MINI REVIEW

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Electrochemistry of porphyrins and related macrocycles

Abstract The electrochemistry of metallomacrocycles is known to depend on a variety of factors, some of which are related to the nature of the macrocycle, some to the central metal ion and some to the solution conditions. This present paper presents a brief overview of metalloporphyrin and metallocorrole redox reactivity while outlining the most important structural factors which influence the reversible half-wave potentials for oxidation or reduction of these complexes in non-aqueous media.

Keywords Porphyrins · Metalloporphyrins · Metallocorroles · Electrochemistry

Introduction

A large number of metalloporphyrins and related macrocycles have been investigated as to their electrochemical properties in non-aqueous media [1]. These compounds are all electroactive and all undergo multiple redox processes, with the exact number depending upon the potential range of the utilized solvent, the type of macrocycle and/or the type of axially coordinated ligands. The half-wave potentials at which these redox processes occur and the site of electron transfer itself (metal, macrocycle or axial ligand) will vary with several parameters, some of which are related to the type and planarity of the macrocycle, some to the type and oxidation state of the central metal ion and some to the type

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and number of coordinated axial ligands [1]. The aim of this paper is to provide a few examples as to how these different parameters affect the redox potentials and/or the site of electron transfer in selected porphyrins and related corroles. Examples for these two types of metallomacrocycles are shown in Scheme 1, which illustrates the structurally similar (TriPC)M and (TPP)M on the one hand and (OEC)M and (OEP)M on the other.

## Effect of macrocycle on porphyrin redox potentials

The first synthetic porphyrins to be electrochemically investigated in detail contained the tetraphenylporphyrin (TPP) or octaethylporphyrin (OEP) macrocycles shown in Scheme 1. The electrochemistry of these compounds was generally similar in that almost all of the compounds could be stepwise oxidized or stepwise reduced by two electrons at the π-ring system to give π-cation radicals and dications and π-anion radicals and dianions, although the more basic OEP derivatives were invariably easier to oxidize and harder to reduce than their TPP analogues [1]. Early electrochemical studies of the OEP and TPP complexes utilized in large part cyclic voltammetry to measure half-wave potentials of each electrode reaction and demonstrated that most of the porphyrins exhibited a constant potential difference between the first and second macrocycle-centered oxidations or first and second macrocycle-centered reductions as well as a similar HOMO-LUMO gap of 2.25 ± 0.15 V which is represented in Fig. 1 as $\Delta|\text{Red}_1 - \text{Ox}_1|$. These constant separations in potentials between half-wave potentials were then used as diagnostic criteria to distinguish macrocycle-centered reactions from metal-centered ones.

It was also pointed out that no more than a maximum of two macrocycle-centered oxidations and two macrocycle-centered reductions could be observed for any metalloporphyrin in non-aqueous media, despite the fact that additional electrode reactions had been theoretically predicted. We now know that the above absolute

(TriPC)M   (TPP)M

(OEC)M   (OEP)M
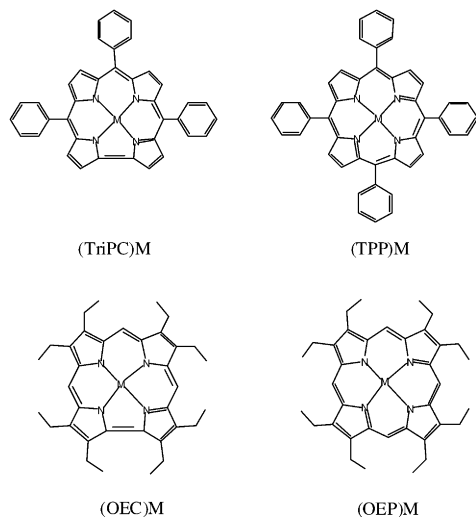
Scheme 1

statement is not absolute and that additional redox reactions can sometimes be experimentally observed, depending upon the number and type of electron-donating or electron-withdrawing substituents at the β-pyrrole and *meso* positions of the porphyrin macrocycle. The nature of these substituents can also greatly affect the magnitude of the HOMO-LUMO gap, as well as the value of the reversible half-wave potentials which might vary by more than 1.0 V in a positive or negative direction for a specific metal- or macrocycle-centered redox reaction [1].

