Iron Porphyrins as Models of Cytochrome *c* Oxidase

David Ricard,[a] Maurice L'Her,[b] Philippe Richard,[a] and Bernard Boitrel*[a]

Abstract: A series of iron porphyrins has been synthesized as models of cytochrome *c* oxidase; their activity as $4e^-$ catalysts in the reduction of dioxygen has been studied at pH 7. These compounds have been obtained by grafting very different residues onto the same iron complex, namely tripodal tetraamines, pickets, and straps, in order to change the environment of the metal center. In the case of porphyrins bearing a tripodal cap, the secondary amines have been alkylated with different substituents so as to modify the electronic environment of the distal pocket. Surprisingly, when the iron porphyrin is functionalized with four identical acrylamido pickets, the resulting complex exhibits biomimetic activity in that it catalyzes oxygen reduction with almost no production of hydrogen peroxide. The crystal structure of the redox-inactive zinc(II) analogue is reported; this shows how the metal influences the spatial arrangement of the four pickets through axial coordination and hydrogen bonding. Even a bis-strapped iron porphyrin, for which no dimerization or self-aggregation can occur at the electrode surface, acts as a $4e^-$ catalyst for O_2 reduction. It is thus demonstrated that at pH close to physiological values, the iron porphyrin is an intrinsically efficient catalyst for the reduction of oxygen to water.

Keywords: cytochrome *c* oxidase · dioxygen activation · electrochemistry · heme proteins · model compounds · structure–activity relationships

Introduction

In nature, the four-electron reduction of dioxygen is effected by cytochrome *c* oxidase (C*c*O). For this reduction process, of eight protons effectively taken out of the mitochondria through the membrane, only four are consumed, so that the enzyme is also referred to as "proton-pumping oxido-reductase".[1] The structure of its active site was unambiguously elucidated in 1995.[2] However, the role of the copper Cu_B in the vicinity of the heme a_3 remains a subject of debate. According to some authors, the Cu center plays an essential role in the catalytic process so that a model cannot be regarded as biomimetic unless it includes both an iron porphyrin and a copper complex. This led to intense activity in the design and synthesis of many elaborate molecules, which have been cleverly designed and skillfully made and which all have two metal coordination sites close to each other to favor the binding of an O_2 molecule.[3] On the other hand, the possibility that the copper ion does not participate in the catalytic reduction of O_2 has been considered by Rousseau.[4] The refinement (at 2.35 Å) of the structure of the enzyme led Yoshikawa[5] to almost the same conclusion, even though the role attributed to copper by these two authors was not exactly the same. We have previously reported the results of some experiments on porphyrins capped with a tris(2-aminoethyl)-amine (tren) motif[6] as functional models for cytochrome *c* oxidase; we examined their potential as catalysts for the electrochemical reduction of O_2. These studies showed that the presence of an intramolecular nitrogen base as a potential axial ligand for the iron of the heme is not a prerequisite for the catalytic activity. A surprising finding was that the iron-only complexes, without copper bound to the tren, proved to be efficient catalysts for the $4e^-$ reduction of O_2. As cooperativity between the two metals of the enzymatic redox center in O_2 reduction, through the μ-bonding of O_2, is a sound hypothesis, we suggested that in a model system without copper, a hydrogen bond between the O_2 molecule bound to the heme and the protonated secondary amino groups could favor the $4e^-$ reduction process.

At this point of our study of synthetic models of cytochrome *c* oxidase (C*c*O), it appeared crucial to assess the various hypotheses concerning the redox center and its efficiency as a catalyst in the reduction of O_2. It was important to know which conditions are essential to drive the reduction through the $4e^-$ process at a pH close to physiological value.

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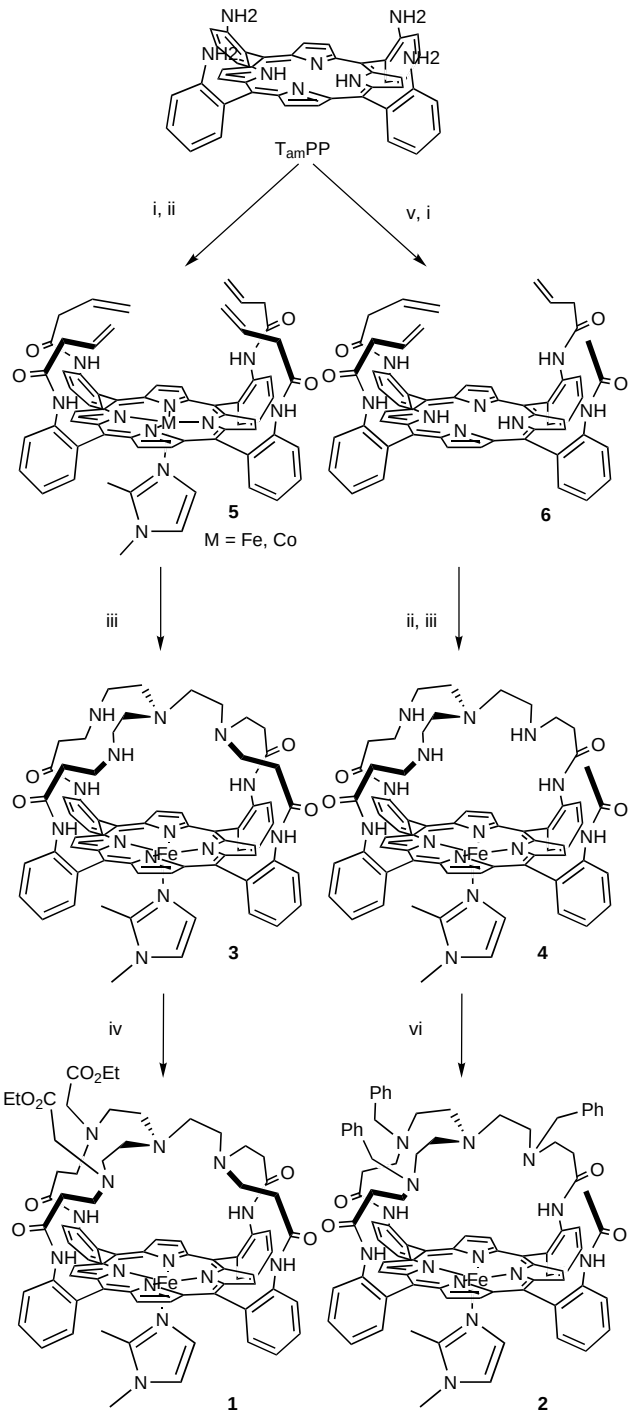
The following questions need to be addressed: i) Are the amino groups of the tren-capped porphyrins involved? ii) Does the tren tripod structure provide a hydrophobic environment above the iron porphyrin, favorable to the binding of O_2 and to its reduction? iii) As the moiety mimicking the heme a_3 of the enzyme is an Fe porphyrin, and as some Co porphyrins, under particular conditions, are known to be efficient catalysts for the reduction of O_2, is iron essential? These questions prompted the present studies on alkyl-tren capped, picket, and bis-strapped iron and cobalt porphyrins. We set out to ascertain whether they are efficient for the reduction of O_2 to H_2O and whether they represent synthetic analogues of the heme a_3 active site of C*c*O.

