

It is not clear, however, whether a peptide oxygen or a water molecule occupies the second axial site of $\text{Ni}^{\text{III}}(\text{H}_2\text{L})(\text{H}_1\text{L})^{2-}$. A bridging cyanide would probably not replace a peptide oxygen before electron transfer but might replace a water molecule, as is the case for the mono complexes. CPK models indicate that coordination of the peptide oxygen is possible. Furthermore, coordination of the peptide oxygen would provide an additional chelate ring and thus stabilize the $\text{Ni}^{\text{III}}(\text{H}_2\text{L})(\text{H}_1\text{L})^{2-}$ complex. The cross-exchange rate constants of $\text{Ni}^{\text{III}}(\text{H}_2\text{G}_3)(\text{H}_1\text{G}_3)^{2-}$ are only 5-42 times larger than those of $\text{Ni}^{\text{III}}(\text{H}_2\text{G}_3)_2^{3-}$. This factor appears to be too small to be due to an inner-sphere pathway where factors of up to 10^5 were found. Therefore, the $\text{Ni}^{\text{III}}(\text{H}_2\text{G}_3)(\text{H}_1\text{G}_3)^{2-}$ electron-transfer reactions are proposed to be outer sphere and the peptide oxygen coordinated axially. However, this argument is based on the assumption that the reduction potential of $\text{Ni}^{\text{III}}(\text{H}_2\text{G}_3)_2^{3-}$ is less than or equal to that of $\text{Ni}^{\text{III}}(\text{H}_2\text{G}_3)(\text{H}_1\text{G}_3)^{2-}$, which is likely but as yet not proven.

Conclusions

Bis(tripeptido)nickelate(III) complexes of non sterically hindered peptides can be expected to form in neutral or alkaline

solution whenever there is excess tripeptide present. These complexes are less reactive than the mono complexes in both electron-transfer and redox decomposition reactions but react rapidly with acid to give the mono complexes. The reduction potentials of the bis complexes are significantly (at least 0.56 V) lower than those of the mono complexes.

Acknowledgment. This investigation was supported by Public Health Service Grant No. GM 12152 from the National Institute of General Medical Sciences and by a fellowship from Chevron Research (G.E.K.).

Registry No. $\text{Ni}^{\text{III}}(\text{H}_2\text{G}_3)_2^{3-}$, 97764-72-2; $\text{Ni}^{\text{III}}(\text{H}_2\text{G}_3)(\text{H}_1\text{G}_3)^{2-}$, 97764-73-3; $\text{Ni}^{\text{III}}(\text{H}_2\text{G}_3)$, 97764-74-4; $\text{Ni}^{\text{II}}(\text{H}_2\text{G}_3)^-$, 97764-75-5; $\text{Ni}^{\text{III}}(\text{H}_2\text{AGG})(\text{H}_1\text{AGG})^{2-}$, 97764-76-6; $\text{Ni}^{\text{III}}(\text{H}_2\text{GAG})(\text{H}_1\text{GAG})^{2-}$, 97764-77-7; $\text{Ni}^{\text{III}}(\text{H}_2\text{GGA})(\text{H}_1\text{GGA})^{2-}$, 97764-78-8; $\text{Ni}^{\text{III}}(\text{H}_2\text{AGA})(\text{H}_1\text{AGA})^{2-}$, 97764-79-9; $\text{Ni}^{\text{III}}(\text{H}_2\text{AGG})$, 97764-80-2; $\text{Ni}^{\text{III}}(\text{H}_2\text{GAG})$, 97764-81-3; $\text{Ni}^{\text{III}}(\text{H}_2\text{GGA})$, 97764-82-4; $\text{Ni}^{\text{III}}(\text{H}_2\text{AGA})$, 97781-33-4; G_3 , 556-33-2; G_2 , 20238-94-2; G_2 , 556-50-3; $\text{Ni}^{\text{III}}(\text{H}_2\text{A}_3)$, 97764-83-5; $\text{Ni}^{\text{II}}(\text{H}_2\text{G}_3)(\text{H}_1\text{G}_3)^{3-}$, 97764-84-6; $\text{Ni}^{\text{II}}(\text{H}_2\text{G}_3)_2^{4-}$, 97764-85-7; $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$, 13408-63-4; $\text{W}^{\text{IV}}(\text{CN})_8^{4-}$, 18177-17-8; $\text{Cu}^{\text{II}}(\text{H}_3\text{Aib}_3\text{a})^-$, 85926-43-8; $\text{Cu}^{\text{II}}(\text{H}_2\text{Aib}_3)^-$, 89438-84-6; 2,5-piperazinedione, 106-57-0; ascorbic acid, 50-81-7.