The half-wave potentials for reduction or oxidation of porphyrins containing eight bulky or highly electron-withdrawing groups at the β-pyrrole positions of the macrocycle will depend not only upon the electronic properties of the β-pyrrole and *meso* substituents but also upon the planarity of the macrocycle. A good illustration of this is seen when comparing potentials for oxidation and reduction of complexes containing the tetraphenylporphyrin (TPP), octaethyltetraphenylporphyrin

(Et$_8$TPP or OETPP), octabromotetraphenylporphyrin (Br$_8$TPP) and (pentafluorophenyl)octabromotetraphenyl-porphyrin (Br$_8$F$_{20}$TPP) macrocycles. For example, the oxidation potentials shift from $E_{1/2} = 0.82$ V in the case of (TPP)Zn in methylene chloride to 0.47 V for the first oxidation of the non-planar OETPP complex and then to more positive half-wave potentials of 0.96 and 1.57 V vs. SCE for the non-planar Zn(II) derivatives of Br$_8$TPP and Br$_8$F$_{20}$TPP [2], both of which contain bulky electron-withdrawing substituents [1].

In many cases, the electrochemical behavior of the (Et$_8$TPP)M complexes is similar to that of the analogous (TPP)M or (OEP)M derivatives, but the non-planar Et$_8$TPP derivatives are systematically easier to oxidize than the related planar porphyrins containing the OEP or TPP macrocycles. At the same time, reduction potentials of the (Et$_8$TPP)M complexes are usually similar to those of the (OEP)M derivatives under the same solution conditions, thus giving a smaller HOMO-LUMO gap for the case of the non-planar porphyrins.

The $E_{1/2}$ values for reduction of the (TPP)M and (DPP)M complexes are often similar to each other [1, 2, 3] [e.g. −1.32 and −1.33 V vs. SCE for (DPP)Cu and (TPP)Cu or −1.34 and −1.38 V for (DPP)Zn and (TPP)Zn in CH$_2$Cl$_2$], but the first ring-centered oxidations of the DPP derivatives occur at $E_{1/2}$ values which are shifted cathodically by 190 to 520 mV with respect to half-wave potentials for oxidation of porphyrins in the corresponding TPP series [3]. The shift in $E_{1/2}$ of reduction upon going from (TPP)M to (Br$_8$TPP)M and then to (Br$_8$F$_{20}$TPP)M is usually large for a given complex, and for the case of M = Zn the first reduction in CH$_2$Cl$_2$ varies from −1.33 V (TPP) to −0.82 V (Br$_8$TPP) to −0.48 V (Br$_8$F$_{20}$TPP) as a function of the electronic effect of the Br and/or F groups on the macrocycle [1, 2]. This contrasts to what is observed for oxidation of the same species, where smaller substituent effects are obtained, as discussed above. This is due to a competition between two opposite effects; one is the

Fig. 1 Cyclic voltammogram showing the HOMO-LUMO gap of (TPP)M in CH$_2$Cl$_2$

HOMO-LUMO
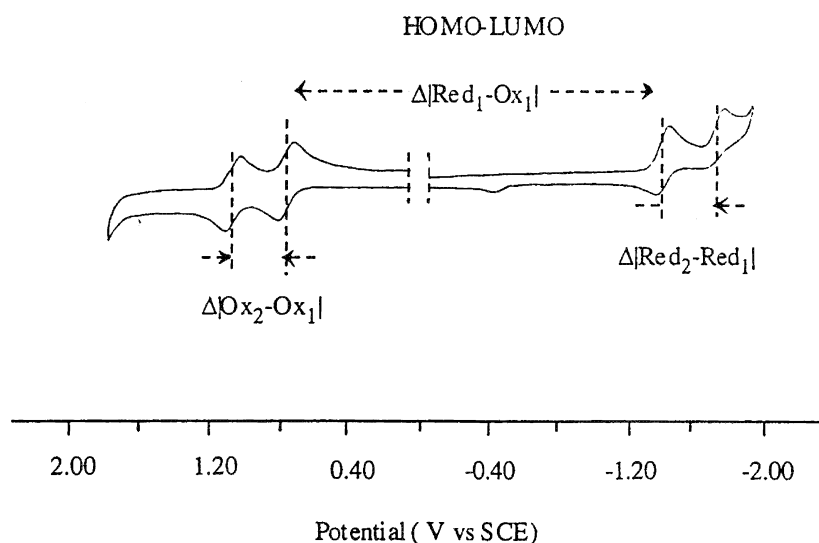
non-planarity of the macrocycle and the other is the electron-withdrawing effect of the Br and F atoms.