Results and Discussion

If the amino groups of the tren-capped porphyrins participate in the O_2 activation, through hydrogen bonding between the protonated amine and O_2 bound to the iron porphyrin, then substituents on the amino groups should significantly influence the catalytic activity at the surface of an electrode. The effect of the surrounding environment of the heme has been precisely studied for cytochrome *c* models;[7] slight electronic effects in the distal cage should, of course, substantially affect the activity of the C*c*O model catalyst. Of the alkyl-tren capped porphyrins which have been synthesized to date, two new complexes have distal structures that differ only in the nature of the alkyl group grafted onto the amine functions of the tren[8] (compounds **1** and **2**, Scheme 1). Compounds **1** and **2** were prepared by a simple synthetic pathway which has previously been used to obtain **3**, the compound that we will consider in this work as a reference catalyst for the $4e^-$ reduction of O_2[9] [actually, at physiological pH, almost no hydrogen peroxide is produced when **3** is used as a catalyst, an efficiency comparable with that of $[Co_2(FTF4)]$ (FTF4 = face-to-face 4-atom-bridged porphyrin) at low pH].[10] Compounds **1** and **2** were prepared by attaching a tren moiety to the picket-porphyrins **5** and **6**, followed by alkylation of the

Abstract in French: *Plusieurs porphyrines de fer ont été synthétisées comme modèles de la cytochrome c oxydase; leur activité, en tant que catalyseur de la réduction à $4e^-$ de l'oxygène moléculaire a été étudiée à pH 7. Ces composés ont été obtenus par greffage de motifs structuraux très différents sur la même porphyrine de fer, afin de changer l'environnement de celle ci par des tétraamines tripodales, des piquets, et des anses. Dans le cas des porphyrines portant un tripode, les amines secondaires ont été alkylées par différents substituants afin de modifier l'environnement électronique de la poche distale. De façon surprenante, quand la porphyrine de fer est fonctionnalisée par quatre piquets identiques de type acrylamido, le complexe obtenu présente une activité biomimétique, puisqu'il catalyse la réduction de l'oxygène moléculaire avec une très faible production de peroxyde d'hydrogène. La structure radiocristallographique de l'analogue de zinc(II), électrochimiquement inactif, est décrite; elle montre comment le métal influence l'arrangement spatial des quatre piquets par l'intermédiaire de la coordination axiale et de liaisons hydrogène. Même une porphyrine de fer à deux anses, pour laquelle aucune dimérisation ou agrégation ne peut avoir lieu à la surface de l'électrode, est un catalyseur à $4e^-$ pour la réduction de l'oxygène moléculaire. Il est donc démontré qu'à un pH proche des valeurs physiologiques, la porphyrine de fer, en elle-même, est un catalyseur efficace pour la réduction de l'oxygène en eau.*



Scheme 1. Synthesis of two substituted iron(II) tren-capped porphyrins. i) CH_2=$CHCOCl$, NEt_3, THF; ii) $FeBr_2$ or $CoCl_2$, 2,6-lutidine, THF, 55 °C, glove-box; iii) tren, MeOH, 50 °C; iv) $BrCH_2CO_2Et$, DBU, THF, 55 °C; v) CH_3COCl, NEt_3, THF, 0 °C; vi) benzyl bromide, THF, NEt_3.

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secondary amino groups of **3** and **4**, respectively, with ethyl 2-bromoacetate or benzyl bromide; the general procedure for this synthesis is summarized in Scheme 1. Porphyrin **2** was prepared with two different goals in mind, the first being to test the activity of the iron-only complex, in view of the fact that the iron–copper analogue is an efficient $4e^-$ catalyst.[3c, 3f] The second goal was to compare it with the iron complexes **1** and **3**, in order to verify whether electronic effects on the distal cage, due to different substituents on the amino groups (H-, benzyl, or ethyl acetate), affect the activity of the catalyst. The compounds were tested as catalysts for O_2 reduction by using a rotating ring–disk electrode (RRDE). The molecules were adsorbed on the disk electrode, which was the section of a highly ordered graphite rod, the planes of graphite being perpendicular to the surface of the electrode (this is often called an edge-plane graphite electrode, EPGE). The potential of this modified graphite electrode was scanned from high to lower values so as to record the voltammogram for the reduction of O_2. Under the experimental conditions used for these experiments (see Experimental Section), a $2e^-$ reduction of O_2 produced a plateau current of about 350 μA. The graphite electrode was surrounded by a platinum ring electrode, the potential of which was set at a fixed value such that H_2O_2 eventually produced at the disk was oxidized; when O_2 was completely reduced to H_2O_2, the ring current reached a plateau at 175 μA. As illustrated by curve c in Figure 1, the

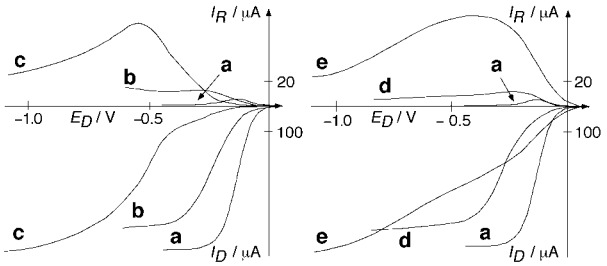

Figure 1. Rotating ring–disk voltammograms for O_2 reduction; graphite disk impregnated with **3** (a), **1** (b), **2** (c), **5Fe** (d), and **5Co** (e) with 1,2-Me_2Im as an exogenous base; pH 6.86; I_R and I_D = current of the ring and disk, respectively; E_D = electropotential of the disk; Nr = 100 rpm; reference: SCE; $p(O_2)$ = 1 atm; potential of the platinum ring electrode: 0.8 V. At disk: reduction of O_2 to H_2O or H_2O_2. At ring: oxidation of H_2O_2 produced at disk.