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Electrochemical Redox Properties and Spectral Features of Supermolecular Porphyrins

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Received December 28, 1984

meso-(Tetrakis(benzo-15-crown-5)porphyrin (TCP) and its metal (Mg(II), V^{IV} O, Ni(II), Cu(II), Zn(II), and Mn(III)) derivatives form dimers on complexation with K^+ ions. The porphyrin ring oxidations of these dimers are found to occur at less anodic potentials relative to the oxidations of the corresponding monomers. The electrochemical redox states of these dimers in conjunction with their electronic absorption and emission features have been used to arrive at the electronic structures. Supermolecular formalism has been proposed to describe the properties of these dimers. EPR data on the oxidized dimer radical cations indicate that the unpaired electron is localized on one of the porphyrin π systems unlike those found in the reaction-center complex, "special pair" bacteriochlorophyll (BChl) molecules, of the bacterial photosynthetic system.

Introduction

Supermolecular systems constitute two identical molecular entities coexisting together without the assistance of a covalent linkage. The notable features of these systems are (i) they exhibit spectral features different from those of the individual molecular units and (ii) they display reactivity patterns incommensurate with those of the component molecular entities. Polynuclear aromatic hydrocarbons are well-known to form supermolecular systems.¹ In our earlier studies on tetrakis(5,10,15,20-benzo-15-crown-5)-porphyrin (TCP) and its metal derivatives (MTCP), we demonstrated² the formation of dimeric porphyrins when TCP or MTCP is complexed with cations, e.g. K^+ , Ba^{2+} , and NH_4^+ (Figure 1). These molecules are described as supermolecules since the two porphyrin units are joined by noncovalent interactions and exhibit optical absorption and emission properties different from those of the monomeric porphyrin units. In the anticipation that these dimeric porphyrins should exhibit different redox properties relative to those of the monomeric units, we carried out electrochemical redox potential measurements on these dimers. It is known³ that the potentials of reversible one-electron oxidations and reductions of conjugated aromatic systems provide a good experimental

estimate of the relative energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. In view of the close analogy between the π systems of the conjugated aromatic hydrocarbons and porphyrins, the redox potentials of the latter should yield the energies of the HOMO and LUMO, which would be useful in the supermolecular description of the crown porphyrin dimers.

The objectives of this study are (i) to seek the manner in which the ring oxidation potentials (energies of the HOMO) of the dimers change with respect to corresponding monomeric species, (ii) to investigate the effect of the central metal ion on the redox properties of the dimers, and (iii) to study the influence of spatial constraint of the dimers on the electronic spectral features and the magnitudes of oxidation potentials. For this reason, we have chosen only those metallic crown porphyrins [$\text{M} = \text{Mg}(\text{II})$, $\text{V}(\text{IV})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Zn}(\text{II})$, and $\text{Mn}(\text{III})$] where the first oxidation potential corresponds to one-electron transfer from the porphyrin ring to the electrode. Moreover, the optical and magnetic resonance studies of the dimers carried out in the present study provide a basis for the supermolecular description of these dimeric crown porphyrins.

