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# Using polyethyleneimine (PEI) as a scaffold to construct mimicking systems of [FeFe]hydrogenase: preparation, characterization of PEI-based materials, and their catalysis on proton reduction

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Ten branched polymeric materials (PEI-P-Fe<sub>2</sub>s) derived from polyethyleneimine (PEI) functionalized with [Fe<sub>2</sub>(CO)<sub>5</sub>]-units to mimic [FeFe]-hydrogenase were prepared. Before the functionalization, PEI was first premodified using diphenylphosphinamine (NPPh<sub>2</sub>) group. In the premodification, three approaches were employed: (i) using PEI with an average molecular weight of 1800 and 600, respectively; (ii) grafting NPPh<sub>2</sub> group by either direct reaction of chlorodiphenylphosphine with PEI or Br(CH<sub>2</sub>)<sub>11</sub>OPPh<sub>2</sub>; and (iii) further premodification with BrCH<sub>2</sub>COOH after immobilization of the NPPh<sub>2</sub> group. Reaction of the premodified PEI with diiron hexacarbonyl complexes, [Fe<sub>2</sub>( $\mu$ -S)<sub>2</sub>(CO)<sub>6</sub>] (1), or [Fe<sub>2</sub>( $\mu$ -S<sub>2</sub>C<sub>2</sub>H<sub>4</sub>)(CO)<sub>6</sub>] (3) produced 10 functionalized materials, PEI-P-Fe<sub>2</sub>s. These materials were characterized using a variety of spectroscopic techniques, FTIR, NMR, TGA, and cyclic voltammetry. Spectral comparison with two control complexes, [Fe<sub>2</sub>( $\mu$ -S)<sub>2</sub>(CO)<sub>5</sub>PPh<sub>3</sub>] (2) and [Fe<sub>2</sub>( $\mu$ -S<sub>2</sub>C<sub>2</sub>H<sub>4</sub>)(CO)<sub>5</sub>PPh<sub>3</sub>] (4), suggested that the immobilized diiron units of PEI-P-Fe<sub>2</sub>s were dominantly pentacarbonyl analogous to complexes 2 and 4, although tetracarbonyl units may also exist because the amine groups of PEI could also be involved in substituting CO, as was the NPPh<sub>2</sub> group. The catalysis of these materials on proton reduction was examined in 0.1 mol I<sup>-1</sup> [NBut<sub>4</sub>]BF<sub>4</sub>/DMF containing acetic acid by using cyclic voltammetry. Our results indicated that both the presence of carboxylic acid and dangling the diiron units at the end of a long aliphatic chain improved catalytic efficiency by one-fold. The improvement was attributed to the increase in flexibility of the catalytic center and enhancement of proton transfer during the catalysis. Copyright © 2013 John Wiley & Sons, Ltd.

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Keywords: [FeFe]-hydrogenase; PEI-based materials; proton reduction; catalysis

### Introduction

The structure of [FeFe]-hydrogenase, a metalloenzyme catalyzing hydrogen evolution reversibly and rapidly, was revealed over one decade ago. The enzyme exhibits one significant feature, performing both hydrogen oxidation and evolution by employing those elements widely available and relatively abundant in the crust of our planet, e.g. iron, sulfur (Fig. 1).<sup>[1–4]</sup> This is in striking contrast to the practice in industry where precious metals – platinum and palladium – are required. These well-known metals are in extremely low abundance.

The extraordinary feature of the natural system and the relevance of hydrogen as a future energy vector have tremendously inspired synthetic chemists to mimic the dimetallic center of the enzyme. Indeed, exploring bio-inspired mimetic chemistry has not attempted to duplicate the active site. Instead, the main concerns of modeling the metal center of the enzyme lie in (i) understanding the catalytic mechanism of the enzyme at the molecular level and, more specifically, how this natural 'machinery' consisting of 'cheap building blocks' can achieve its marvelous catalytic function, and thus, general principles of the enzymatic catalysis can be drawn; and (ii) being inspired by those general principles, artificial systems may be constructed to have functionalities comparable to the natural system. In the past decade, a large number of diiron complexes of the core,  $[Fe_2(CO)_{6-x}]$  (x = 1, 2), have been prepared.<sup>[5-13]</sup> Those diiron complexes, in one way or another, resemble the diiron center of the enzyme. In mimicking the natural systems, particular attention has been paid to the preparation of mimics possessing a basic group either directly coordinating to the diiron center or locating in the secondary coordination sphere because it is believed that such a group may play a role in proton transfer in the process of proton reduction and hence improve catalytic efficiency. Wherever the base groups are located in the mimics, studies demonstrated that those groups were actively involved in the protonation of the mimics.<sup>[4,14–18]</sup> An important consideration is that the base group in a model complex may initiate a proton-coupled electron transfer process in catalysis. In natural systems, this is one of the key processes employed

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Figure 1. Schematic view of the H-cluster of [FeFe]-hydrogenase in its rest state.

by nature to reduce the reaction energy barrier.<sup>[19–24]</sup> Transition metal complexes bearing a pendant base functioning as a proton relay are not unprecedented.<sup>[25,26]</sup> A recent report by Rauchfuss and his coworkers demonstrated well that the azo group of the bridging head of a diiron model helped activate hydrogen via the PCET mechanism at a significantly lower potential compared to an analogous system without such a base group.<sup>[20]</sup> This is probably thus far the most concrete experimental evidence providing rationalization for assigning the uncertain X (Fig. 1) to an NH group.