iron-only complex of porphyrin **2** is a $4e^-$ catalyst, even if a significant amount of H_2O_2 is produced before the plateau is reached. This result is particularly important because it demonstrates that the presence of copper in the distal coordination site is not essential. The second observation concerns the reduction overpotential, which is larger for **1** (curve b) and much more important for **2** (curve c) than it is for **3** (curve a). It seems that alkylation of the secondary amine by an ethyl acetate group does not significantly modify the activity of the catalyst, whereas alkylation by a benzyl group induces a 0.5 V shift of the overpotential. Nevertheless, both $2e^-$ (catalase-like) and $4e^-$ (C*c*O-like) mechanisms are simultaneously operative for **1** and **2**. Apparently, the catalyst is more efficient when it bears secondary amino groups instead of tertiary amines. However, these results should be interpreted with caution as the substitution could influence the adsorption of the catalysts on graphite and, thus, the number of catalytic sites on the electrode, which would modify the overpotential.

Based on these observations, it seems reasonable to consider other structures different from these tren-capped porphyrins. Could it be possible that a simpler structure, without the amino groups present in compounds **1**–**4**, might also induce the four-electron reduction? If so, compound **8**, the milestone picket-fence porphyrin, known to favor the binding of O_2 by creating a hydrophobic distal cage, should be an active model of C*c*O.[11] This should also be the case for the iron complex of the picket porphyrin **5**, the precursor of the capped porphyrin **3**. Curve d in Figure 1 indicates that the iron derivative **5Fe** is a rather effective $4e^-$ catalyst for O_2 reduction, just as effective as **3**. Surprisingly, **8** exhibits a predominantly $2e^-$ reduction, as shown by curve g in Figure 2,

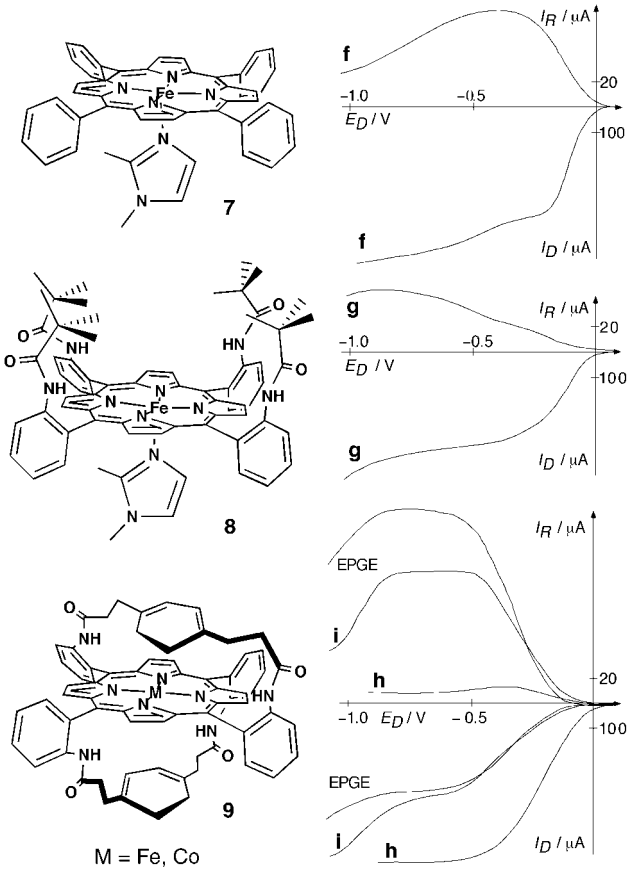

Figure 2. Three known porphyrins evaluated as potential catalysts by rotating ring–disk voltammetry; **9Fe** (h), **9Co** (i), bare graphite electrode (EPGE).

with a disk limiting current even lower than that observed for [Fe(TPP)(1,2-Me_2Im)] (**7**: TPP = tetraphenylporphyrin, 1,2-Me_2Im = 1,2-dimethylimidazole; curve f, Figure 2). From the very different behavior of the two picket porphyrins examined, **5** and **8**, we conclude that the picket-fence does not play a decisive role. However, it has to be noted that the acrylamido pickets of **5** could adopt a conformation inacces-

sible to the pivalamido pickets of **8**. The crystal structure of **5Zn**, an analogue of **5Fe** with a redox-inactive metal, shows that the porphyrin is slightly saddle-shaped and that the coordinated water molecule is stabilized by a hydrogen-bond network (Figure 3).[12] However, this simple observation is not

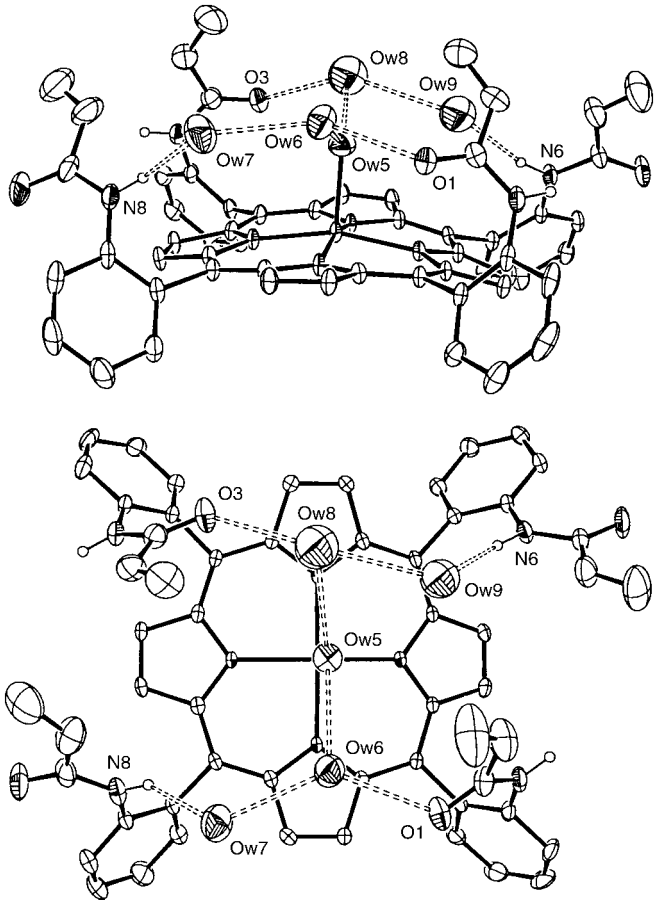

Figure 3. ORTEP representation of the solid-state structure of **5Zn** (top: side view; bottom: apical view; for clarity, ellipsoids are drawn at a 30% probability level).