The shift in redox potentials between neutral and positively or negatively charged macrocycles (i.e. TPP, TMPyP or TPPS) depends on the conjugation between the positively or negatively charged group at the porphyrin periphery and the π-ring system. This has been illustrated by a number of electrochemical studies on different metal complexes [1], two of which involve (TMpyP)VO and (TPPS)VO [4, 5]. The tetra-positively charged TMpyP derivative is substantially easier to reduce than (TPP)VO under the same solution conditions, while the tetra-negatively charged TPPS complex undergoes reductions at $E_{1/2}$ values which are virtually identical to potentials for reduction of the TPP compounds.

Electrochemical studies of corroles [6] have demonstrated significant shifts in $E_{1/2}$ for reduction or oxidation of these species as compared to metalloporphyrins containing the same central metal ion. The metallocorroles are generally harder to reduce and easier to oxidize than metalloporphyrins with the same central metal ion [6] and this is due to the fact that the formal charge on the macrocycle is –2 in the case of porphyrins and –3 in the case of corroles. The corroles in many cases will also undergo three ring-centered oxidations, giving a corrole trication as compared to only two ring-centered oxidations in the case of the analogous porphyrins, which form only dications under the same solution conditions. Examples of these different reactivity patterns are illustrated for the structurally related porphyrins and corroles in the two series shown by Scheme 1. The three ring-centered oxidations of (OEC)Sn^{IV}Cl occur at 0.67, 1.22 and 1.65 V vs. SCE in CH$_2$Cl$_2$ while the first ring-centered reduction of the corrole is located at –1.46 V in CH$_2$Cl$_2$. These values can be compared to the macrocycle-centered oxidations and reductions of (OEP)Sn^{IV}Cl$_2$, which are found at $E_{1/2}$ = 1.36, –1.08 and –1.48 V under the same experimental conditions. Both (OEC)Sn^{IV}Cl$_2$ and (OEP)Sn^{IV}Cl have a similar HOMO-LUMO gap but the corrole is harder to reduce and easier to oxidize than the porphyrin [6].

A large difference in electrochemical behavior is also seen between (TriPC)Cu and (TPP)Cu, whose structures are illustrated in Scheme 1. The three macrocycle-centered oxidations of (TriPC)Cu occur at 0.78, 1.37 and 1.57 V in CH$_2$Cl$_2$, while the related porphyrin is oxidized in two steps at potentials of 1.00 and 1.25 V under the same solution conditions. Again, the corrole is easier to oxidize than the analogous porphyrin.

Another difference between the two series of copper compounds is that the porphyrin contains a formal Cu(II) central ion and the corrole a formal Cu(III) ion. The corrole also undergoes a Cu(III)/Cu(II) process which occurs at –0.20 V for (TriPC)Cu in CH$_2$Cl$_2$ [7], but no such reaction has ever been observed in the case of a related Cu(II) porphyrin. A single macrocycle-centered reduction of the electrogeneratated Cu(II) corrole is seen at –1.94 V in CH$_2$Cl$_2$ at –75 °C, as compared to two (room temperature) reductions of (TPP)Cu at –1.32

and –1.74 V in CH$_2$Cl$_2$ (Kadish KM, unpublished results). Thus, the π-anion radical of the Cu(II) corrole is more difficult to generate by over 600 mV as compared to the π-anion radical of the porphyrin.

