The above example illustrates the power of this approach for kinetic purposes. Let us kow discuss the potentialities of this method for preparative scopes. As summarized above, in poor H atoom donor solvents the main deactivation steps for the chain reaction in Scheme I are the various possible pathways for Ar· reduction.[6] For the approach based on redox catalysis, the yield in ArNu thus depends on the parameter $k_2[\mathrm{Nu}^-]/(k_d[\mathrm{P}]_0)$ whereas it depends[2] on $k_2[\mathrm{Nu}^-]/k_1$ (when[16,9b] $k_1 \gg (k_d[\mathrm{ArX}]_0)^{2/3}\theta^{-1/3}$) or on $k_2[\mathrm{Nu}^-]k_1{}^{1/2}\theta^{1/2}/(k_d[\mathrm{ArX}]_0)$ (for the converse situation) in the context of the direct electrochemical approach. It is thus seen that the approach via redox catalysis will be preferable when either $k_1 \gg k_d[\mathrm{P}]_0$ (for large k_1) or $k_1\theta \ll ([\mathrm{ArX}]_0/[\mathrm{P}]_0)^2$ (for smaller k_1). Obviously the latter condition is not truly realistic since the redox catalysis phenomenon needs $k_1\theta \gg 1$ to be effective.[17] Thus we can conclude that the approach based on redox catalysis will be advantageous when compared to the direct method as soon as $k_1 \gg k_d[\mathrm{P}]_0$, i.e., for the cases involving very frangible anion radicals, such as $\mathrm{PhX}^{-}\cdot$, X = Cl, Br, I.[2,13] When the converse situation is obtained the direct approach is preferable for preparative scopes.

However, as examplified by the example of 2-chlorobenzonitrile with PhS^- presented in this paper, the approach based on redox catalysis may be extremely worthwhile as a kinetic tool for determination of rates of nucleophilic attack close to the diffusion limit. Application of this method to the comparative investigation of the reactivity in an extended series of Ar·/nucleophile systems is currently in progress.

Experimental Section

The experimental setup, electrochemical cell, and procedures for purifying the solvent were the same as previously described.[3d] The working electrode for the CV in Figure 1 was a gold disk of diameter 1 mm, polished on alumina before use. The data in Figure 2 and in Table I were obtained at a hanging mercury drop for a lesser contribution of the background current and capacitive current on the i_p and $i_p{}^0$ measurements. The reference electrode was an $\mathrm{Ag}/\mathrm{Ag}^+$ 0.01 M electrode in liquid ammonia. The supporting electrolyte was KBr, 0.1 M.

The starting materials were from commercial origin. 2-Chlorobenzonitrile was sublimed prior to use.

2-Cyanodiphenyl sulfide was prepared by refluxing for 15 h 0.01 mol of 2-chlorobenzonitrile and 0.01 mol of sodium benzenethiolate in DMF. After filtration of NaCl and evaporation of the solvent, the white product was purified by recrystallization in dilute methanol, mp 58 °C. Anal.: mass spectrum (m/e) 213 (5), 212 (18), 211 (100), 210 (43), 185 (8), 184 (34), 183 (5), 109 (13), 108 (10), 92 (11), 77 (34).

Registry No. 2-Chlorobenzonitrile, 873-32-5; benzenethiolate, 13133-62-5; 4-cyanopyridine, 100-48-1.

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(17) This condition corresponds to a fast irreversible cleavage of $\mathrm{ArX}^{-}\cdot$ in the time scale considered. This requirement is needed to allow a continuous displacement of the reversible electron transfer in eq 3. See ref 11.

Molecular Environment Effects in Redox Chemistry. Reversible Multielectron Oxidation of Amide-Linked, Basket-Handle Metalloporphyrins

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Abstract: Electrochemical oxidation of Cu, Zn, and Mg amide-linked, basket-handle porphyrins involves the simultaneous reversible uptake of two electrons leading directly to the dication as opposed to what happens with the parent tetraphenylporphyrin (TPP) complexes where two one-electron steps separated by several hundreds of millivolts are observed. Comparison with tetra-*o*-methoxy- and tetra-*o*-nitro-substituted TPP and with ether-linked, basket-handle porphyrin complexes shows that this is a manifestation of the presence of amide groups in the chains. Amide-linked, basket-handle Cu and Mg dimers bound by two NHCONH groups undergo a simultaneous four-electron reversible uptake leading directly to the dimeric tetracation. Possible reasons for this new and spectacular effect of the amide groups located in the immediate vicinity of the porphyrin ring are discussed.