supportive of the latter hypothesis. On the other hand, it has recently been reported that, in the case of the cobalt picket-fence porphyrin, that is, the cobalt(II) analogue of **8** with 1-methylimidazole as the fifth ligand instead of 1,2-dimethylimidazole, at low pH, the four bulky pickets seem to hinder the catalytic activity in the electroreduction of O_2.[13]

None of the features that we have carefully examined seems to be essential for the catalysis of the electroreduction of O_2 to H_2O other than the iron porphyrin that mimics the heme a_3 of C*c*O. Metalloporphyrins other than the iron derivatives are potential catalysts for O_2 reduction; the properties of these compounds depend on environmental factors such as pH or their ability to form μ-oxo derivatives. For example, [Fe(TPP)], which is known to be a $4e^-$ catalyst at pH 1,[14] is not as efficient at pH 6.86 when coordinated by one molecule of 1,2-dimethylimidazole (compound **7**, curve f, Figure 2).[15] It is for this reason that the catalytic behavior of porphyrin **5Co** has been investigated. From the comparison of curves d and e in Figure 1, it is evident that the cobalt derivative becomes a $4e^-$ catalyst only at very negative potentials and produces much more H_2O_2 than the iron complex **5Fe** when the O_2 reduction starts. It has previously been reported that the replacement of iron by cobalt in such monometallic systems leads to loss of the $4e^-$ reduction activity.[16] Consequently, it seems that for this type of catalyst, iron cannot be replaced by cobalt, and, hence, is a requisite element. It might be argued that the $4e^-$ reduction occurs through self-assembly into dimeric structures on the electrode surface, as has been demonstrated in several studies.[17] This may happen for all the $4e^-$ catalysts studied in the present work (Scheme 1), by O_2 fixation on the side of the porphyrin opposite to the picket-fence or the tren pocket after decoordination of the proximal nitrogen base. This possibility also exists for all the functional models previously described in the literature.[3] For this reason, compound **9** (Figure 2) has been studied. This basket-handle porphyrin, initially synthesized by Momenteau et al.,[18] has no axial base at all; it is known that this molecule cannot form a μ-oxo derivative and is not oxidized by O_2 according to an intermolecular mechanism.[19] From curve h in Figure 2, it would appear that **9Fe** is a $4e^-$ catalyst as efficient as **3**, with no production of H_2O_2 at the potential at which the plateau is reached. Unquestionably, this result indicates that, at pH 6.86, the reduction of O_2 to H_2O can be mediated by a single iron porphyrin and occurs without the formation of any dimer. The cobalt analogue **9Co**, however, exhibits almost the same catalytic efficiency as the bare electrode (curve i, Figure 2), confirming that single cobalt porphyrins can apparently only act as $4e^-$ active catalysts through self-assembly on the electrode surface.[17c]

Conclusion

The experiments described herein have clearly established some facts about the electroreduction of O_2 catalyzed by molecules designed as models of cytochrome *c* oxidase. The main target of these studies has been to ascertain the characteristics of the enzyme that facilitate the $4e^-$ reduction. The chosen molecules have been tested on graphite electrodes, in contact with an aqueous medium, at pH close to physiological values. It has clearly been shown that the nature of the distal structure of the chemical models is not of great consequence, that a fifth ligand for the iron porphyrin is not necessary, and that the possibility of the O_2 molecule binding to Fe at one end and to Cu at the other, or to another center through a hydrogen bond, is not indispensable. Indeed, only the iron porphyrin itself seems to be essential. It has been shown that cobalt porphyrins, known for their catalytic properties in acidic media, are inefficient at this pH. That an iron porphyrin is an efficient catalyst for O_2 reduction at $pH \approx 7$ is not such a trivial result as it might first appear: through the experiment with the basket-handle iron porphyrin, it has been shown that the formation of a μ-derivative (Fe–O_2–Fe) is not necessary, and that an Fe–O_2 adduct could be the intermediate in the $4e^-$ catalytic process.

These results call into question biomimetic models, or more specifically, on what they can tell us. Our conclusions regarding the electro-reduction of O_2 mediated by molecules

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modeling the behavior of C*c*O are that an iron porphyrin adsorbed on an electrode is an intrinsically efficient catalyst for the reduction. This does not mean that Cu_B and Tyr_{244} play no role in the enzyme. The reduction necessitates that O_2 binds to the iron porphyrin and requires electrons and protons to be delivered rapidly to the O_2 complex; these requirements are apparently fulfilled when an electrode modified by an iron porphyrin is in contact with an aqueous solution at pH 7. When O_2, H^+, and e^- have to reach the heme a_3 of cytochrome *c* oxidase, the mechanism should be different and can be expected to be influenced by the other parts of the enzyme. The role of Cu_B in the enzyme needs to be scrutinized through different experimental approaches. Observations on any molecule synthesized as a model of an enzyme must be interpreted carefully, considering both the experiments and the methodology itself.

Experimental Section

General: ^{1}H NMR spectra were recorded at 500.13 MHz on a Bruker Avance DRX 500 spectrometer and referenced to the residual proton signals of the solvents. Mass spectra were measured on an MS/MS ZABSpec TOF spectrometer at the University of Rennes I (C.R.M.P.O.). UV/visible spectra were recorded on Varian Cary 1E and Bruker IFS 66 spectrophotometers. All solvents (ACS for analysis) were purchased from Carlo Erba. THF was distilled from potassium metal; methanol was distilled from magnesium turnings. CH_2Cl_2 was used as received. Triethylamine was distilled from CaH_2. The starting materials were generally used as received (Acros, Aldrich) without further purification. All reactions were performed under argon atmosphere and were monitored by TLC (silica; CH_2Cl_2/MeOH). Flash column chromatography was performed on silica gel (Merck TLC-Kieselgel 60 H, 15 μm). Elemental analyses were obtained on an EA 1108 analyzer from Fisons Instruments.