While the number of mimics of the diiron core,  $[Fe_2(CO)_{6-x}]$ (x = 1, 2), has increased exponentially in recent years, studies to address concerns beyond the diiron subunit, e.g. the peripheral environment in which the H-cluster is harbored, have been relatively rare. It is undoubted that the surrounding protein domains of the active site of the enzyme are indispensable for the enzyme to exhibit its catalytic function. This nonmetallic part of the enzyme not only offers a safe guard for the fragile and highly oxygen-sensitive active site but also functions as a platform to construct a channel to shuttle the substrate in and the product out. Nature devises the channel in such a way that those processes are thermodynamically downhill to avoid extra energy expenses in the catalysis. Jones and her coworkers grafted a diiron carbonyl unit onto a short peptide chain a few years ago, and this was probably the very first attempt employing an approach analogous to nature to address this issue.<sup>[27]</sup>

Such a peripheral component is also useful in assembling an electrode by using mimics. But developing mimicking systems of this kind needs to draw further attention because only a handful examples have been reported to date.<sup>[28-32]</sup> One of the difficulties is the integration of the diiron mimics into such a peripheral environment, which can be used as a scaffold in the assembly. Selecting an appropriate scaffold is another nontrivial task. In the reported systems, forming a monolayer of the mimics on the surface of a vitreous carbon electrode was one of the approaches to construct an electrode.<sup>[33,34]</sup> Further improvement was achieved by anchoring diiron models into pro-polymerized polypyrrole film via diffusion and then chemical reaction.[35,36] Recently, we reported polymeric systems functionalized with diiron mimics prepared either by polymerizing diiron models possessing alkynyl group(s) <sup>[14,37,38]</sup> or by joining the model to an organic diazide via 'click' chemistry.<sup>[39]</sup> Those functionalized polymers were successfully employed to construct film electrodes that exhibited electrochemical responses in the presence or absence of an acid. However, the tedious, time-consuming, and perhaps costly nature of their synthesis poses a disadvantage for their further development. To bypass this hurdle, it is suggested that utilizing materials commercially available may be an option in this regard. It was reported that resin was successfully employed to support diiron models.<sup>[40]</sup> Recently, we exploited the functionality of the C-Cl bond

of polyvinyl chloride (PVC), a plastic found in many applications in industry and is available at low cost, to achieve artificial systems to mimic the enzyme.<sup>[37]</sup> By doping the functionalized polymers with multiwall carbon nanotubes, film electrodes were assembled with the aid of Nafion.

Obviously, in addition to availability and low cost, an ideal material into which a diiron mimic is to be incorporated should exhibit flexibility in tailoring its properties, for example, solubility, hydrophilicity, and protonability. Being inspired by our recent success in exploiting the PVC plastic,<sup>[37]</sup> we turned to another commercially available polymeric material - polyethyleneimine (PEI) - which is an additive widely used in industry. Herein, we report our exploration of the reactivity of the primary and secondary amine groups (NH<sub>2</sub> and NH, respectively) of PEI to prepare PEI-based materials functionalized with diiron carbonyl mimics. Through premodifying PEI with diphenylphosphinamine  $(NPPh_2)$ , diiron models,  $[Fe_2(\mu-S)_2(CO)_6]$  (1) or  $[Fe_2(\mu-S_2C_2H_4)(CO)]$ <sub>6</sub>] (**3**), were chemically grafted onto PEI skeleton via substitution of the bound CO by the premodified NPPh<sub>2</sub> groups. The resultant materials were characterized using NMR, Fourier transform infrared spectroscopy, and TGA techniques. Cyclic voltammetry was employed to investigate the electrochemistry of the materials and their catalysis on proton reduction in DMF-acetic acid medium. It was found that increasing the flexibility of the catalytic center (the diiron unit) and immobilization of carboxylic acid onto PEI could improve the electrocatalytic efficiency.

