Effect of Ring Distortion upon Redox Potentials of Metalloporphyrins: Electrochemical Studies of Metallododecaphenylporphyrins

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Redox potentials of nonplanar metallododecaphenylporphyrins (MDPP) are determined by cyclic voltammetry. Oxidation processes of MDPP are selectively shifted to negative potentials in comparison with those of planar metalloporphyrins.

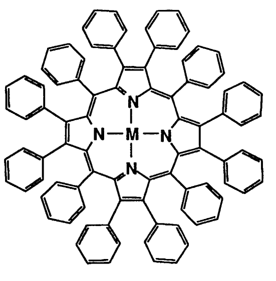
Porphyrin ring distortions are of special importance in understanding the biological functioning of tetrapyrrole pigments such as heme, chlorophyll, factor F430, and cobalamin.[1] Several nonplanar heme prosthetic groups have been substantiated by X-ray diffraction.[2-4] Aquometmyoglobin has a domed or bowl-shaped heme,[2] while the heme prosthetic groups in oxidized tuna cytochrome *c*,[3] yeast cytochrome *c* peroxidase (CCP),[4a] and CCP compound I[4b] are distorted to saddle-like conformation. The nonplanar conformation of the porphyrin macrocycle must modulate the redox properties as well as the axial ligand affinities of the central iron, thus playing an important role in the special functioning of the hemoproteins. We have recently reported the synthesis and properties of nonplanar 2,3,5,7,8,10,12,13,15,17,18,20-dodecaphenylporphyrin (H_2DPP), which has a unique nonplanar macrocycle of saddle type distortion.[5]

In this letter, we report the redox properties of metallododecaphenylporphyrins (MDPP),[6] which are compared with those of planar 5,10,15,20-tetraphenylporphyrin metal complexes (MTPP). The compounds reported here include (1) redox-nonactive metal complexes (M = Mg, Zn, Cu, Ni, Pd, and Pt) and (2) redox-active complexes (M = Co, Fe, and Mn). The redox potential data of MDPP and MTPP are summarized in Table 1. The electrochemical studies were performed by cyclic voltammetry on a Pt electrode (area: 0.025 cm^2) using CH_2Cl_2 as solvent and 0.1 M (1 M = 1 mol dm^{-3}) tetrabutylammonium perchlorate (TBAP) as supporting electrolyte.

Table 1. Redox potentials (V vs. SCE) of DPP metal complexes in CH_2Cl_2[a]

	ring oxidation		metal redox		ring reduction	
compound	$E_{1/2}(2)$	$E_{1/2}(1)$	III/ II	II/ I	$E_{1/2}(1)$	$E_{1/2}(2)$
MgDPP	0.46	0.33			-1.49[b]	c
MgTPP	0.95	0.66			-1.49[b]	c
ZnDPP	0.64	0.48			-1.34	-1.70[b]
ZnTPP	1.14	0.82			-1.33	c
CuDPP	1.00	0.55			-1.32	-1.60
CuTPP	1.36	1.07			-1.20	c
NiDPP	0.94	0.78			-1.38	-1.70
NiTPP	1.17	1.04			-1.26	c
PdDPP	1.22	0.93			-1.32	-1.68
PdTPP	1.62	1.20			-1.24	c
PtDPP	1.36	1.05			-1.20	-1.57
PtTPP	1.65	1.30			-1.21	-1.79[b]
CoDPP	1.03	0.77	0.52	-0.97	-1.54[b]	c
CoTPP	1.15	0.96	0.80	-0.92	-1.43[b]	c
Fe(DPP)Cl	1.24	0.79	-0.41[b]	-1.13[b]	c	c
Fe(TPP)Cl	1.49	1.19	-0.29[d]	-1.04	c	c
Mn(DPP)Cl	1.10	0.92	-0.47		-1.68[b]	c
Mn(TPP)Cl	1.55[d]	1.16	-0.29		-1.68[b]	c

[a]Measured, unless otherwise noted, in 2 mM solutions containing 0.1 M TBAP. Redox potentials are evaluated as $(E_{pc}+E_{pa})/2$. [b]Irreversible process. Cathodic peak potential at sweep rate 100 mVs^{-1} is shown. [c]Redox potentials could not be obtained by the solvent limitation. [d]Quasi-reversible process.



M =	
Mg	MgDPP
Zn	ZnDPP
Cu	CuDPP
Ni	NiDPP
Pd	PdDPP
Pt	PtDPP
Co	CoDPP
FeCl	Fe(DPP)Cl
MnCl	Mn(DPP)Cl

In general, the free base porphyrins and their redox-nonactive metal complexes (M = Mg, Zn, Cu, Ni, Pd and Pt) undergo two successive ring-centered one-electron oxidations and two successive ring-centered one-electron reductions.[7] However, for free base H_2DPP, only one oxidation process and one reduction process are observed, both of which are completely irreversible even at high sweep rates. This is probably due to presence of associated chemical processes in nonplanar H_2DPP.