The diameter of the graphite disk of the RRDE (Pine Instruments) was 6 mm; a bipotentiostat (Solea-Tacussel) was used to control its potential and maintained the platinum ring potential at 0.8 V so as to detect, through its oxidation, H_2O_2 produced by the reduction of O_2 at the graphite electrode. The voltammograms were recorded on a SEFRAM T.2Y $x-yy$ recorder. All the potentials are referred to SCE (KCl satd.). The aqueous solution in contact with the electrode was buffered at pH 6.86 (0.025 M KH_2PO_3, 0.025 M Na_2HPO_3) and saturated with O_2 at 1 atm. The electrode was abraded with wet SiC paper (grade 600), sonicated in deionized water for 1 min, washed with water and acetone, and dried. It was then modified by the catalysts: 10 μL of a solution of the catalyst in $CHCl_3$ or CH_2Cl_2 was deposited on the graphite surface and the solvent was evaporated.

The previously known compounds **5**, **7**, **8**, and **9** were prepared as described in the literature and their identities were confirmed by comparison with the reported data. Nevertheless, the critical experimental procedure for obtaining **9** is fully detailed.

***α*-5,10,15,20-{*o*-{3,3′,3″,3‴-[*N*,*N*,*N*′,*N*″-Tris(2-aminoethyl)amine](*N*′,*N*″-diethoxycarbonylmethyl)tetrapropionamido}tetraphenyl}porphyrin (1)**: In a 250 mL two-necked round-bottomed flask under argon, compound **3** (200 mg, 0.19 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (80 μL, 0.76 mmol) were dissolved in freshly distilled THF (100 mL). The solution was heated to 55 °C, whereupon ethyl 2-bromoacetate (430 μL, 0.38 mmol) was slowly added by means of a syringe. Stirring was maintained for 24 h, and then the mixture was concentrated to dryness in vacuo. The residue was redissolved in dichloromethane, and the resulting solution was washed with 5% aqueous NaOH (2 × 10 mL). The organic phase was concentrated in a rotary evaporator, and the concentrate was applied to the top of a column of 15 μm silica gel (3 × 10 cm). The desired product was eluted with 1.5% MeOH/CH_2Cl_2. After concentration of the appropriate fraction to dryness, 120 mg of powder was collected (yield 50%). ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ = 9.76 (s, 2H; NHCO), 8.92 (d, ^3J(H,H) = 5.0 Hz, 2H; $H_{\beta\text{-pyr}}$), 8.89 (d, ^3J(H,H) = 4.7 Hz, 2H; $H_{\beta\text{-pyr}}$), 8.84 (s, 2H; $H_{\beta\text{-pyr}}$), 8.70 (s, 2H; $H_{\beta\text{-pyr}}$), 8.66 (d, ^3J(H,H) = 8.5 Hz, 2H; H_{arom}), 8.57 (d, ^3J(H,H) = 8.5 Hz, 2H; H_{arom}), 8.07 (s, 2H; NHCO), 8.02 (d, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.0 Hz, 2H; H_{arom}), 7.86 (t, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.5 Hz, 2H; H_{arom}), 7.81 (t, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.5 Hz, 2H; H_{arom}), 7.52 (m, 4H; H_{arom}), 7.37 (t, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.0 Hz, 2H; H_{arom}), 3.92 (q, ^3J(H,H) = 7.0 Hz, 4H; $-CH_{2\,ester}$), 2.58 (d, ^2J(H,H) = 16.5 Hz, 2H; CH_2), 2.51 (m, 2H), 2.37 (m, 2H), 2.12 (m, 4H), 2.01 (m, 2H), 1.86 (m, 2H), 1.70 (m, 4H), 1.10 (t, ^3J(H,H) = 7.5 Hz, 6H; CH_3), 0.91 (m, 2H), 0.66 (m, 4H), 0.55 (m, 4H), −1.72 (m, 4H), −2.55 (s, 2H; NH_{pyr}); ^{13}C NMR (125 MHz, [D$_5$]pyridine, 50 °C): δ = 171.4, 171.0, 170.7, 137.3, 136.7, 133.7, 131.2, 130.0, 129.6, 124.4, 124.0, 123.6, 123.3, 60.8, 56.0, 52.4, 51.6, 51.3, 51.0, 49.4, 47.5, 35.5, 32.6, 14.3; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 421 (271 100), 514 (16 700), 547 (5100), 588 (6000), 645 nm (2200); MS (FAB): *m*/*z* (%): 1209.9 (100) $[M-H]^+$; elemental analysis calcd (%) for $C_{70}H_{72}N_{12}O_4$: C 69.52, H 6.00, N 13.90; found C 69.21, H 6.07, N 13.81.

Iron complex (1Fe): MS (MALDI/TOF, linear mode): *m*/*z* (%): 1263.8 (100) $[M-H]^+$.

***α*-5,10,15-{*o*-{3,3′,3″-[*N*,*N*′,*N*″-Tris(2-aminoethyl)amine](*N*,*N*′,*N*″-tribenzyl)tripropionamido}triphenyl}-*α*-20-(*o*-acetylamidophenyl)porphyrin (2)**: The procedure described above for **1** was applied to **4** by using benzyl bromide instead of ethyl 2-bromoacetate. The main difference was that the eluent used had a composition of 2% MeOH/CH_2Cl_2. Yield: 108 mg (44%); ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ = 10.13 (s, 1H; NHCO), 9.67 (s, 2H; NHCO), 9.02 (d, ^3J(H,H) = 5.0 Hz, 2H; $H_{\beta\text{-pyr}}$), 8.99 (d, ^3J(H,H) = 5.0 Hz, 2H; $H_{\beta\text{-pyr}}$), 8.92 (d, ^3J(H,H) = 5.0 Hz, 2H; $H_{\beta\text{-pyr}}$), 8.71 (d, ^3J(H,H) = 5.0 Hz, 2H; $H_{\beta\text{-pyr}}$), 8.37 (d, ^3J(H,H) = 8.5 Hz, 2H; H_{arom}), 8.18 (d, ^3J(H,H) = 8.0 Hz, 1H; H_{arom}), 7.86–7.76 (m, 8H; H_{arom}), 7.51 (t, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.0 Hz, 4H; H_{arom}), 7.43 (t, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.0 Hz, 2H; H_{arom}), 7.23–7.16 (m, 4H), 7.13 (m, 5H), 6.82 (d, ^3J(H,H) = 7.0 Hz, 3H; H_{arom}), 6.67 (m, 3H), 2.82 (d, ^2J(H,H) = 20.0 Hz, 4H; $-CH_{2\,benzyl}$), 2.41 (d, ^2J(H,H) = 15.0 Hz, 2H; $-CH_{2\,benzyl}$), 2.02–1.63 (m, 12H; CH_2), 1.31 (s, 3H; CH_3), 0.56 (m, 2H), −0.06 (m, 4H), −1.58 (m, 4H), −2.10 (m, 2H), −2.48 (s, 2H; $-NH_{pyr}$); ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C, DEPT 135): δ = 137.9, 136.8, 130.5, 129.7, 129.5, 129.0, 128.8, 128.7, 128.0, 127.8, 126.5, 125.1, 124.3, 123.9 (CH), 58.9, 57.4, 53.0, 50.4, 50.2, 50.0, 49.8, 33.82, 33.44, 30.4 (CH_2); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 422 (325 300), 516 (20 800), 550 (8100), 590 (7700), 646 nm (4600); MS (FAB): *m*/*z* (%): 1294.6 (100) $[M]^+$; elemental analysis calcd (%) for $C_{82}H_{78}N_{12}O_4 \cdot H_2O$: C 74.98, H 6.14, N 12.80; found C 75.03, H 6.01, N 12.62.