### **Experimental**

#### **Reagents and Equipment**

Reactions and manipulations were performed using standard Schlenk technique under argon atmosphere when necessary. All solvents were dried following standard procedures prior to use and stored under argon atmosphere. PEI (branched,  $M_{\rm w} = 1800$ and 600) and chlorodiphenylphosphine were purchased from Alfa Aesar and triphenylphosphine from Sinopharm Chemical Reagent Co., Ltd. General chemicals were purchased from local commercial suppliers and further purified when necessary. Complexes  $[Fe_2(\mu-S)]$  $_{2}(CO)_{6}$ ] (1), [Fe<sub>2</sub>( $\mu$ -S)<sub>2</sub>(CO)<sub>5</sub>PPh<sub>3</sub>] (2), [Fe<sub>2</sub>( $\mu$ -S<sub>2</sub>C<sub>2</sub>H<sub>4</sub>)(CO)<sub>6</sub>] (3), and  $[Fe_2(\mu-S_2C_2H_4)(CO)_5PPh_3]$  (4) (refer to ESI) were synthesized following published procedures.<sup>[41–43]</sup> Infrared (IR) spectra were recorded on a Scimitar 2000 (Varian). NMR spectral data were collected on an Avance 600 or 400 (Bruker) in CDCl<sub>3</sub>. TGA measurement was carried out on a NETZSCH STA 409 PC/PG at a heating rate of 10°C min<sup>-1</sup> under nitrogen purging. Electrochemical investigation was performed under argon in a customized glass cell with a threeelectrode system as described elsewhere.<sup>[44]</sup> In the setup, the working electrode was a glassy carbon disk ( $\phi = 5$  mm), and a glassy carbon strip electrode was used as a counter electrode. The reference electrode was Aq/AqCl with an inner reference solution of  $[NBut_4]BF_4$  (0.45 mol I<sup>-1</sup>) and  $[NBut_4]CI$  (0.05 mol I<sup>-1</sup>) in dichloromethane (DCM). All potentials were quoted against a ferrocenium/ferrocene couple.

#### Functionalization of PEI with Diphenylphosphine

#### PEI-P-A

To a solution of PEI (4.30 g) and anhydrous  $NEt_3$  (7 ml, 50 mmol) in DCM (80 ml) cooled in an ice bath,  $CIPPh_2$  (9 ml, 50 mmol) in DCM (20 ml) was slowly added dropwise under vigorous stirring.

After the addition, the reaction was stirred for a further 4 h at room temperature. Removal of the solvent under reduced pressure gave an off-white solid, which was redissolved in DCM (5 ml). To the solution was added hexane (500 ml) under stirring. Upon the addition, precipitates formed instantly and suspended in the solution. The mixture was left standing for 2 h to settle the product at the bottom of the reaction vessel. A pale-yellow solid (i.e. PEI-P-A) was collected by filtration, washed with anhydrous ethanol, and then dried under vacuum to a constant weight (10.6 g). IR (KBr): 3407 (NH), 3051, 1586, 1479, 1435 cm<sup>-1</sup> (benzene). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  22.01, 61.60, 62.21 ppm. Other functionalized polymers – PEIs, PEI-P-B, PEI-P-B', PEI-P-C, PEI-P-D, and PEI-P-E – were analogously prepared (Table 1).

#### PPh2-O-(CH2)11-Br

A solution of HO-(CH<sub>2</sub>)<sub>11</sub>-Br (2.24 g, 8.9 mmol) and Et<sub>3</sub>N (0.63 ml, 8.9 mmol) were mixed in anhydrous THF (50 ml) at 0°C. To the precooled solution, ClPPh<sub>2</sub> (1.6 ml, 8.9 mmol) in THF (2 ml) was slowly added dropwise under vigorous stirring. After the addition, the reaction was stirred for a further 1 h at low temperature. Removal of the solvent followed by purification using flash chromatography (eluent, ethyl acetate/petroleum ether = 20%/80%) produced a white solid (1.56 g, 40%). IR (KBr): 1592, 1485, 1439 (benzene), 3058 (benzene C-H), 2929, 2855 (CH<sub>2</sub>) cm<sup>-1</sup>. <sup>31</sup>P NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  31.34 ppm.

#### PEI-(CH<sub>2</sub>)<sub>11</sub>-O-P

 $PPh_2$ -O-(CH<sub>2</sub>)<sub>11</sub>-Br (550 mg, 1.26 mmol), Et<sub>3</sub>N (1.3 mmol, 0.18 ml), and PEI (143 mg) were reacted in DCM (10 ml). The reaction was similarly performed and worked up as described earlier to produce a yellow oily liquid (Table 1).

#### HOOCCH<sub>2</sub>-PEI-P

BrCH<sub>2</sub>COOH (278 mg, 2 mmol) was reacted with PEI-P-B (540 mg) in DCM (20 ml) in the presence of anhydrous  $K_2CO_3$  (300 mg, 2.18 mmol). The reaction was similarly performed and worked up as described earlier to produce a white solid (Table 1).

# Preparation of the Polymer Functionalized with Diiron Models

#### PEI-P-Fe<sub>2</sub>-A

PEI-P-A (2.00 g) in anhydrous THF (5 ml) was added to a solution of complex 1 (2.54 g, 7.4 mmol) in anhydrous THF (70 ml) under rapid stirring. After the addition, the reaction mixture was refluxed and stirred for a further 24 h at 70°C. When the reaction was completed as monitored using thin-layer chromatography, the mixture was filtered, and the filtrate was collected. Removal of the solvent produced a residue, which was redissolved in anhydrous DCM (5 ml). The solution was added to hexane (500 ml) dropwise under vigorous stirring to precipitate the product. The product (dark brown, 3.1 g) was collected via filtration, washed with anhydrous ethanol, and dried under reduced pressure. The product was kept under Ar atmosphere for further use. IR (KBr): 2054, 2013, 1995 1985, 1972, 1934 cm<sup>-1</sup> (CO). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 600 MHz): δ 32.97, 69.66, 71.45 ppm. PEI-P-Fe<sub>2</sub>-A: found S 11.10, Fe 19.33. The other polymers functionalized with diiron mimics were analogously prepared (Table 2).

