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## COMMUNICATION

## Distant protonated pyridine groups in water-soluble iron porphyrin electrocatalysts promote selective oxygen reduction to water†

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Fe(III)-*meso*-tetra(pyridyl)porphyrins are electrocatalysts for the reduction of dioxygen in aqueous acidic solution. The 2-pyridyl derivatives, both the triflate and chloride salts, are more selective for the desired  $4e^-$  reduction than the isomeric 4-pyridyl complexes. The inward-pointing pyridinium groups influence proton delivery despite their distance from the iron centre.

Fuel cells are an attractive approach to improved energy efficiency but their widespread application will require inexpensive catalysts rather than the current use of substantial amounts of platinum. Catalysis of the oxygen reduction reaction (ORR), eqn (1), is particularly challenging because of the complexity of the  $4e^-/4H^+$  reaction, the high thermodynamic potential, and the need for high selectivity.<sup>1</sup> The competing  $2e^-/2H^+$  reduction of  $O_2$  to  $H_2O_2$  is less exoergic and the  $H_2O_2$  is potentially corrosive and hazardous.



Described here are soluble iron *meso*-tetra(pyridyl)porphyrin electrocatalysts for the ORR in acidic water. Iron-porphyrin compounds have been widely used for the ORR.<sup>2,3</sup> We have included pyridyl groups with the goal of affecting proton addition to  $O_2$ -derived ligands at the iron centre. Proton relays have less frequently been used for the ORR, from with the early ‘hangman’ porphyrin and corrole ORR electrocatalysts of Nocera.<sup>4</sup> The phosphine–amine ligands of DuBois are well-positioned for  $O_2$  chemistry but are not oxidatively stable.<sup>5–7</sup> Iron *meso*-tetra(2-carboxyphenyl)porphyrin is an unusually selective ORR electrocatalyst, apparently due to the positioning of the carboxylic acid groups.<sup>8</sup>

Fe(III)-*meso*-tetra(2-pyridyl)porphyrin (**1**, Fig. 1) is an unlikely addition to this group of electrocatalysts because the inward-pointing pyridyl nitrogens are quite distant from

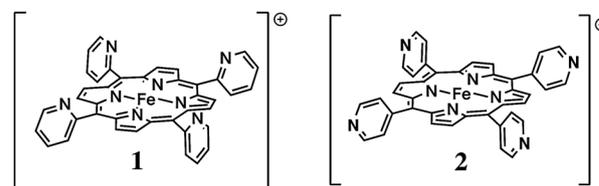


Fig. 1 Electrocatalysts **1** and **2**, triflate ions omitted.

the iron centre (see below). To test the influence of these pyridyl groups, **1** is compared with the outward pointing 4-pyridyl isomer **2**. These complexes, and their chloride analogues **1Cl** and **2Cl**, are active and selective catalysts for the ORR in acidic water, albeit at substantial overpotentials. Despite the poor positioning of the 2-pyridyl substituents, **1** and **1Cl** are significantly more selective for the desired  $4e^-$  reduction of  $O_2$  than **2/2Cl**.

The triflate derivatives **1/2** have been prepared by treatment of **1Cl/2Cl** with AgOTf (see ESI†). These complexes have not been previously examined as ORR electrocatalysts, although Kuwana has studied the ORR by the tetra-*N*-methylated-4-pyridyl derivative.<sup>3</sup> Compounds **1** and **2** are soluble in aqueous solutions that are sufficiently acidic to protonate the pyridyl groups ( $pH < 2$ ).

Cyclic voltammograms (CVs) of **1** or **2**, 0.30 mM in pH 0.3 aqueous triflic acid (HOTf), have been obtained using a glassy carbon working electrode (Ag/AgCl/sat. KCl reference electrode; all potentials reported vs. NHE). Both compounds show a quasi-reversible Fe(III/II) couple, at 250 mV and 150 mV,<sup>11</sup> respectively (Fig. 2 and Fig. S6 and S7, ESI†). In the presence of  $O_2$ , CVs of the same solutions show irreversible waves with much larger currents,  $\sim 20$  and  $\sim 50$  times larger for **1** and **2** under 1 atm  $O_2$ . The currents are larger under 1 atm of pure  $O_2$  vs. under air (1.3 vs. 0.27 mM  $O_2$ ).<sup>12</sup> The onsets of the cathodic currents correspond well with those of the corresponding Fe(III/II) couples. Taken together, the loss of reversibility, the large increase in reductive current, and the  $O_2$ -dependence all indicate rapid electrocatalytic oxygen reduction.