Iron complex (2Fe): MS (MALDI/TOF, linear mode): *m*/*z* (%): 1348.96 (100) $[M]^+$.

***α*-5,10,15,20-{*o*-{3,3′,3″,3‴-[*N*,*N*,*N*′,*N*″-Tris(2-aminoethyl)amine]tetrapropionamido}tetraphenyl}porphyrin (3)**: Under argon, a 100 mL two-necked round-bottomed flask was charged with the Michael acceptor **5** (0.45 mmol, 400 mg) and MeOH (40 mL), and the mixture was heated at 55 °C for 45 min. The ligand tren (0.45 mmol, 72 μL) was then directly added by means of a Hamilton syringe and heating was continued for 48 h. The mixture was cooled, concentrated, and directly applied to a column of 15 μm silica gel column (5 × 20 cm). The desired product was eluted with 4% MeOH/CH_2Cl_2. After concentration of the appropriate fraction to dryness, 234 mg of a purple powder was collected (yield 43%). ^{1}H NMR (500 MHz, [D$_5$]pyridine, 50 °C): δ = 11.42 (s, 2H; NHCO), 9.17 (s, 2H; NHCO), 9.08 (d, ^3J(H,H) = 4.5 Hz, 2H; $H_{\beta\text{-pyr}}$), 9.06 (m, 2H; H_{arom}), 9.02 (d, ^3J(H,H) = 5.0 Hz, 2H; $H_{\beta\text{-pyr}}$), 8.96 (s, 2H; $H_{\beta\text{-pyr}}$), 8.81 (m, 4H; H_{arom}, $H_{\beta\text{-pyr}}$), 8.09 (d, ^3J(H,H) = 6.5 Hz, 2H; H_{arom}), 7.87 (t, ^3J(H,H) = 7.5 Hz, 2H; H_{arom}), 7.83 (t, ^3J(H,H) = 7.5 Hz, 2H; H_{arom}), 7.77 (d, ^3J(H,H) = 7.5 Hz, 2H; H_{arom}), 7.55 (t, ^3J(H,H) = 7.0 Hz, 2H; H_{arom}), 7.46 (t, ^3J(H,H) = 7.0 Hz, 2H; H_{arom}), 2.35–2.12 (m, 10H), 2.09–1.99 (m, 4H), 1.86–1.80 (m, 2H), 1.09 (m, 2H), 0.84 (m, 2H), 0.70 (m, 2H), 0.47 (m, 2H), 0.01 (m, 2H), −0.13 (m, 2H), −1.57 (m, 2H), −2.29 (s, 2H; NH_{pyr}); ^{13}C NMR (125 MHz, [D$_5$]pyridine, 50 °C): δ = 139.0, 137.0, 135.0, 131.4, 131.2, 126.0, 125.0, 124.5, 81.0, 56.0, 50.5, 45.0, 44.8, 43.5, 36.5, 35.5, 34.2, 27.0, 26.8; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 421 (180 400), 515 (9000), 548 (3100), 588 (3400), 644 nm (1800); HRMS (LSIMS): *m*/*z* calcd for $C_{62}H_{61}N_{12}O_4$: 1037.4939 $[M-H]^+$; found 1037.4929; elemental analysis calcd (%) for $C_{62}H_{60}N_{12}O_4 \cdot 2H_2O$: C 69.38, H 6.01, N 15.66; found C 68.81, H 5.54, N 15.79.

Iron complex (3Fe): HRMS (LSIMS): *m*/*z* calcd for $C_{62}H_{59}N_{12}O_4Fe$: 1091.4132 $[M-H]^+$; found 1091.4160.

***α*-5,10,15-{*o*-{3,3′,3″-[*N*,*N*′,*N*″-Tris(2-aminoethyl)amine]tripropionamido}triphenyl}-*α*-20-(*o*-acetylamidophenyl)porphyrin (4)**: The previous procedure for **3** was used, but with **6** instead of **5**. Yield 37%; ^{1}H NMR (500 MHz,