# **Results and Discussion**

# Pre-functionalization of PEI with Diphenylphosphine and Their Reaction with the Diiron Models

It is well known that phosphine ligand substitutes readily the CO of diiron hexacarbonyl complexes, and numerous mimics have been prepared in this manner.<sup>[43,45–49]</sup> To functionalize PEI with diiron mimics, we exploited this reactivity by first premodifying PEI through its reaction with CIPPh<sub>2</sub> and then reacting with diiron hexacarbonyl complexes. In this study, four types of premodified PEI were prepared (Table 1). PEI-P-A, PEI-P-B, PEI-P-C, PEI-P-D, and PEI-P-E were prepared by reacting CIPPh<sub>2</sub> with PEI of average molecular weight 1800. These premodified PEIs differed in the content of chemically anchored diphenylphosphine (Table 1). The second type was PEI-P-B', which was prepared using PEI with a smaller molecular weight (600). To allow more flexibility for immobilized diiron models, we linked the diphenylphosphine to PEI via a long aliphatic chain. Reacting 11-bromoundecanol with

Table 1. The ratio of (PEI) and chlorodiphenylphosphine (CDPP) in the preparation of functionalized PEIs, their physical properties, and <sup>13</sup> P NMR						
PEI-P	PEI (g)/CIPPh <sub>2</sub> (mmol)	Physical properties	<sup>13</sup> P NMR (CDCI <sub>3</sub> )	Yield (g)		
PEI-P-A	4.3/50	Pale-yellow solid	22.01, 61.60, 62.21	10.6		
PEI-P-B	4.3/38	Pale-yellow solid	21.94, 62.16	8.7		
PEI-P-C	4.3/15	White solid	21.40, 23.55, 35.39, 36.82, 40.78, 62.12	4.1		
PEI-P-D	2.15/4	Pale-yellow oily liquid	18.23, 21.89, 24.77, 29.95, 30.44, 36.09,	1.6		
			37.03, 40.94, 41.30, 62.68			
PEI-P-E	4.3/2	Pale-yellow oily liquid	18.46, 21.92, 24.12, 24.33, 24.58, 30.34, 36.03,	0.50		
			36.97, 41.06, 41.40, 62.82			
PEI-P-B <sup>/a</sup>	4.3/38	Pale-yellow solid	21.47, 35.38, 36.69, 40.06, 40.79, 61.90, 61.12, 61.67	2.52		
PEI-(CH <sub>2</sub> ) <sub>11</sub> -O-P <sup>b</sup>	4.3/38	Yellow viscous liquid	31.05	0.24		
HOOCCH <sub>2</sub> -PEI-P <sup>c</sup>		White solid	17.06, 24.04, 27.60, 28.42, 29.86, 30.54, 32.32, 50.16	0.23		

<sup>a</sup>PEI with a molecular weight of 600 was employed.

<sup>b</sup>No <sup>13</sup>P NMR data were available for PEI-(CH<sub>2</sub>)<sub>11</sub>-O-P, but <sup>13</sup>P NMR of its precursor (PPh<sub>2</sub>-O-(CH<sub>2</sub>)<sub>11</sub>-Br) showed a signal at 1.34 ppm. <sup>c</sup>PEI-P-B: BrCH<sub>2</sub>COOH = 0.54 g : 2 mmol and 1729 cm<sup>-1</sup> (KBr) for the carboxyl group.