The traditional shape of the CV under  $N_2$  (Fig. 2 inset) suggests a soluble electrocatalyst, and we tested for adsorption on the glassy carbon electrode (as occurs with hydrophobic iron-porphyrins<sup>13</sup> but is less likely for the polycationic **1** and **2** in acid<sup>14</sup>). A scan was done under catalytic conditions, the electrode was removed, rinsed with deionized water and placed

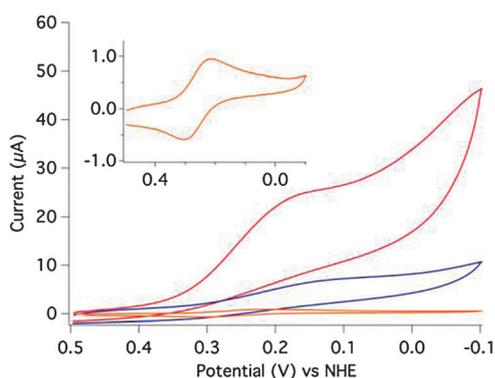
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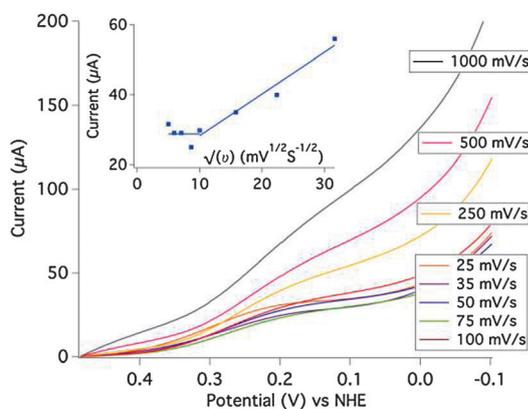


**Fig. 2** CVs of **1** (0.30 mM, 0.5 M HOTf) under: N<sub>2</sub> (orange [bottom]), air (blue [middle], 0.27 mM O<sub>2</sub>) and 1 atm of O<sub>2</sub> (red [top], 1.3 mM O<sub>2</sub>). Inset: CV under N<sub>2</sub> enlarged.

in a fresh 0.5 M HOTf solution. Scans on these unpolished electrodes showed an irreversible wave under air of similar shape to that seen in the presence of dissolved **1** or **2**, but with a significantly lower current (Fig. S8, ESI<sup>†</sup>). Thus some adsorption to the glassy carbon electrode may be occurring but it does not appear to be the primary contributor to the electrocatalysis.

The turnover frequency (TOF) of a soluble electrocatalyst can be calculated from the ratio of catalytic ( $i_c$ ) to non-catalytic currents ( $i_p$ ) when the catalysis occurs under kinetic conditions where substrate diffusion is not limiting<sup>15</sup> (see ESI<sup>†</sup>). To achieve kinetic conditions, CVs of **1** and **2** were obtained in a pressure vessel under 68 atm O<sub>2</sub> to achieve high substrate : catalyst ratios: 88 mM O<sub>2</sub> : 500 mM H<sup>+</sup> : 0.10 mM **1**. Under these fairly extreme conditions, the catalytic currents were independent of scan rate between 25 and 100 mV s<sup>-1</sup> (Fig. 3), indicating kinetic conditions. With the assumption that **1** is acting purely as a soluble catalyst, the  $i_c/i_p$  of  $\sim 110 + 0.2 \text{ V}$  at 100 mV s<sup>-1</sup> implies a TOF of  $\sim 600 \text{ s}^{-1}$  (see ESI<sup>†</sup>). In contrast, CVs of the 4-pyridyl catalyst **2** under the same conditions are still limited by diffusion (Fig. S15 and S16, ESI<sup>†</sup>). This implies that higher dioxygen pressures would further increase the peak current, and indicates that **2** is a faster electrocatalyst than **1**.

While **1** and **2** are rapid electrocatalysts for the ORR, they operate at quite high overpotentials. The onset of the reductive



**Fig. 3** Background-corrected linear sweep voltammograms of 0.10 mM **1** in 0.5 M HOTf under 68 atm O<sub>2</sub> at varying scan rates  $v$ . For non-background-corrected versions, see Fig. S11–S20, ESI<sup>†</sup>. Inset: Plot of  $i$  at  $+0.2 \text{ V}$  vs.  $v^{1/2}$ .