It has been shown previously[2] that the presence of ether-linked or amide-linked, basket-handle chains exerts a pronounced influence on the redox and coordination chemistry of iron porphyrins. Of particular interest is the behavior exhibited by the amide-linked compounds owing to their approximate resemblance with metalloproteins. It was observed that the negatively charged complexes formed upon successive reduction of the starting $\mathrm{Fe}^{\mathrm{III}}$ porphyrins are destabilized by the presence of the ether-linked chains as a result of steric hindrance to solvation. The same effect also exists with the amide-linked, basket-handle complexes but is overcompensated by dipolar interactions with the NHCO groups acting as acceptors. An overall stabilization of the negatively charged species ensues resulting in opposite shifts of standard potentials and complexation constants as compared to what happens with the ether-linked derivatives.

In the present preliminary report, we describe an even more spectacular effect of amide-linked, basket-handle structures on the redox chemistry of metalloporphyrins. It concerns the formation upon electrochemical oxidation of the cation radicals and the dications of Cu, Zn, and Mg porphyrins.

With the standard tetraphenylporphyrin (TPP) complexes, two well-separated, one-electron reversible electron-transfer steps[3] are

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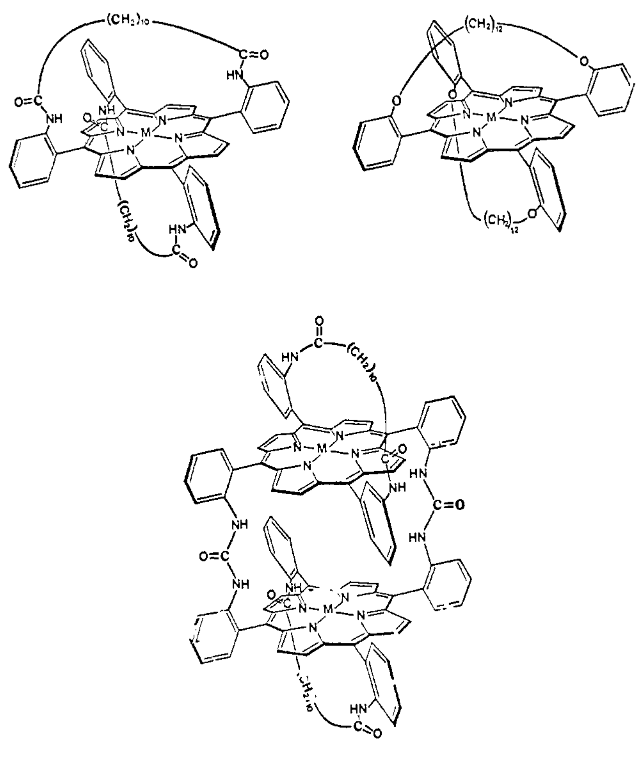
Table I. Electrochemical Oxidation Characteristics of Standard and Superstructured Cu and Zn Porphyrins[a]

		oxidation waves			
		1st		2nd	
porphyrin	solv[b]	$E°$,[c] V vs. SCE	ΔE_p,[d] mV	$E°$,[c] V vs. SCE	ΔE_p,[d] mV
Cu complexes					
TPP	CH_2Cl_2[e]	1.15	60	1.44	70
	PhCN[e]	1.095	72	1.42	93
tetra-*o*-methoxy-TPP	CH_2Cl_2	1.075	90	1.39	75
tetra-*o*-nitro-TPP	PhCN	1.295	70	1.505	90
e-$(C12)_2$-CT	CH_2Cl_2	1.03	110	1.445	90
a-$(C12)_2$-CT	CH_2Cl_2	1.195[f]	70		
	PhCN	1.19[f]	60		
tetra-*o*-pivalamido-TPP	CH_2Cl_2	1.22[f]	95		
(a-C12-CT) dimer	CH_2Cl_2	1.12[g]	50		
Zn complexes					
TPP	CH_2Cl_2[e]	0.91	60	1.21	65
	PhCN[e]	0.925	70	1.265	78
a-$(C12)_2$-CT	CH_2Cl_2	1.03[f]	45		
	PhCN	1.00[f]	85		
(a-C12-CT) dimer	CH_2Cl_2	1.01[g]	100		
Mg complexes					
TTP[h]	PhCN	0.755	50	1.072	55
a-$(C12)_2$-CT	PhCN	0.895[f]	60		

[a] At 20 °C in the presence of 0.1 M BF_4NBu_4 on glassy carbon electrode. [b] The water content was ca. 0.1 M H_2O. [c] As determined from the midpoint between the anodic and cathodic peak potential. [d] Potential separation between anodic and cathodic peaks. [e] The data listed here are not directly comparable to those reported in the litterature[6] since the supporting electrolyte we used (BF_4NBu_4) was different (ClO_4NBu_4). We observed that the whole oxidoreduction pattern was shifted positively by ca. 100 mV when passing from ClO_4NEt_4 to BF_4NBu_4 in CH_2Cl_2. [f] Two-electron wave. [g] Four-electron wave. [h] Tetratolylporphyrin.