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Table 2. Ratio of PE	-P over complex 1 or 3 in the prep	paration of functionaliz	ed polymers,	their physical properties, IR absorption	bands, reduction poten	tials $(E_p)^c$ , and <sup>13</sup> P NMR	
Polymer	PEI-P (g) over 1 or 3 (mmol)	Physical properties	S%, Fe%	IR $(cm^{-1})^a$	$E_{\rm p}$ (V) <sup>c</sup>	<sup>13</sup> P NMR (CDCl <sub>3</sub> )	Yield (g)
PEI-P-Fe <sub>2</sub> -A	PEI-P-A/1, 2.0/7.4	Dark-brown solid	11.1, 19.3	2054, 2013, 1995 1985, 1972, 1934	-1.53, -1.30, -0.98	32.97, 69.66, 71.45	3.1
PEI-P-Fe <sub>2</sub> -B	PEI-P-B/1, 2.0/7.4	Dark-brown solid	8.1, 14.1	2055, 2039, 2013, 1986, 1973, 1932	-1.54, -1.32, -0.99	32.97, 59.06, 68.65, 70.55, 76.55	2.9
PEI-P-Fe <sub>2</sub> -B-2	PEI-P-B/ <b>3</b> , 2.0/7.4	Orange solid	7.3, 12. 8	2042, 1981, 1952, 1929	-1.80	21.41, 30.32, 68.19, 75.74	2.5
PEI-P-Fe <sub>2</sub> -C	PEI-P-C/1, 0.8/2.9	Dark-brown solid	10.9, 19.0	2054, 2047, 2016, 1998, 1985, 1933	-1.59, -1.32, -1.19	32.52, 36.64, 59.34, 68.73	0.35
PEI-P-Fe <sub>2</sub> -D	PEI-P-D/1, 1.0/3.7	Dark-brown solid	11.1, 19.4	2044, 2030, 1998.8, 1933	-1.41, -1.28	59.28, 70.43	1.1
PEI-P-Fe <sub>2</sub> -E	PEI-P-E/1, 0.563/0.78	Dark-brown solid	2.5, 4.4	2045, 2000, 1985, 1963, 1931	-1.79	59.54, 65.63, 70.16	0.28
PEI-P-Fe <sub>2</sub> -B'	PEI-P-B'/1, 2.0/7.4	Dark-brown solid	7.4, 13.0	2055, 2014, 1985, 1975, 1935	-1.56, -1.34, -1.01	32.21, 59.28, 68.66, 70.58	1.34
PEI-P-Fe <sub>2</sub> -B'-2	PEI-P-B'/ <b>3</b> , 0.248/0.92	Orange solid	8.6, 14.9	2043, 2019, 1981, 1955, 1931	-1.80	23.31, 27.49, 31.67, 59.12,	0.12
						68.50, 71.12	
PEI-(CH <sub>2</sub> ) <sub>11</sub> -O-P-Fe <sub>2</sub>	PEI-(CH <sub>2</sub> ) <sub>11</sub> -O-PPh <sub>2</sub> / <b>1</b> , 0.21/1.44	Dark-brown solid	7.6, 13.2	2067, 2043, 2034, 2009, 1973	-1.53, -1.26	31.10	0.33
HOOCCH <sub>2</sub> -PEI-P-Fe <sub>2</sub>	HOOCCH <sub>2</sub> -PEI-P/1, 0.5/1.74	Dark-brown solid	11.2, 19.4	2060, 2039, 2018, 1996, 1944	-1.60, -0.96	30.31, 56.96	0.21
Complex 1		Red solid		2079, <sup>b</sup> 2043, 2003	-1.23, -2.24		
Complex <b>3</b>		Red solid		2077, <sup>b</sup> 2037, 2001, 1996	—1.30, <sup>d</sup> —1.84		
<sup>a</sup> KBr.							
<sup>b</sup> Dichloromethane.							
<sup>c</sup> Benzene-d <sub>6</sub> .							
<sup>d</sup> (vs. NHE, MeCN).							

CIPPh<sub>2</sub> produced PPh<sub>2</sub>-O-(CH<sub>2</sub>)<sub>11</sub>-Br, which further reacted with PEI to achieve the third premodified PEI, PEI-(CH<sub>2</sub>)<sub>11</sub>-O-P. In the last premodified PEI (HOOCCH<sub>2</sub>-PEI-P), a carboxylic group was introduced by reacting PEI-P-B with bromoacetic acid. An absorption band at 1729 cm<sup>-1</sup> of the resultant product indicated the successful immobilization of the carboxyl group. All the preparations of PEI-Ps are illustrated in Schemes 1 and 2.

Polyethyleneimine is a hygroscopic liquid. As shown in Table 1, the premodified PEIs were solid in most cases. When the content of the chemically grafted NPPh<sub>2</sub> was relatively low or a long aliphatic chain was introduced, the pre-functionalized PEIs could be oily liquids. These PEIs are soluble in common organic solvents such as DMF, THF, and DCM. The premodification was confirmed by IR (supporting information, Fig. S1) and <sup>13</sup>P NMR spectroscopies (supporting information, Fig. S2). The PEIs grafted with NPPh<sub>2</sub> showed a number of signals of <sup>13</sup>P NMR ranging from 15 to 65 ppm, which is in agreement with the multiple reaction sites of PEI with CIPPh<sub>2</sub> and the coupling between P and the N atoms of the backbone.

Reaction of the PEIs premodified with NPPh<sub>2</sub> (PEI-P) in THF with the diiron complexes (1 or 3) led to the polymers functionalized with diiron mimics (PEI-P-Fe<sub>2</sub>) in good yields in most cases (Table 2). Unlike the PEI-Ps, all the PEI-P-Fe<sub>2</sub>s were dark solids and soluble in organic solvents such as dichloromethane and DMF. For the same reasons as for PEI-Ps (Table 1), they also showed



**Scheme 1.** Illustrative representations and preparation of the premodified PEIs and their further functionalization with diiron models (see Tables 1 and 2 for detailed denotations of the macromolecules).