The "tuning" of porphyrins redox potentials by varying electronic effects of the substituents on the macrocycle has long been investigated for a number of different compounds and similar studies are now being carried out for metallocorroles having the formula [Br$_8$(C$_6$F$_5$)$_3$Cor]M (Kadish KM, unpublished results). This study showed that the electronic effects of the Br groups on the corrole reduction potentials are similar in magnitude to what is seen in the case of related porphyrins such as (Br$_8$TPP)M [1].

Effect of metal ion

The electrochemistry of metalloporphyrins with close to 80 different central metal ions has been discussed in a recent review [1], although not all the 80 metal ions were incorporated into the same type of macrocycle under the same solution conditions. Metalloporphyrins containing electroinactive Cu(II) or Zn(II) metal ions undergo only reactions involving the π-ring system, but metal-centered and ring-centered processes are both observed in the case of Fe, Co or Mn derivatives (see Table 1).

An early study of how changes in metal ions effect the redox potentials of OEP complexes showed that reversible potentials for the first ring-centered oxidation and first ring-centered reduction were both linearly related to the divalent central metal ion electronegativity [1]. Only a few metalloporphyrins containing an electroactive metal ion, such as (OEP)Mn and (OEP)Mo, did not follow this trend and this was because these compounds were actually reduced and/or oxidized at the metal center as opposed to the π-ring system, which was the case for all of the other investigated compounds.

Plots of $E_{1/2}$ vs. the central metal ion electronegativity have also been made for reduction of metalloporphyrins of the type (TPP)M(C$_6$H$_5$) [8] and related correlations have been made for oxidation and reduction of metallocorroles of the type (OEC)M [9]. Again, linear relationships are observed and, perhaps surprisingly, a

Table 1 Examples of porphyrin metal-centered redox processes

Metal	Redox processes				
Ti	Ti$^{IV/III}$				
V	V$^{IV/III}$	V$^{III/II}$			
Cr	Cr$^{V/IV}$	Cr$^{IV/III}$	Cr$^{III/II}$		
Mo	Mo$^{VI/V}$	Mo$^{V/IV}$			
Mn	Mn$^{V/IV}$	Mn$^{IV/III}$	Mn$^{III/II}$		
Fe	Fe$^{IV/III}$	Fe$^{III/II}$	Fe$^{II/I}$		
Ru	Ru$^{VI/V}$	Ru$^{V/IV}$	Ru$^{IV/III}$	Ru$^{III/II}$	Ru$^{II/I}$
Os	Os$^{V/IV}$	Os$^{IV/III}$	Os$^{III/II}$		
Co	Co$^{IV/III}$	Co$^{III/II}$	Co$^{II/I}$		
Rh	Rh$^{III/II}$	Rh$^{II/I}$			
Ni	Ni$^{IV/III}$	Ni$^{III/II}$	Ni$^{II/I}$		
Ag	Ag$^{III/II}$	Ag$^{II/I}$			

Fig. 2 Plots of $E_{1/2}$ vs. the number of Br groups for **a** the first oxidation and **b** the first reduction of (Br$_x$TPP)FeCl ($x = 0$–8) in PhCN, 0.1 M TBAP [Figure adapted from Kadish KM, D'Souza F, Villard A, Autret M, Van Caemelbecke E, Bianco P, Antonini A, Tagliatesta P (1994) Inorg Chem 33:5169]
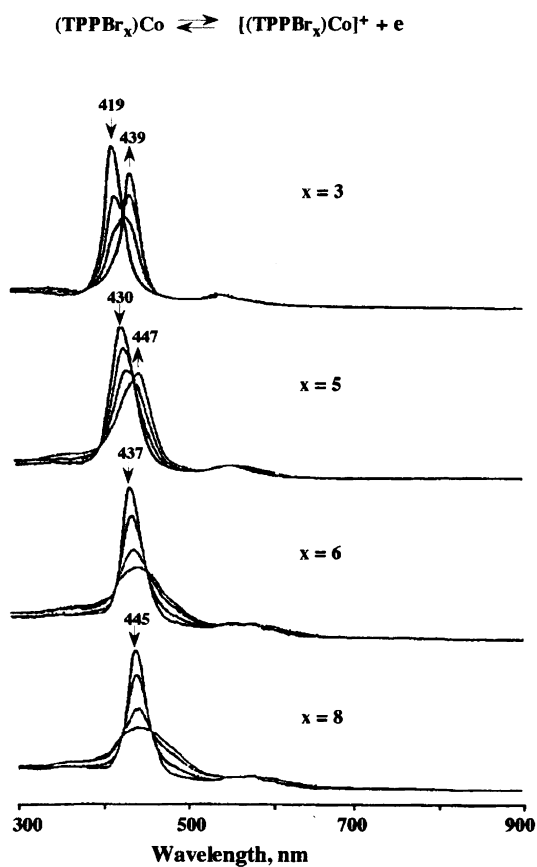