Experimental Section

TCP and its metal derivatives [V^{IV} O, Ni(II), Cu(II), and Zn(II)] were synthesized according to the methods described.² Mn(III) and Mg(II) derivatives were synthesized according to the published procedures.⁴ Dimeric crown porphyrins were produced on addition of excess KCl (AR

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- (a) Thanabal, V.; Krishnan, V. *J. Am. Chem. Soc.* **1982**, *104*, 3643-3650. (b) Thanabal, V.; Krishnan, V. *Inorg. Chem.* **1982**, *21*, 3606-3610.
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Table I. Electrochemical Data for Monomers and Dimers of Crown Porphyrins^a

compd	$E_{1/2}(\text{monomer}),^b$ V	$E_{1/2}(\text{dimer}),$ V	compd	$E_{1/2}(\text{monomer}),^b$ V	$E_{1/2}(\text{dimer}),$ V
TCP	0.90	0.70	ZnTCP	0.70	0.55
MgTCP	0.57	0.90			0.75
		0.68	Mn ^{III} TCP	1.10	0.97
VO(TCP)	1.00	0.87			1.32
		1.02	ZnTCP + NaCl	0.74	
NiTCP	1.01 ^c	0.90	[TCPH ₄] ²⁺	1.6	<i>d</i>
		1.06	[TCP] ²⁻	0.50 ^e	<i>d</i>
CuTCP	0.96	0.84			
		1.06			

^aCyclic voltammograms were run at 24 ± 1 °C. Potentials are with respect to SCE. The error involved is ± 20 mV. ^bOnly first ring oxidation could be measured in the solvent system used. ^cCurrent values do not strictly correspond to one-electron transfer. Both the anodic and the conjugate cathodic peaks are broad, possibly due to the cooccurrence of ring and metal oxidations. ^dIll-defined voltammograms are obtained in the solvent systems used. ^eThe solvent employed is THF.

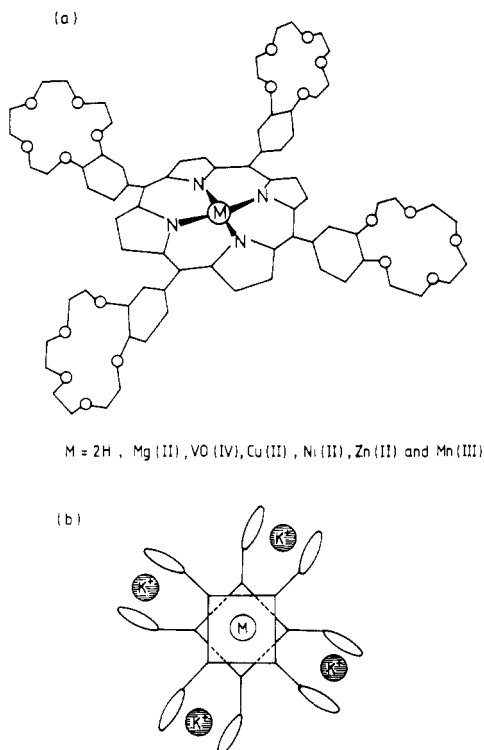


Figure 1. (a) Chemical structure of 5,10,15,20-tetrakis(benzo-15-crown-5)porphyrin (TCP) and its metal derivatives (MTCP). (b) Schematic representation of the K⁺-ion-induced dimers (TCP)₂/(MTCP)₂.

grade) to the monomers in CH₃OH/CH₂Cl₂ (1:1 v/v) solvent mixture. Absence of monomers in solutions of dimers was ascertained by absorption and emission spectroscopy.

Spectrometers employed were already described.² For measurements of EPR parameters, DPPH was used as the standard.

Cyclic voltammetry was carried out by using a three-electrode potentiostatic circuit and a MPI Model MP 1042 voltammetry controller. A Plotmatic 715M (MFE) X-Y recorder was employed to record the current voltage output. The working electrode was a platinum-button electrode (area ~ 0.25 cm²) while the counter electrode was a Pt wire. A Beckman saturated calomel electrode (SCE) was used as the reference electrode. This was separated from the bulk of the solution by a fritted bridge filled with solvent and supporting electrolyte to avoid liquid-junction potentials.

Solvents used in this study are specially purified according to the standard methods. Concentration of the supporting electrolyte (TBAP) was ~ 100 mM for a ~ 1 mM concentration of the test solution. All solutions were deaerated just before the measurements by using highly purified N₂ gas. Under these conditions, a consistent value of 0.78 V (SCE) was observed for the first ring oxidation potential of ZnTPP, in CH₂Cl₂.

