 (s, 4H, PCH<sub>2</sub>N), 3.40 (s br, 2H NCH<sub>2</sub>N), 2.11 (s br, 16H, 4CH<sub>3</sub> and 2SCH<sub>2</sub>), 1.84 (s, 2H, CCH<sub>2</sub>C). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 213.57, 170.10, 169.45, 67.20, 61.97, 52.26, 47.92, 43.22, 30.42, 29.83, 24.32, 21.61. <sup>31</sup>P{<sup>1</sup>H} NMR: δ 7.49. Anal. Calc. for C<sub>25</sub>H<sub>38</sub>N<sub>6</sub>O<sub>8</sub>P<sub>2</sub>S<sub>2</sub>Fe<sub>2</sub> · C<sub>2</sub>H<sub>5</sub>OH: C, 38.86; H, 5.31; N, 10.07. Found: C, 38.68; H, 5.19; N, 9.85%. TOF-ESI-MS: *m/z* calc. (found) for [M+H]<sup>+</sup>, 789.0445 (788.9816); [M+Na]<sup>+</sup>, 811.0264 (810.9710).

### 4.4. Synthesis of (μ-pdt)[Fe(CO)<sub>2</sub>(PTA)][Fe(CO)<sub>2</sub>(DAPTA)]

Complex (μ-pdt)[Fe(CO)<sub>3</sub>][Fe(CO)<sub>2</sub>PTA] (0.26 g, 0.51 mmol) and the DAPTA (0.23 g, 1.0 mmol) were dissolved in CH<sub>3</sub>CN (40 mL), and the mixture was refluxed for 24 h. After removal of solvent, the product was separated by column chromatography on silica gel. The mixed solution of CH<sub>2</sub>Cl<sub>2</sub>/C<sub>2</sub>H<sub>5</sub>OH (10:1, v/v) was used to remove the PTA-monosubstituted diiron complex, and subsequently CH<sub>2</sub>Cl<sub>2</sub>/C<sub>2</sub>H<sub>5</sub>OH (5:1, v/v) was used to elute the product. Yield: 0.16 g (44%). IR (CHCl<sub>3</sub>): ν(CO) 1985, 1947, 1902, 1644 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.82 (s br, 1H, PCH<sub>2</sub>NC(O)), 5.52 (s br, 1H, NCH<sub>2</sub>NC(O)), 4.96 (s br, 1H, NCH<sub>2</sub>NC(O)), 4.51 (s br, 8H, 1H for NCH<sub>2</sub>NC(O), 1H for PCH<sub>2</sub>NC(O) and 6H for the NCH<sub>2</sub>N of PTA), 4.12 (s, 6H, the PCH<sub>2</sub>N of PTA), 3.94 (s br, 2H, PCH<sub>2</sub>NC(O)), 3.67 (s, 2H, the PCH<sub>2</sub>N of DAPTA), 3.39 (s br, 1H, NCH<sub>2</sub>NC(O)), 2.10 (s br, 10H for 2CH<sub>3</sub> and 2SCH<sub>2</sub>), 1.83 (s, 2H, CCH<sub>2</sub>C). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 213.97, 169.41, 159.58, 72.90, 67.29, 62.06, 55.63, 52.43, 48.07, 43.33, 37.71, 30.58, 24.49, 21.81. <sup>31</sup>P{<sup>1</sup>H} NMR: δ 7.56, −16.81. Anal. Calc. for C<sub>22</sub>H<sub>34</sub>N<sub>6</sub>O<sub>6</sub>P<sub>2</sub>S<sub>2</sub>Fe<sub>2</sub> · C<sub>2</sub>H<sub>5</sub>OH: C, 37.81; H, 5.29; N, 11.02. Found: C, 38.13; H, 5.14; N, 11.09%.

TOF-ESI-MS:  $m/z$  calc. (found) for  $[M+H]^+$ , 717.0234 (717.0241).

#### 4.5. Electrochemistry

Measurements were recorded using a BAS-100B electrochemical potentiostat. Cyclic voltammograms were obtained in a three-electrode cell under argon. The working electrode was a glass carbon disc polished with 1  $\mu\text{m}$  diamond paste and sonicated for 15 min prior to use, and the auxiliary electrode was a platinum wire. The reference electrode was an Ag/Ag<sup>+</sup> electrode (0.01 M AgNO<sub>3</sub> in CH<sub>3</sub>CN). A solution of 0.05 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN or a mixture of 0.05 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN and 0.05 M KCl in water were used as electrolyte. The potentials were reported relative to the normal hydrogen electrode using Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup> as reference except those measure in pure water. When the experiments were performed in water, an Ag/AgCl electrode was used as reference electrode and a saturated solution of KCl in water was used as electrolyte. The reference potential of an Ag/AgCl electrode vs. normal hydrogen electrode in a saturated aqueous solution of KCl is 0.198 V at 25 °C [22].

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