Scheme 2. Illustrative representations and preparation of  $PEI-(CH_2)_{11}$ -O-P and HOOCCH<sub>2</sub>-PEI-P (see Table 1 for detailed denotations of the premodified PEIs).

multi-signals in their <sup>13</sup>P NMR spectra (Table 2 and supporting information, Fig. S3). Recently, we reported a number of polymers functionalized with diiron mimics.<sup>[14,37–39]</sup> Those polymers grafted with either diiron hexacarbonyl units or diiron pentacarbonyl units all exhibited characteristic spectral profiles corresponding to the grafted diiron mimics, although broadening was observed because of a polymeric effect. However, for the polymers reported in this work, the IR spectra are more complicated (Figs 2 and 3). By comparing the spectra of the control complexes (2 and 4, Table 2), it is obvious that the diiron pentacarbonyl units are dominant. However, a sharp absorption band at about 2020  $\text{cm}^{-1}$  suggests that further substitution may be possible to form diiron tetracarbonyl units.<sup>[43]</sup> Either a free NPPh<sub>2</sub> group or N atom from the PEI backbone could complete the second substitution. Therefore, the multiplicity of IR spectra of the polymers is caused not only by the polymeric effect but also by the existence of diiron tetracarbonyl units.

Analyzing iron content suggests a maximum iron content of ~20% and lowest iron content of ~5% (Table 2). It seems that increasing the content of CIPPh<sub>2</sub> in the preparation of PEI-Ps did not proportionally increase the diiron mimics on the PEI-P backbone, but the molar ratios between the Fe and S were calculated as  $0.997 \pm 0.006$ : almost a perfect value of 1:1. This



Figure 2. IR spectra of PEI-P-Fe<sub>2</sub>-A, -B, -C, -D, -E (KBr) and complex 2 (DCM).



**Figure 3.** IR spectra of PEI-P-Fe<sub>2</sub>-B, PEI-P-Fe<sub>2</sub>-B', PEI-P-Fe<sub>2</sub>-B-2, PEI-P-Fe<sub>2</sub>-B'-2, PEI-(CH<sub>2</sub>)<sub>11</sub>-O-P-Fe<sub>2</sub>-B, HOOCCH<sub>2</sub>-PEI-P-Fe<sub>2</sub> (KBr).

suggested that the mimics grafted onto the PEI skeleton via the diphenylphosphine were maintained as a diiron unit.

#### Thermal Stabilities of PEI-Ps and PEI-P-Fe<sub>2</sub>s

The thermal stability of the polymer was evaluated using TGA between 298 and 1073 K under a steady flow of nitrogen. The thermal decomposition of the polymers is shown in Fig. 4. For comparison, TGA of PEI-P was also performed. Like in the case of the polymers with diiron mimics that we reported before,<sup>[14,37–39,43]</sup> attaching the diiron mimics onto the polymers compromises thermal stability. By comparison with the thermal gravimetric trace of PEI-P, the first stage of thermal decomposition of the functionalized polymers was attributed to the diiron carbonyl units. This assignment was further supported by examining the IR absorption bands of CO after the polymers were heated to about 573 K. The residue obtained from heating did not show any CO absorption bands. Compared with analogous functionalized polymers that we reported previously,<sup>[38,39]</sup> the starting temperature of decomposition was evidently higher. This showed that the functionalized polymers with PEI backbone have better thermal stability. The improvement in thermal stability could be attributed to intramolecular and intermolecular hydrogen interactions. Furthermore, flexible PEI chains could also offer a shielding effect against thermal decomposition.<sup>[14]</sup>



**Figure 4.** (a) TGA traces of the polymers PEI-P-Fe<sub>2</sub>-A, -B, -C, -D, -E and PEI-P recorded in nitrogen flow (heating rate  $10^{\circ}$ C min<sup>-1</sup>). (b) TGA traces of the polymers PEI-P-Fe<sub>2</sub>-B, PEI-P-Fe<sub>2</sub>-B', PEI-P-Fe<sub>2</sub>-B-2, PEI-P-Fe<sub>2</sub>-B', 2, PEI-(CH<sub>2</sub>)<sub>11</sub>-O-P-Fe<sub>2</sub>-B, HOOCCH<sub>2</sub>-PEI-P-Fe<sub>2</sub> and PEI-P recorded in nitrogen flow (heating rate  $10^{\circ}$ C min<sup>-1</sup>).

# Electrochemistry of the Functionalized Polymers, PEI-P-Fe<sub>2</sub>s and Their Catalysis on Proton Reduction

Because the functionalized polymers were not sufficiently soluble in acetonitrile, electrochemistry of the functionalized polymers was performed in DMF. Because our main concern was the reduction process and its catalysis on proton reduction, oxidation of these polymers was not examined. Cyclic voltammograms (CVs) of the functionalized polymers and reduction potentials are shown in Fig. 5 and Table 2, respectively. In the CVs shown in Fig. 5, the normalized current (J,  $\mu$ A mg<sup>-1</sup>) is defined as current (i,  $\mu$ A) divided by iron content (mg) calculated using the iron percentage (Fe%, Table 2) to eliminate the influence of the variation in content of the chemically grafted diiron mimics. As shown in the CVs, the electrochemical behavior of these polymers was affected by the content of diiron mimics, the presence of carboxylic acid (HOOCCH<sub>2</sub>-PEI-P-Fe<sub>2</sub>), the distance of the diiron mimics to the PEI backbone (PEI-(CH<sub>2</sub>)<sub>11</sub>-O-P-Fe<sub>2</sub>), and the diiron mimics.