Results and Discussion

The cyclic voltammograms of a representative monomer, ZnTCP, and its dimer (obtained by addition of KCl) in

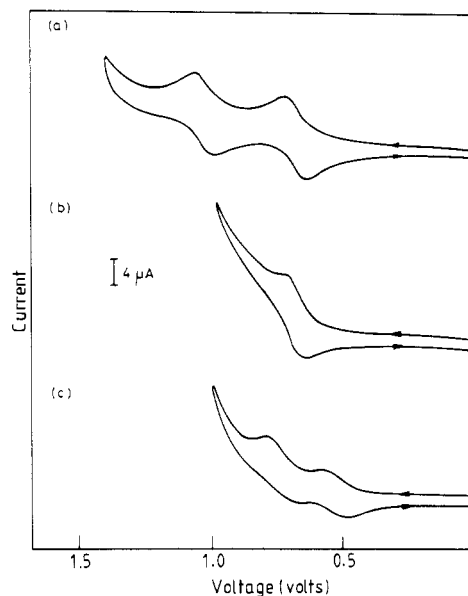


Figure 2. Cyclic voltammograms of ZnTCP in (a) CH₂Cl₂, (b) CH₂Cl₂/CH₃OH (1:1), and (c) (ZnTCP)₂ produced by addition of KCl to ZnTCP. The concentration of ZnTCP in parts a and b is ~ 1 mM, while the concentration of the dimer, (ZnTCP)₂, is ~ 0.5 mM. Scan rate is 0.05 V/s. Potentials are with respect to SCE.

CH₃OH/CH₂Cl₂ (1:1 v/v) are shown in Figure 2. This choice of a solvent mixture for potential measurements is necessitated owing to the restricted solubility of KCl in nonpolar solvents. An employment of this solvent mixture limits the access of potentials to the range 0.0 to ~ 1.5 V (with respect to SCE). The potentials of both the monomeric and dimeric porphyrins are found to be Nernstian and refer to one-electron transfer.⁵ Well-defined current-voltage curves with a peak separation ($\Delta E_{a,c}$) of ~ 60 mV are observed in the sweep-rate range 20–200 mV/s. A linear plot of i_p vs. $v^{1/2}$ for all the electron-transfer reactions is found. Coulometric studies carried out on the first oxidation steps for both ZnTCP and its dimer confirmed that these steps involve only one electron transfer. The potentials are calculated as the average of cathodic and anodic peaks.

First, we shall consider the ring oxidation potentials of TCP and MTCPs with reference to the analogous tetraphenylporphyrin (TPP) and its metal derivatives (MTPPs). An examination of Table I reveals that the ring oxidation potentials of TCP and MTCPs occur at a less anodic potential than those of the corresponding TPP and MTPPs.⁶ This may possibly be due to the effect of crown ether appendage in the meso positions of the porphyrins.⁷ The trend in the magnitudes of the oxidation po-

(5) Nicholson, R. S.; Shaine, I. *Anal. Chem.* **1964**, *36*, 706–712.

(6) Ring oxidation potentials of TPP and MTPPs are either taken from ref 3 or measured in this laboratory.

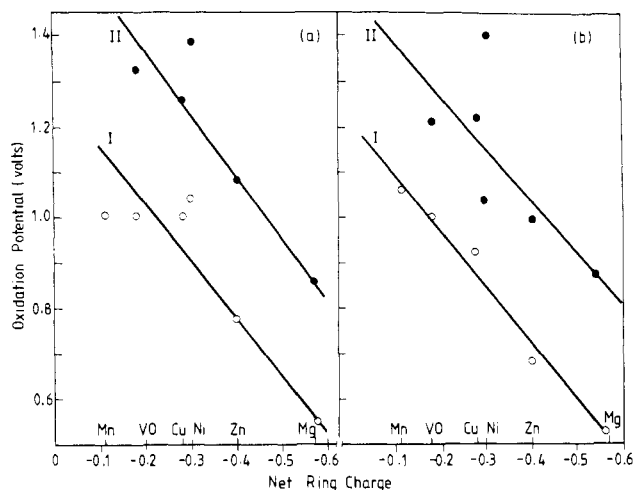


Figure 3. Plots of first (I) and second (II) porphyrin ring oxidation potentials of (a) MTPP and (b) MTCP in the solvent (CH_2Cl_2) vs. the net charge on the porphyrin ring of the respective porphyrins. The metal ions are in the divalent state except manganese, which is in the Mn(III) state.