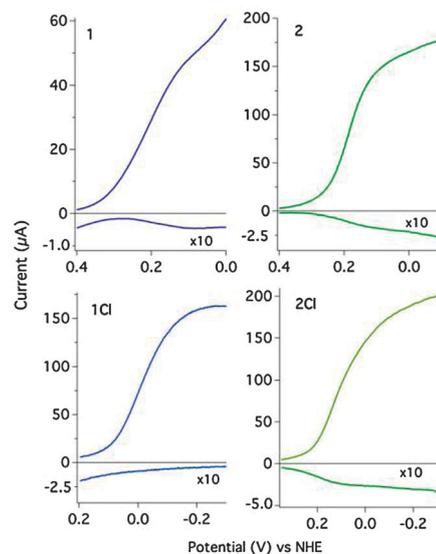
wave for **1**,  $\sim +0.4 \text{ V}$  vs. NHE, is  $\sim 0.8 \text{ V}$  below the thermodynamic potential. Complex **2** has a  $\sim 100 \text{ mV}$  higher overpotential. High overpotentials are typical for iron porphyrin ORR catalysts, with even cytochrome *c* modified electrodes having  $\geq 0.7 \text{ V}$  onset overpotentials at pH 7.<sup>16</sup>

The selectivity of these dioxygen reduction catalysts was probed using rotating ring-disk voltammetry (RRDV), following Kuwana's study of the closely related iron *meso*-tetra(*N*-methyl-4-pyridinium porphyrin).<sup>3</sup> The potential of the disk electrode was scanned while the ring electrode was poised at  $+1.19 \text{ V}$  to oxidize the H<sub>2</sub>O<sub>2</sub> formed. For **1** and **2**, a ring current was observed that closely mirrors the ORR current at the disk (Fig. 4), indicating H<sub>2</sub>O<sub>2</sub>. Quantitative analysis of the currents and the collection efficiency of the RRD (see ESI<sup>†</sup>) indicates that **1** produces 5% H<sub>2</sub>O<sub>2</sub>. Complex **2** produces over twice this amount, 11% H<sub>2</sub>O<sub>2</sub>.

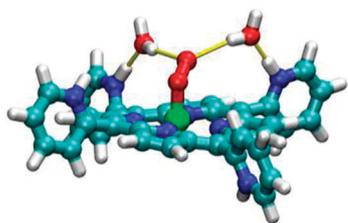
The chloride complexes **1Cl** and **2Cl** are also rapid ORR electrocatalysts in acidic water (in this case 0.25 M HCl/0.5 M KCl; see ESI<sup>†</sup>). RRDV experiments under 1 atm O<sub>2</sub> show the 4-pyridyl isomer **2Cl** produces  $\sim 15\%$  H<sub>2</sub>O<sub>2</sub>, similar to **2** in HOTf. The 2-pyridyl isomer **1Cl**, however, shows essentially no onset of ring current as the disk is scanned through the O<sub>2</sub>-reduction wave (Fig. 4 bottom left).

The high selectivities of these pyridyl catalysts for 4e<sup>-</sup> reduction of O<sub>2</sub> are in marked contrast with Kuwana's results on the closely related *meso*-tetrakis(*N*-methyl-4-pyridinium)-porphyrin catalyst.<sup>3</sup> Essentially all of the O<sub>2</sub> reduction with that catalyst proceeded *via* H<sub>2</sub>O<sub>2</sub>, from pH 1–13 (in H<sub>2</sub>SO<sub>4</sub>, phosphate or borate buffers, or NaOH). Their RRDV experiments at pH 9 showed 95% H<sub>2</sub>O<sub>2</sub>.<sup>3b</sup>

It is remarkable that there is such a dramatic effect upon changing from CH<sub>3</sub><sup>+</sup> to H<sup>+</sup> at the 4-pyridyl nitrogen that is very distant from the iron centre. It is also interesting that the 2-pyridyl catalysts have higher selectivities than the 4-pyridyl isomers. Electrocatalysis by **1** makes half as much H<sub>2</sub>O<sub>2</sub> as that by **2**, and **1Cl** makes essentially no H<sub>2</sub>O<sub>2</sub> while **2Cl** gives



**Fig. 4** RRDVs under 1 atm O<sub>2</sub>, with the ring current magnified  $\times 10$ . Top: **1** (left) and **2** (right) (0.3 mM, 0.5 M HOTf) with a rotation rate  $\omega$  of 2000 rpm and a disk scan rate  $v$  of 250 mV s<sup>-1</sup>. Bottom: **1Cl** and **2Cl** (0.3 mM) in 0.5 M KCl/0.25 M HCl solutions, with  $\omega = 3000 \text{ RPM}$  and  $v = 250 \text{ mV s}^{-1}$ .