The variation in average molecular weight of PEI did not seem to exert any influence on the electrochemistry (PEI-P-Fe<sub>2</sub>-B and PEI-P-Fe<sub>2</sub>-B'). Conversely, the diiron hexacarbonyl precursor showed a significant influence on the resultant polymers. Reaction of complex **3** with PEI-P resulted in polymers PEI-P-Fe<sub>2</sub>-B-2 and PEI-P-Fe<sub>2</sub>-B'-2, which possessed diiron units analogous to complex **4**. Electrochemically, they behaved very much like complex **4** (Table 2). When complex **1** was used, however, the electrochemical responses of the resultant polymers (PEI-P-Fe<sub>2</sub>-A



**Figure 5.** (a) Cyclic voltammograms of PEI-P-Fe<sub>2</sub>-A (28.6 mg in 3.5 mL) PEI-P-Fe<sub>2</sub>-B (7.9 mg in 3.5 mL), PEI-P-Fe<sub>2</sub>-C (9.0 mg in 3.5 mL), PEI-P-Fe<sub>2</sub>-D (10 mg in 3.5 mL), PEI-P-Fe<sub>2</sub>-E (29 mg in 3.5 mL), PEI-P(7.9 mg in 3.5 mL) and complex **2** ( $C = 4.79 \times 10^{-3} \text{ mol L}^{-1}$ ) in 0.1 mol L<sup>-1</sup> [NBu<sub>4</sub>]BF<sub>4</sub>/DMF at a scanning rate of 0.1 V s<sup>-1</sup> under Ar atmosphere at 298 K. (b) Cyclic voltammograms of PEI-P-Fe<sub>2</sub>-B (7.9 mg, 3.5 mL), PEI-P-Fe<sub>2</sub>-B' (9 mg, 3.5 mL), PEI-P-Fe<sub>2</sub>-B' (9 mg, 3.5 mL), PEI-P-Fe<sub>2</sub>-B' (9 mg, 3.5 mL), PEI-P-Fe<sub>2</sub>-B' (7.9 mg, 3.5 mL), mol L<sup>-1</sup> [NBu<sub>4</sub>]BF<sub>4</sub>/DMF at a scan rate of 0.1 V s<sup>-1</sup> under Ar atmosphere at 298 K.

to PEI-P-Fe<sub>2</sub>-E) were much more complicated (Fig. 6a, b). The most distinctive feature of their electrochemistry, as shown in Fig. 5, was that a few reduction processes appeared at more positive potentials, in addition to the process analogous to that of complex 2 at about -1.4 V. These additional processes were not observed when the content of diiron mimics decreased (PEI-P-Fe<sub>2</sub>-E). As indicated by its reduction potential and IR spectral absorption bands (Table 2), complex 1 and hence 2 are stronger nucleophiles than complexes 3 and 4, respectively. Considering the electron-withdrawing nature of the diiron units in the polymers, supposedly mostly pentacarbonyl, the reduction potential of a diiron unit would be driven positively by its surrounding diiron units. Such an effect would certainly be less important when the diiron content decreased (PEI-P-Fe<sub>2</sub>-E), and therefore, its reduction behaved more simply compared with those of the others (Fig. 5a). Increasing the distance of the diiron units to the PEI backbone did not show any drastic change in electrochemistry, as shown by the CV of polymer PEI-(CH<sub>2</sub>)<sub>11</sub>-O-P-Fe<sub>2</sub>-B (Fig. 5b).

To examine the catalytic behavior of the functionalized polymers, we performed their electrochemical catalysis on proton reduction in DMF in the presence of acetic acid. As already



**Figure 6.** (a) Curve of PEI-P-Fe<sub>2</sub>-A (5.8 mg in 3.5 mL), PEI-P-Fe<sub>2</sub>-B (7.9 mg in 3.5 mL), PEI-P-Fe<sub>2</sub>-C (9 mg in 3.5 mL), PEI-P-Fe<sub>2</sub>-D (10 mg in 3.5 mL), PEI-P-Fe<sub>2</sub>-E (29 mg in 3.5 mL) and complex **2** ( $C = 4.79 \times 10^{-3}$  mmol mL<sup>-1</sup>) in 0.1 mol L<sup>-1</sup> [NBu<sub>4</sub>]BF<sub>4</sub>/DMF at a scanning rate of 0.1 V s<sup>-1</sup> under Ar atmosphere at 298 K. (b) Curve of PEI-P-Fe<sub>2</sub>-B (7.9 mg, 3.5 mL), PEI-P-Fe<sub>2</sub>-B' (8.6 mg, 3.5 mL), PEI-P-Fe<sub>2</sub>-B (2.8 mg, 3.5 mL), PEI-P-Fe<sub>2</sub>-B'-2 (7.5 mg, 3.5 mL), PEI-P-Fe<sub>2</sub>-B (8.5 mg, 3.5 mL), HOOCCH<sub>2</sub>-PEI-P-Fe<sub>2</sub> (5.7 mg, 3.5 mL) and complex **2** (4.79 × 10<sup>-3</sup> mmol mL<sup>-1</sup>) in 0.1 mol L<sup>-1</sup> [NBu<sub>4</sub>]BF<sub>4</sub>/DMF at a scanning rate of 0.1 V s<sup>-1</sup> under Ar atmosphere at 298 K.