tentials of TCP and MTCP bears many similarities with that found for the corresponding TPP and MTPPs. Thus, the difference between the first and second ring oxidation potentials of TCP and MTCPs is found to be ~ 0.30 V, close to that found for the analogous TPP and MTPPs. The influence of metal ion on the first ring oxidation potentials of TCP and MTCPs is compared with those of the corresponding TPP and MTPPs in Figure 3, where the net-charge on the ring⁸ is plotted against the $E_{1/2}$ values. The close similarities of the plots suggest that the electronic structure of the crown porphyrins is not significantly different from that of the tetraphenylporphyrins as a result of crown ether substitution in the meso positions.

The dimeric porphyrins obtained by complexing TCP or MTCP with K^+ ions exhibit dramatic changes in the ring oxidation potentials relative to the those of monomeric species (Table I). A comparison of these potentials reveals that both the first and the second ring oxidations of the dimers occur at less anodic potentials with reference to the respective potentials of the monomers. This is in contrast to the studies reported on the covalently linked bis(porphyrin) systems.⁹ It is found that the difference between the first and second oxidation potentials for the dimers is ~ 0.20

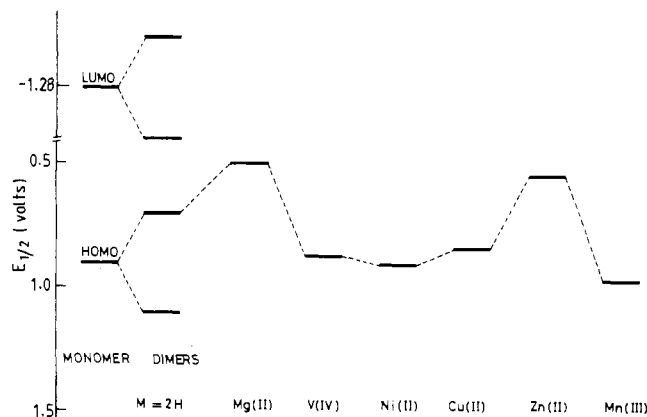


Figure 4. Splitting of the HOMO energy level of monomeric crown porphyrins on dimerization.

Table II. Ring Oxidation Potentials and Optical Properties of the Crown Porphyrin Dimers

compd	$E_{1/2}$, ^a V	λ_{max} , ^b cm^{-1}	$\Delta\lambda$, ^c cm^{-1}	V , ^d cm^{-1}
(TCP) ₂	0.20	15 100	270	162
(MgTCP) ₂	0.07	17 670	430	2830
[VO(TCP)] ₂	0.13	17 670	510	3640
(NiTCP) ₂	0.11	18 550	260	1580
(CuTCP) ₂	0.12	18 180	300	2160
(ZnTCP) ₂	0.15	17 730	260	1540
Mn ^{III} TCP ₂	0.13	15 850	600	2000

^aDifference between the formal electrode potentials of the first oxidations of the monomer and the dimer (see Table I). ^bAbsorption maximum of one of the prominent Q bands of the dimer. ^cDifference between the energies of absorption maxima corresponding to the Q bands of the monomer and the dimer. ^dExciton coupling parameter calculated at the reported absorption maxima.

V, while this value is ~ 0.30 V in the case of monomeric species. The assertion that the ring oxidation potentials are due only to dimer formation of the crown porphyrins is borne out from the following observation. The cyclic voltammogram of ZnTCP containing NaCl in a $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ (1:1 v/v) mixture reveals that the ring oxidation potentials do not show much change relative to those of the uncomplexed ZnTCP (Table I). This indicates that axial ligation of the chloride and/or the presence of Na^+ ion in the crown ether cavity has minimum influence on the π -electronic manifold of the porphyrin ring.¹⁰ These observations can be rationalized in terms of supermolecular formation.