a) First oxidation

b) First reduction
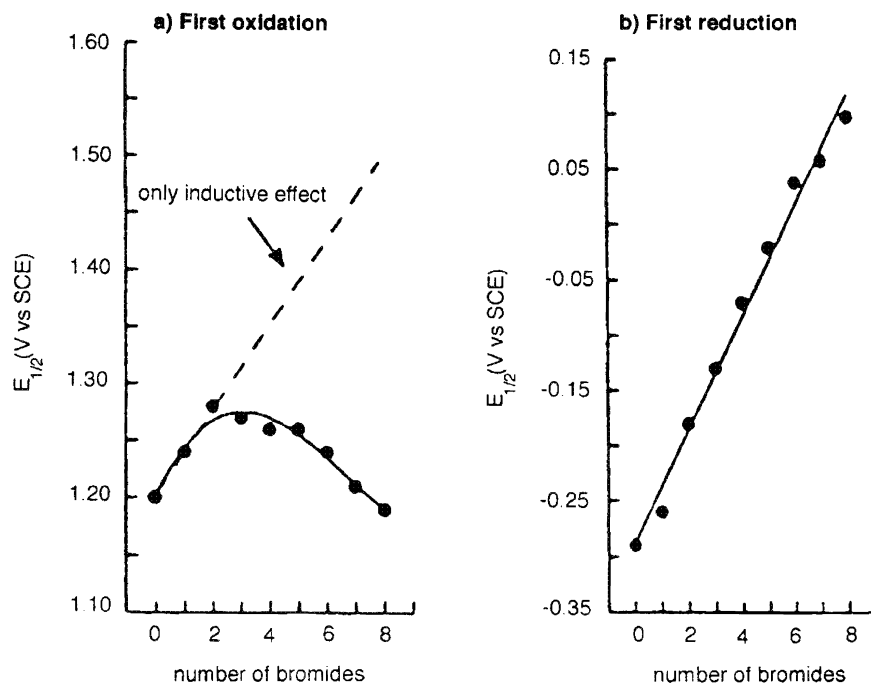
HOMO-LUMO gap of 2.32 ± 0.09 V is seen for the octaethylcorroles, as is also the case for the related octaethlyporphyrins.

Effect of axial ligation

The type of axial ligand coordinated to a metal ion in a metalloporphyrin is known to influence the site of electron transfer and/or the $E_{1/2}$ values at which the compound is reduced or oxidized [1]. Over 250 different axial ligands are known to bind to a porphyrin central metal ion (see Table III of [2]), with the most often examined being pyridine, imidazole and other nitrogenous bases. The best examples of how $E_{1/2}$ values shift with the type and number of axial ligands are given in the case of iron and cobalt porphyrins [1], with (TPP)Co and (TPP)FeCl being perhaps the most studied among the cobalt and iron porphyrin derivatives.