mentioned in the discussion of their electrochemistry, catalytic currents were normalized by dividing the current by the iron content. All CVs of the catalysis are shown in the supporting information, Figs S4 and S5. As shown by the CVs, all the functionalized polymers showed no substantial catalysis in response to the reduction processes of potentials more positive than about -1.8 V in the presence of acetic acid. Instead, a catalytic process was often observed at about -2.2 V. In some cases, catalytic current increased so strongly that no wave-shaped process could be observed. To compare the catalytic efficiency of the functionalized polymers, we plotted normalized current  $(J, \mu A mg^{-1})$  against added acetic acid. Considering that not in all cases could a peak catalytic current be read, a current at -2.17 V in all cases was read and divided by the iron content in the sample. For reasons of clarity and categorization, plots of normalized current J versus acetic acid volume (µl) for polymers PEI-P-Fe<sub>2</sub>-A to PEI-P-Fe<sub>2</sub>-E and the others are shown in Fig. 6(a) and (b), respectively.

The normalized current versus the volume of the acid added as shown in Fig. 6(a) suggests that the functionalized polymers (PEI-P-Fe<sub>2</sub>-A, PEI-P-Fe<sub>2</sub>-C, and PEI-P-Fe<sub>2</sub>-D, Table 2) with high iron content show better catalytic performance. There is no straightforward explanation for this. One possible cause is that evolution of one hydrogen molecule via catalytic reduction of proton involves the transfer of two proton and electrons stepwise, respectively. Synergistic actions among the diiron units could enhance the catalysis and, therefore, high-density polymers (high iron content) showed better catalytic efficiency.

Interesting results are further found in Fig. 6(b). As indicated by the normalized current at 70 µl of the acid, either varying PEI (average molecular weight of 1800 and 600, respectively) or diiron complex (1 and 3, respectively) in the functionalization of the polymers did not significantly improve the catalytic performance. The other two functionalized polymers - PEI-(CH<sub>2</sub>)<sub>11</sub>-O-P-Fe<sub>2</sub>-B and HOOCCH<sub>2</sub>-PEI-P-Fe<sub>2</sub> – however, showed improvement in catalytic performance. In particular, the latter was derived using the same PEI-P-B precursor as for the preparation of PEI-P-Fe<sub>2</sub>-B, but its normalized current increased by over one-fold. For PEI-(CH<sub>2</sub>)<sub>11</sub>-O-P-Fe<sub>2</sub>-B, the long aliphatic chain, -(CH<sub>2</sub>)<sub>11</sub>-, increases the flexibility of the catalytic site (diiron center). This flexibility could be beneficial to the catalysis because the involvement of transfer of multiple protons and electrons per hydrogen molecule requires structural rearrangement of the catalyst during catalysis. The results show that the basic groups of PEI help in improving catalytic efficiency by taking part in proton transfer. Carboxylic acid ought to be a better proton donor than the protonated amine group. Therefore, it is not surprising that the functionalized polymer, HOOCCH<sub>2</sub>-PEI-P-Fe<sub>2</sub>, exhibited much higher catalytic efficiency than PEI-P-Fe<sub>2</sub>-B.

## Conclusions

In this study, we employed PEI to construct a mimicking system for [FeFe]-hydrogenase. PEI was not only used as a scaffold to support diiron mimics but also its basicity was exploited to improve proton transfer in catalysis. Electrochemical investigation into the seven functionalized polymers suggests that the amine groups of PEI played a role in increasing catalytic efficiency by improving proton transfer. Further enhancement in proton transfer was achieved by introducing carboxylic acid onto the skeleton of PEI, and the catalytic performance was improved by over one-fold. By dangling the catalytic unit onto the backbone of PEI via a long aliphatic chain, catalytic efficiency was also improved because of the increase of flexibility of the catalytic units (diiron mimics). The flexibility allows a feasible structural rearrangement of the catalytic center, which during catalysis, is required by the catalytic process involving multiple proton and electron transfers for the evolution of each hydrogen molecule. Compared with the system based on PVC we reported recently,<sup>[37]</sup> the PEI-derived functionalized polymers enjoy several advantages: (i) These polymers are highly hydrophilic. (ii) The rich primary and secondary amine groups allow diverse functionalization to further tailor the PEI-based systems, for example, immobilizing quantum dot to construct a photocatalytic system or functionalizing with an electron mediator to enhance electron transfer. Thus, utilizing PEI to develop artificial systems inspired by [FeFe]-hydrogenase deserves further exploration.

### Supporting information

Supporting information may be found in the online version of this article.

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