$CDCl_3$, 50 °C): $\delta = 11.31$ (s, 1H; NHCO), 10.78 (s, 2H; NHCO), 8.93 (d, $^3J(H,H) = 7.5$ Hz, $^4J(H,H) = 1.2$ Hz, 2H; H_{arom}), 8.91 (d, $^3J(H,H) = 5.0$ Hz, 2H; $H_{\beta\text{-pyr}}$), 8.88 (d, $^3J(H,H) = 5.0$ Hz, 2H; $H_{\beta\text{-pyr}}$), 8.86 (d, $^3J(H,H) = 8.0$ Hz, 2H; H_{arom}), 8.85 (d, $^3J(H,H) = 5.0$ Hz, 2H; $H_{\beta\text{-pyr}}$), 8.76 (br s, 2H; $H_{\beta\text{-pyr}}$), 7.89 (m, 1H; H_{arom}), 7.83–7.79 (m, 5H; H_{arom}), 7.67 (d, $^3J(H,H) = 7.7$ Hz, $^4J(H,H) = 1.5$ Hz, 2H; H_{arom}), 7.51 (m, 1H; H_{arom}), 7.41–7.35 (m, 3H; H_{arom}), 7.27 (s, 1H; NHCO), 2.12–1.95 (m, 12H; CH_2), 1.30 (s, 3H; CH_3), 0.95 (m, 2H; NH_{tren}), 0.71 (m, 2H; $CH_{2\,tren}$), 0.62 (m, 2H; $CH_{2\,tren}$), 0.24 (m, 2H; $CH_{2\,tren}$), −0.16 (m, 2H; $-CH_{2\,tren}$), −1.04 (m, 2H; $CH_{2\,tren}$), −1.25 (m, 3H; $CH_{2\,tren}$, NH), −2.53 (s, 2H; NH_{pyr}); ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C): $\delta = 171.9$, 171.8, 163.2, 139.8, 139.0, 137.2, 136.7, 135.8, 132.2, 131.6, 131.0, 130.3, 130.0, 122.9, 122.7, 122.2, 121.8, 117.5, 117.2, 115.5, 49.6, 47.2, 43.9, 43.3, 42.5, 41.2, 35.4, 34.8, 30.1; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 421 (221 700), 515 (11 800), 552 (3000), 589 (3200), 646 nm (1300); HRMS (LSIMS): *m/z* calcd for $C_{61}H_{61}N_{12}O_4$: 1025.4939 $[M-H]^+$; found 1025.4915; elemental analysis calcd (%) for $C_{61}H_{60}N_{12}O_4 \cdot H_2O$: C 70.22, H 5.99, N 16.12; found C 69.96, H 5.89, N 16.44.

Iron complex (4Fe): HRMS (LSIMS): *m/z* calcd for $C_{61}H_{59}N_{12}O_4Fe$: 1079.4132 $[M-H]^+$; found 1079.4133.

***α*-5,10,15,20-Tetrakis(*o*-acrylamidophenyl)porphyrin (5)**: This compound was prepared according to the original method.[21]

Iron complex 5Fe: In a glove-box, compound **5** (20 mg) was dissolved in THF, and the resulting solution was heated at 55 °C. Then, ten drops of 2,6-lutidine and a fivefold excess of iron(II) bromide were added. After 5 h, the mixture was concentrated to dryness, the residue was redissolved in CH_2Cl_2, and this solution was filtered through a Celite plug. The filtrate was then concentrated to dryness once more. The complex was stabilized as a five-coordinate derivative by the addition of a fifth ligand (1,2-Me_2Im). To ensure that no atropisomerization had occurred, the proton NMR spectrum of the iron picket-porphyrin **5Fe** was recorded in the coordinating [D_5]pyridine, in which a diamagnetic six-coordinate complex is formed. As expected for a complex possessing C_{2v} symmetry, the ^{1}H NMR spectrum featured two triplets and two doublets corresponding to the *meso* aromatic protons.

5Fe·([D_5]Py)$_2$: ^{1}H NMR (500 MHz, [D_5]pyridine, 50 °C): $\delta = 8.82$ (d, $^3J(H,H) = 7.0$ Hz, 4H; H_{arom}) 8.74 (s, 8H; $H_{\beta\text{-pyr}}$), 8.23 (br s, 4H; NHCO), 7.98 (d, $^3J(H,H) = 7.0$ Hz, 4H), 7.77 (t, $^3J(H,H) = 7.5$ Hz, 4H; H_{arom}), 7.47 (t, $^3J(H,H) = 7.5$ Hz, 4H; H_{arom}), 5.90 (d, $^3J(H,H) = 17.0$ Hz, 4H; −CH=), 5.17 (m, 4H; $=CH_2$), 5.06 (m, 4H; $=CH_2$); MS (MALDI/TOF, linear mode): *m/z* (%): 944.3 $[M]^+$ (100).

Cobalt complex 5Co: The cobalt insertion was achieved by following the same procedure as above, but by using cobalt(II) chloride. MS (MALDI/TOF, linear mode): *m/z* (%): 1043.9 (100) $[M - H - 1,2\text{-}Me_2Im]^+$.