Chart I



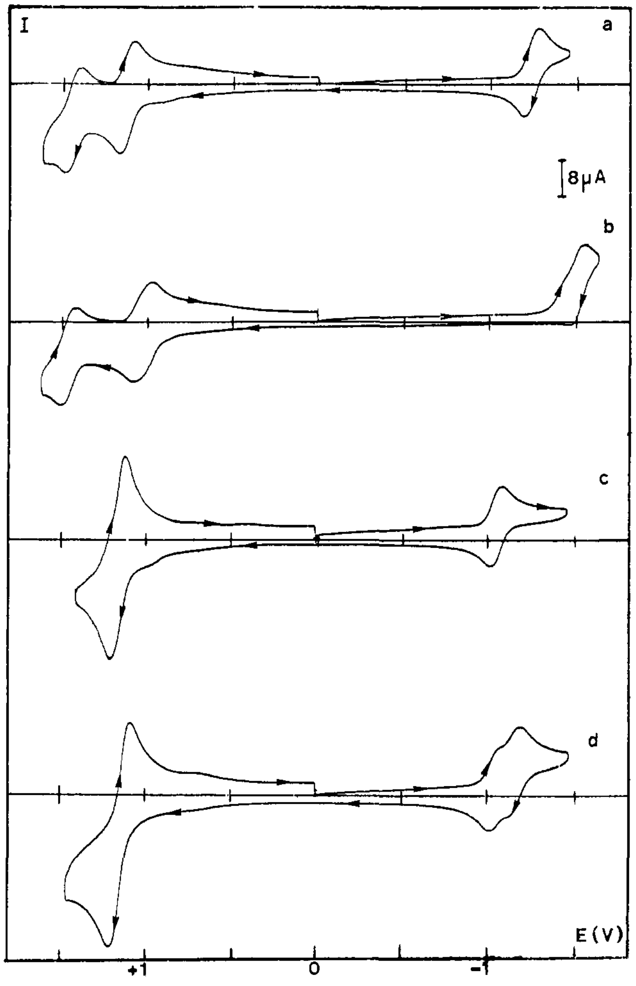


Figure 1. Cyclic voltammetry of Cu porphyrin complexes in CH_2Cl_2 + 0.1 M NBu_4BF_4 at room temperature: (a) CuTPP; (b) Cu-e-$(C12)_2$-CT; (c) Cu-a-$(C12)_2$-CT; (d) Cu_2-[(a-C12-CT) dimer]. In all cases the porphyrin concentration was 1 mM.

observed leading to the stepwise formation of the cation radical and the dication (Figure 1; Table I). With the amide-linked, basket-handle complexes Cu-a-$(C12)_2$-CT, Zn-a-$(C12)_2$-CT, and Mg-a-$(C12)_2$-CT[4] (Chart I) *a single two-electron reversible* wave is observed featuring the direct formation of the dication from the starting complex (Figure 1). The two electrons per molecule stoichiometry was confirmed by coulometry in the case of the Cu and Zn complexes. Spectroelectrochemical experiments carried out with the same complexes showed that the spectra obtained at a potential slightly positive to the anodic peak potential were

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(4) a is the presence of amide linkages, C12 the number of carbon atoms in each chain and CT the cross-trans configuration of the two basket-handle chains (Chart I).

nearly the same as those of the dications of the corresponding TPP complexes.[5]

That the two-electron character of the oxidation wave results from the presence of the amide functionalities in the chains, rather than from the very presence of the chains, is demonstrated by comparison with the ether-linked, basket-handle analogue complexes e-(C12)$_2$-CT (Chart I). With the latter Cu complex (Table I), two well-separated, one-electron reversible waves are obtained, even more separated (415 mV) than in the case of TPP (290 mV). On the other hand, the appearance of a two-electron reversible oxidation process is not critically dependent upon the nature and configuration of the chains provided they are linked via amide groups: a very similar cyclic voltammetric pattern is obtained with copper tetrakis(*o*-pivalamidophenyl)porphyrin ("picket-fence") porphyrins[8]) although the anodic to cathodic peak potential separation (95 mV) is slightly larger than in the case of the a-(C12)$_2$-CT complexes (70 mV) (Table I).