**Fig. 5** Representative structure for  $[\text{Fe}\{\text{porphyrin}(\text{pyH})_4\}(\text{O}_2)(\text{H}_2\text{O})_2]^{4+}$  in water.

$\sim 15\%$   $\text{H}_2\text{O}_2$ . These effects are likely due to differences in the proton delivery to  $\text{O}_2$ -derived intermediates in the catalytic cycle. This is reminiscent of the effects of proton delivery to  $\text{FeOOH}$  intermediates in cytochrome P450 enzymes.<sup>17</sup>  $\text{H}^+$  delivery to the distal oxygen facilitates O–O bond cleavage, while mutations allow protonation of the proximal oxygen and lead to  $\text{H}_2\text{O}_2$ .

Proton delivery is kinetically significant under the high pressure conditions discussed above: reducing the HOTf concentration from 0.5 to 0.25 M reduces the catalytic current by a roughly a factor of two (Fig. S17 and S18, ESI†). In contrast, under 1 atm  $\text{O}_2$  when currents are limited by diffusion of  $\text{O}_2$  to the electrode, changes in acid concentration from pH 0 to 1 caused little change in the CVs of **1** or **2**.

Computations have explored how the 2-pyridyl substituents in **1** affect proton delivery. Density functional theory calculations (see ESI† for relevant details) indicate that the tetraprotonated Fe(II) derivative binds  $\text{O}_2$ , and that the pyridinium protons are much too far to hydrogen-bond to the  $\text{O}_2$  ligand. In a representative conformer of  $[\text{Fe}\{\text{porphyrin}(\text{pyH})_4\}(\text{O}_2)]^{4+}$ , the closest  $\text{pyH}^+\cdots\text{O}$  distance is 3.80 Å, with an  $\text{N}\cdots\text{O}$  distance of 4.56 Å. Complexes with added water molecule(s) optimize to place  $\text{H}_2\text{O}$  in between the pyridinium and the bound  $\text{O}_2$ ; one such structure is shown in Fig. 5. Even in this structure, the  $\text{OH}\cdots\text{O}$  hydrogen bonding is weak, with long  $\text{H}\cdots\text{O}$  distances of 2.2 and 2.3 Å. When more water molecules are included, the pyridinium ions seem to organize them into a cluster around the  $\text{O}_2$  ligand, but additional computations are needed to better define the solvation structure around the  $\text{O}_2$  ligand.

In the iron(II) complex  $[\text{Fe}\{\text{porphyrin}(\text{pyH})_4\}]^{4+}$ , the computed  $\text{p}K_{\text{a}}$  for the pyridinium groups is about 4.4. The protons needed for the reduction of  $\text{O}_2$  thus may come from the acidic solution (pH  $\sim 0.5$ ) rather than from the pyridinium groups. This would imply that the pyridinium cations act not as proton relays but in a more subtle fashion, affecting other protons in the second coordination sphere. Computations to explore this issue are in progress.

Iron *meso*-tetra(pyridyl)porphyrin complexes are rapid and selective electrocatalysts for the ORR. Under 68 atm  $\text{O}_2$  (88 mM) in 0.5 M HOTf, cyclic voltammograms for **1** and **2** suggest turnover frequencies of *ca.* 600  $\text{s}^{-1}$  or more. Electrocatalysts **1** and **1Cl**, with the pyridyl nitrogens pointing toward the iron centre, are  $>95\%$  selective for the desired  $4e^-$  reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}$ . The isomeric 4-pyridyl complexes have somewhat lower selectivity ( $\sim 85\text{--}89\%$ ) and the related *tetrakis*-4-methyl-pyridinium derivative was found by Kuwana to give almost exclusively  $\text{H}_2\text{O}_2$ .<sup>3</sup>

The substantial effects of the regiochemistry of the pyridinium acids and of replacing  $\text{H}^+$  for  $\text{CH}_3^+$  are surprising given

the large distances of the pyridyl nitrogens from the iron centre. Unlike previous electrocatalysts with proton relays, the pyridyls are very poorly positioned to serve that function. The ability of the protonated ligands to affect the proton delivery is especially surprising because catalysis occurs in acidic water, pH  $< 1$ , where proton transfer would be expected to be particularly facile. These results point toward a more subtle role for groups introduced as proton relays in multielectron/multiproton catalysis.

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