On the other hand, reversible well-defined redox couples are observed for redox-nonactive metal complexes of DPP. Comparison of reduction potentials of DPP complexes with those of TPP complexes reveals that respective reduction processes occur within a few hundred millivolts of each other. The potentials for ring oxidation process of DPP complexes, however, are significantly different from those of TPP complexes. For example, Figure 1 compares the cyclic voltammogram of CuDPP with that of CuTPP. The first reduction process appears at similar potentials (-1.32 V in CuDPP and -1.20 V in CuTPP), whereas the first and second oxidation processes in CuDPP are more negative by 520 and 360 mV in comparison with those in CuTPP. As shown in Table 1, similar results are obtained for the other redox-nonactive metal complexes.

Additional metal-centered redox reactions occur for redox-active metalloporphyrins (M = Co, Fe and Mn). Similar trends are also observed for the ring-centered redox couples. The metal-centered redox couples seem to be insensitive toward the planarity of porphyrin macrocycles. Figure 2 compares the voltammogram of Fe(DPP)Cl with that of Fe(TPP)Cl. The Fe(III)/Fe(II) couple appears at similar potentials for both complexes. However, the Fe(III)/Fe(II) couple in Fe(DPP)Cl is considerably more irreversible than that in Fe(TPP)Cl. This results from the difference in the ability of the iron to bind Cl ligand. Addition of excess tetrabutylammonium chloride

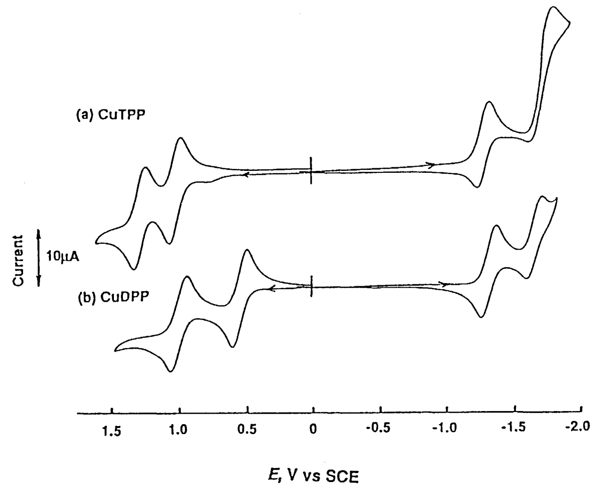


Figure 1. Cyclic voltammograms of (a) CuTPP and (b) CuDPP in CH_2Cl_2 at sweep rate 100 mVs^{-1}.

(TBACl) to the solution of Fe(TPP)Cl causes small change in the voltammogram. In contrast, addition of 1 equivalent of TBACl to the solution of Fe(DPP)Cl causes stepwise appearance of an anodic peak (E_{pc} = -0.31 V) coupled to the cathodic peak at -0.41 V. This result indicates that the binding of Cl ligand to the Fe(II) oxidation state is weaker in DPP than in TPP complex.

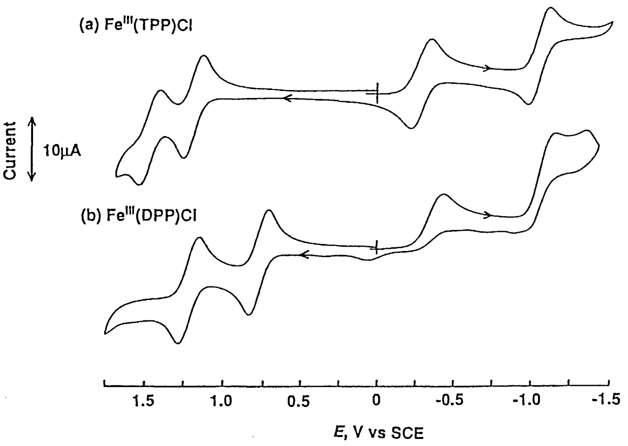


Figure 2. Cyclic voltammograms of (a) Fe(TPP)Cl and (b) Fe(DPP)Cl in CH_2Cl_2 at sweep rate 100 mVs^{-1}.

It is clear from these results that the nonplanar distortion of porphyrin macrocycle selectively shifts the ring oxidation processes to negative potentials. Such results can be interpreted by selective elevation of the HOMO orbital energies of the porphyrin π electron system.[1] This is in accord with the red-shifted visible spectra of the DPP complexes. The distorted macrocycle is well-suited for formation of π-cation radical complexes.[8] The ring distortion does not change significantly the potential of the metal-centered redox couple, but changes the ligand binding affinity of central metal ions.

Further studies on the redox properties of a series of phenyl-substituted planar to nonplanar porphyrins (hexa-, octa-, deca-, and undecaphenylporphyrins)[9] are now underway.

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6 The metal complexes of H_2DPP were prepared using metal acetylacetonates (M = Mg and Zn), metal acetates (M = Cu, Ni, Pd, Co and Mn), and metal halides ($FeBr_2$ for M = Fe and $PtCl_2$ for M = Pt). Detailed procedures and spectral data will be described in the full manuscript.

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