Although the electronic substituent effect of the NHCO group on a benzene ring does not appear to be very different from that of an hydrogen atom,[9] we checked that the merging of the two oxidation steps does not stem from electronic effects transmitted to the porphyrin ring through the benzene groups. The cyclic voltammetry of TPP tetra-substituted in the ortho position by a strong electron-donating group, OCH_3, and a strong electron-withdrawing group, NO_2, was examined in this connection (Table I). As expected the standard potentials are more positive with the nitro derivative than with TPP and less positive with the methoxy derivative than with TPP, but in both cases two well-separated, one-electron reversible waves ($\Delta E° = 315$ mV for OCH_3 and 210 mV for NO_2) are observed.

We also investigated the cyclic voltammetry of cofacial dimeric Cu and Zn porphyrins where the two porphyrin moieties are linked by two ortho-phenyl NHCONH bridges and each bear an amide-linked, C12 basket-handle chain on the opposite face ((a-C12-CT) dimer, Chart I).[10] As anticipated from the above-described behavior of the monomeric basket-handle and picket-fence porphyrins, a *four-electron reversible oxidation* wave leading directly to the corresponding tetracation is observed (Figure 1d; Table 1).[10]

The reversible two-electron oxidation of the amide-linked, basket-handle monomer complexes[12] is compatible with a reaction mechanism in which the first electron transfer is followed by a chemical transformation leading to a species that would be more oxidizable than the starting complex, the next electron transfer step being possibly followed by an additional chemical transformation (ECEC mechanism). The nature of these chemical steps is not presently ascertained. Preliminary kinetic experiments using cyclic voltammetry shows that a decrease in temperature results in a splitting of the rereduction wave. At a given temperature the splitting increases with the sweep rate and decreases with the amount of water present, while the oxidation wave remains two electrons high in all cases. A more systematic investigation of these effects, including the variation of the amide-linked chain structure, is underway. Our working hypothesis is that the ECE (C) process could result from the turning inside out of the CONH dipoles resulting in an easier oxidation of the cation radical and stabilization of the dication. Water would interfere through interaction with the hydrophilic amide groups.[12] Whatever its exact interpretation turns out to be, we wish to emphasize the remarkable effect of the presence of the amide groups in the vicinity of the porphyrin ring leading to a two-electron and a four-electron reversible oxidation in the monomer and dimer, respectively. It would be interesting to investigate the relevance of the latter observation to the four-photon water oxidation process in photosystem II.

Registry No. TPP (Cu complex), 14172-91-9; tetra-*o*-methoxy-TPP (Cu complex), 79502-91-3; tetra-*o*-nitro-TPP (Cu complex), 91900-00-4; e-(ClZ)$_2$-CT (Cu complex), 91900-01-5; a-(ClZ)$_2$-CT (Cu complex), 91900-02-6; tetra-*o*-pivaloyl-TPP (Cu complex), 92007-89-1; (a-ClZ-CT) dimer (Cu complex), 91900-03-7; TPP (Zn complex), 14074-80-7; a-(ClZ)$_2$-CT (Zn complex), 91928-44-8; (a-ClZ-CT) dimer (Zn complex), 91928-45-9; TPP (Mg complex), 91928-46-0; a-(ClZ)$_2$-CT (Mg complex), 91900-04-8.

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(5) The Cu-a-(C12)$_2$-CT two-electron oxidation product exhibits a spectrum with two main bands in the Soret region with equal intensities at λ_{max} 350 (ϵ 37.0) and 450 nm (31.7). This spectrum is very similar to that of the oxidation product of Cu(TPP) at the second oxidation wave (λ_{max} 330 (ϵ 32.2), 450 nm (36.9)). Similar results were obtained with the Zn complexes. The spectrum obtained with Zn(TPP) was the same as previously described in ref 3b and somewhat different from that described in ref 6. The spectra show no definite bands in the near-infrared as exhibited by the parent isoporphyrin complexes;[7] the absorption being much less in the same wavelength region. Rereduction at the foot of the wave gave back the starting complex quantitatively.

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(10) As seen in Figure 1 the cathodic side of the voltammogram displays two closely spaced, one-electron reversible wave pointing to stepwise electron transfers to the two porphyrin moieties. This point will be discussed in a forthcoming publication that also describes the synthesis and characterization of the dimers.

(11) (a) A preliminary investigation of the Fe^{III}-a-(C12)$_2$-CT complex indicates that a two-electron reversible oxidation wave is also obtained in this case.[11b] (b) Lexa, D.; Savéant, J. M.; Xu, F., unpublished results.

(12) The possible formation of an isoporphyrin complex as a cause for the two-electron reversible behavior, as suggested by a reviewer can be excluded by the fact that the characteristic spectrum of these compounds[7] is not observed upon oxidation.[6] Furthermore, the partial irreversibility of the rereduction wave observed at low temperatures does not increase but decreases upon addition of water.