***α*-5,10,15-Tris(*o*-acrylamidophenyl)-*α*-20-(*o*-acetylamidophenyl)porphyrin (6)**: The atropisomer *αααα* of *meso*-tetra(*o*-aminophenyl)porphyrin ($T_{am}PP$)[20] (1.0 g, 1.48 mmol) was monoacetylated by slowly treating it with a solution of acetyl chloride (115 μL, 1.1 mmol) in dry THF (500 mL) over a period of 1 h at 0 °C in the presence of NEt_3 (210 μL, 3.0 mmol). Stirring was maintained for 1 h after the addition, and then the solution was concentrated to dryness in a rotary evaporator. The resulting powder was redissolved in dichloromethane, and this solution was washed with 5% aqueous NaOH (2 × 50 mL). The organic phase was concentrated and applied to the top of a column of 15 μm silica gel (6 × 10 cm) that had been prepared with dichloromethane. The first compound to be eluted (1% MeOH/CH_2Cl_2) was residual *αααα*-TAPP (323 mg). The desired product was then eluted with 1.25% MeOH/CH_2Cl_2 (490 mg, yield 46%). Some other minor bands attributable to polyacylated products remained on the column. ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): $\delta = 8.96$ (br s, 4H; $H_{\beta\text{-pyr}}$), 8.95 (d, $^3J(H,H) = 4.7$ Hz, 2H; $H_{\beta\text{-pyr}}$), 8.81 (d, $^3J(H,H) = 4.7$ Hz, 2H; $H_{\beta\text{-pyr}}$), 8.73 (d, $^3J(H,H) = 8.0$ Hz, 1H; H_{arom}), 8.01 (d, $^3J(H,H) = 7.5$ Hz, 1H; H_{arom}), 7.89 (d, $^3J(H,H) = 7.5$ Hz, 3H; H_{arom}), 7.86 (t, $^3J(H,H) = 8.0$ Hz, 1H; H_{arom}), 7.64 (t, $^3J(H,H) = 8.0$ Hz, 3H; H_{arom}), 7.53 (t, $^3J(H,H) = 8.0$ Hz, 1H; H_{arom}), 7.22 (t, $^3J(H,H) = 7.5$ Hz, 3H; H_{arom}), 7.15 (d, $^3J(H,H) = 7.5$ Hz, 3H; H_{arom}), 6.82 (s, 1H; NHCO), 3.53 (br s, 6H; NH_2), 1.27 (s, 3H; CH_3), −2.66 (s, 2H; NH_{pyr}), MS (FAB): *m/z* (%): 716.7 (100) $[M]^+\bullet$; elemental analysis calcd (%) for $C_{46}H_{36}N_8O \cdot 2H_2O$: C 73.39, H 5.36, N 14.88; found C 73.80, H 4.92, N 15.10. Derivatization of the three remaining amino groups with acryloyl chloride in dry THF, according to the original method,[21] led to the picket porphyrin **6** (yield 63%). ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): $\delta = 9.04$ (d, $^3J(H,H) = 5.0$ Hz, 2H; $H_{\beta\text{-pyr}}$), 8.91 (d, $^3J(H,H) = 5.0$ Hz, 2H; $H_{\beta\text{-pyr}}$), 8.86 (m, 6H; $H_{\beta\text{-pyr}}$, H_{arom}), 8.81 (d, $^3J(H,H) = 8.5$ Hz, 1H; H_{arom}), 8.03 (m, 3H; H_{arom}), 7.92 (t_1 + t_2, $^3J(H,H)_1 = 8.5$ Hz, $^4J(H,H)_1 = 1.5$ Hz, $^3J(H,H)_2 = 7.0$ Hz, $^4J(H,H)_2 = 1.5$ Hz, 2H + 1H; H_{arom}), 7.64 (d, $^3J(H,H) = 7.0$ Hz, $^4J(H,H) = 1.5$ Hz, 1H; H_{arom}), 7.59 (m, 3H; H_{arom}), 7.27 (t, $^3J(H,H) = 7.0$ Hz, $^4J(H,H) = 1.5$ Hz, 1H; H_{arom}), 7.08–6.97 (m, 4H), 6.92 (s, 1H; NHCO), 6.74 (d, $^3J(H,H) = 8.5$ Hz, 1H; H_{arom}), 5.82 (d, $^2J(H,H) = 16.5$ Hz, 2H; $=CH$), 5.77 (d, $^2J(H,H) = 17.0$ Hz 1H; $=CH$), 5.19–5.02 (m, 6H; $=CH_2$), 1.46 (s, 3H; CH_3), −2.53 (s, 2H; NH_{pyr}); ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C): $\delta =$ 163.7, 163.5, 145.9, 145.5, 138.9, 138.8, 135.4, 135.3, 135.2, 131.1, 131.0, 130.3, 129.0, 128.9, 128.1, 127.6, 127.3, 127.2, 126.9, 123.7, 123.6, 122.0, 117.8, 117.0, 116.8, 115.0, 31.0; MS (FAB): *m/z* (%): 879.5 (100) $[M-H]^+$; elemental analysis calcd (%) for $C_{55}H_{42}N_8O_4 \cdot 2CH_2Cl_2$: C 65.27, H 4.42, N 10.68; found: C 64.85, H 4.89, N 10.87.

Iron complex 6Fe: MS (FAB): *m/z* (%): 932.5 (100) $[M]^+$.

***α*-5,15:*β*-10,20-Bis{o-[3,3′-(*p*-phenylene)dipropionamido]diphenyl}porphyrin (9)**: In a 250 mL two-necked round-bottomed flask under argon, NEt_3 (0.56 mL, 4 mmol) was added to freshly distilled THF (120 mL). The atropisomer *αβαβ* of TAPP[18] (674.8 mg, 1 mmol) was dissolved in THF (20 mL), and this solution was used to charge two 10 mL syringes. A third syringe was charged with 10 mL of a solution of the diacyl chloride of benzene-1,4-dipropionic acid (544.2 mg, 2.1 mmol), prepared according to standard methods. The three syringes were driven by a syringe pump capable of adding the three 10 mL solutions together over a 15 h period so as to maintain high-dilution conditions. After the addition, stirring was maintained for 3 h, and the reaction mixture was concentrated to dryness in a rotary evaporator. The residue was redissolved in CH_2Cl_2 and applied to the top of a silica gel column. The expected bis-strapped porphyrin was eluted with 2.5% CH_2Cl_2/MeOH, and the appropriate fraction was concentrated to dryness (439 mg, yield 42%). ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): $\delta = 8.92$ (s, 8H; $H_{\beta\text{-pyr}}$), 8.37 (d, $^3J(H,H) = 7.0$ Hz, 4H; H_{arom}), 8.18 (d, $^3J(H,H) = 8.0$ Hz, 4H; H_{arom}), 7.89 (t, $^3J(H,H) = 8.0$ Hz, $^4J(H,H) = 1.3$ Hz, 4H; H_{arom}), 7.68 (t, $^3J(H,H) = 7.5$ Hz, 4H; H_{arom}), 5.87 (s, 4H; NHCO), 4.49 (s, 8H; H_{arom}), 1.55 (br s, 8H; CH_2), 1.34 (br s, 8H; CH_2), −2.33 (s, 2H; NH_{pyr}); MS (MALDI-TOF): *m/z* (%): 1046.9 $[M]^+$ (100%).

Iron complex 9Fe: MS (MALDI/TOF, linear mode): *m/z* (%): 1101.3 $[M-H]^+$ (100).

Cobalt complex 9Co: MS (MALDI/TOF, linear mode): *m/z* (%): 1104.3 (100) $[M-H]^+$.

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[9] See Figure 1, trace a. Two important criteria have to be simultaneously met for a $4e^-$ catalyst. Firstly, at the disk, a limiting current proportional to the transfer of four electrons must reach a plateau, and, secondly, at the potential of this plateau, no ring current should be detected, indicating a lack of production of hydrogen peroxide at the disk. In accordance with these criteria, our model **2** is an efficient $4e^-$ catalyst at physiological pH with almost no production of hydrogen peroxide. Furthermore, the detection of a small amount of H_2O_2 at the ring occurs before the plateau is reached at the disk.
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[12] In the complex, the zinc atom, which is bound to an axial water molecule, is five-coordinate and lies 0.302(2) Å above the mean plane of the four nitrogen atoms, the porphyrin core being distorted in a saddle-shaped conformation. As shown in Figure 3, the axial water molecule, Ow5, is connected to the four arms through an H-bond network involving four other water molecules. It is noteworthy that this H-bond network ends either on two NH or on two oxygen atoms of the arms. Accordingly, the pickets exhibit different orientations: two of them have their NH groups pointing out of the macrocycle, while the other two have their carbonyl groups oriented towards the outside, thus allowing intermolecular H bonds between macrocycles (NH···OC). This observation is a good illustration of how a single water molecule, coordinated to the central metal, can influence the conformation of the structure tethered on the porphyrin. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-155082. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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