The redox potentials of metallocorroles are also significantly affected by axial ligation of the central metal ion and two examples are given below for iron and cobalt corroles [6]. The formal Fe(III)/Fe(II) reaction of (OEC)FeCl is irreversible and located at $E_{pa} = -1.45$ V in PhCN containing 0.1 M TBAP while the same electrode reactions of (OEC)Fe(C$_6$H$_5$) and (OEC)Fe(NO) are both reversible and located at $E_{1/2} = -1.98$ and -0.41 V, respectively. A similar large variation in $E_{1/2}$ is seen in the case of the cobalt corroles, where the Co(III)/Co(II) reduction process occurs at potentials close to -0.30 V in the case of (OEC)Co but is located at a potential more negative than -2.0 V in the case of (OEC)Co(C$_6$H$_5$).

(TPPBr$_x$)Co $\rightleftarrows$ [(TPPBr$_x$)Co]$^+$ + e

Fig. 3 UV-visible spectroelectrochemical changes upon the first oxidation of (Br$_x$TPP)Co ($x = 3$, 5, 6 and 8) in CH$_2$Cl$_2$, 0.2 M TBAP [Figure adapted from Kadish KM, Li J, Van Caemelbecke E, Ou Z, Guo N, Autret M, D'Souza F, Tagliatesta P (1997) Inorg Chem 36:6292]

The type of axial ligand bound to the metal center can also change the site of electron transfer and one example is given for the case of (OEC)Co and (OEC)-Co(C_6H_5) in CH_2Cl_2 [6]. The σ-bonded complex undergoes a Co(IV)/Co(III) transition at $E_{1/2}$ = −0.23 V in CH_2Cl_2, 0.1 M TBAP, but this metal-centered process is not observed for (OEC)Co which formally contains a Co(III) ion, and is oxidized to a Co(III) π-cation radical as opposed to a Co(IV) species under the same solution conditions [6].

Effect of macrocycle planarity

The redox potentials of metalloporphyrins are known to be influenced by the planarity of the macrocycle, which in turn is affected by the size and number of substituents on the β-pyrrole positions of the macrocycle [10, 11]. Kadish and co-workers [1] have shown that the first oxidation of (Br_xTPP)FeCl where $x = 0–8$ is not linearly related to the number of Br groups on the macrocycle, as would be expected on the basis of purely electronic and resonance effects of the Br substituents. A plot of $E_{1/2}$ versus the number of Br groups on the macrocycle is shown in Fig. 2 and indicates that inductive effects are only dominant for macrocycles containing 1–3 Br groups while a distortion of the macrocycle caused by the bulky substituents dominates the inductive effects of the halogens for the other compounds.

The first reduction of (Br_xTPP)FeCl does, however, vary linearly with the number of Br groups and the difference between substituent effects for oxidation and those for reduction of the same compounds is attributed to a minimum effect of the ring deformation on the reduction potentials, a result which is predicted by theoretical calculations [1].

The site of electron transfer can also be "tuned" by porphyrin ring distortion, with one such example being given for the case of (Br_xTPP)Co in CH_2Cl_2, 0.1 M TBAP, where $x = 0–8$ [1]. This is illustrated in Fig. 3, which shows the thin-layer UV-visible spectral changes which occur during the first one-electron oxidation of (Br_xTPP)Co. As seen in this figure, the first oxidation product of porphyrins with less than five Br groups are characterized by a sharp Soret band, indicative of a Co(III) species, whereas those with more than five Br groups have a broad Soret band and ill-defined visible bands characteristic of a Co(II) porphyrin π-cation radical.

The explanation for these results is that the d orbitals are only sensitive to the inductive effect of the Br groups while the π-ring orbitals are sensitive to both the electronic effect of the halogens and the increased nonplanarity of the porphyrin ring. In fact, the overall oxidative behavior of porphyrins with a Br_xTPP macrocycle is controlled by a combination of factors, including the type of metal ion, the site of electron transfer and the solvent/supporting electrolyte system. Recent electrochemical studies on (Br_xTPP)Zn and (Br_xTPP)MnCl (Kadish KM, Van Caemelbecke E, Ou Z, Shao J, Tagliatesta P, manuscript in preparation) have illustrated this point. Numerous other examples are given in the literature.

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