The electronic structure of a supermolecule can be described in terms of molecular orbitals resulting from a linear combination of π molecular orbitals (HOMO and LUMO) of the individual macrocyclic units. This would lead to the splitting of the energy level(s) of the HOMO of the monomeric porphyrin unit into two energy levels in the dimer, lower and higher with reference to the energy level of the HOMO of the monomer when the dimer assumes a geometry with their π planes parallel and rotated with respect to one another promoting electronic interaction between the two π systems. The energy level of the HOMO of the supermolecular entity predicts lowering of the first ring oxidation potential of the supermolecule with reference to that of the constituent individual molecular units (Figure 4). The present results

- (7) It is known that substituting a $-\text{OCH}_3$ group at the meso-phenyl rings of TPP and its metal derivatives results in electron transfer from the ring at less anodic potentials in comparison with the respective unsubstituted analogues (Kadish, K. M.; Morrison, M. M. *J. Am. Chem. Soc.* 1976, 98, 3326–3328. Kadish, K. M.; Morrison, M. M. *Inorg. Chem.* 1976, 15, 980–984). Appending a crown ether moiety at the meso-phenyl rings is considered equivalent to substituting $-\text{OCH}_3$ groups at meta and para positions, simultaneously.
- (8) Net ring charges on TPP and MTPPs are taken from: (a) Zerner, M.; Gouterman, M. *Theor. Chim. Acta* 1966, 4, 44–63. (b) Zerner, M.; Gouterman, M. *Inorg. Chem.* 1966, 5, 1699–1707. The same values are used for TCP and MTCPs in view of similar absorption spectral features exhibited by the two class of compounds.
- (9) A few reports concerning the redox characteristics of "spatially close" bis(porphyrin)s have appeared in the literature. Williams et al. (Williams, R. F. X.; White, D.; Hambright, P.; Shamin, A.; Little, R. G. *J. Electroanal. Chem. Interfacial Electrochem.* 1983, 10, 69–73) have indicated that the halves of the covalently linked edge-to-edge porphyrin dimers behave as noninteracting units. Electrochemical investigations on both the singly and doubly linked porphyrin dimers (Becker, J. Y.; Dolphin, D.; Paine, J. B.; Wijesekera, T. *J. Electroanal. Chem. Interfacial Electrochem.* 1984, 164, 335–346) have revealed that the two rings are sufficiently independent that no interaction is observed between them. In the bis(cobalt) complexes of cofacial dimers of Collman et al. (Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, H.; Koval, C.; Anson, F. *J. Am. Chem. Soc.* 1980, 102, 6027–6036) and Chang et al. (Chang, C. K.; Lin, H. Y.; Abdalmuhdi, I. *J. Am. Chem. Soc.* 1984, 106, 2725–2726) or bis(phthalocyanines) in a "closed" conformation (Leznoff, C. G.; Greenberg, S.; Marcuccio, S. M.; Minor, P. C.; Seymour, P.; Lever, A. B. P.; Tomer, K. B. *Inorg. Chim. Acta* 1984, 89, L35–38), the redox chemistry at the metal clearly demonstrates a mutual interaction between the two redox centers.

- (10) Axial ligation by chloride ion (tetraalkylammonium chloride) is known to influence the redox chemistry of zinc porphyrins in decreasing the oxidation potential (Waiselewski, M. R.; Niemczyk, M. P.; Svec, W. A. *Tetrahedron Lett.* 1982, 23, 3215–3218. Fajer, J.; Borg, D. C.; Forman, A.; Felton, R. H.; Vegh, L.; Dolphin, D. *Ann. N.Y. Acad. Sci.* 1973, 206, 349). Use of tetrabutylammonium chloride as the backing electrolyte in oxidizing ZnTCP results in two stepwise one-electron transfers at 0.66 and 0.87 V, respectively. However, addition of KCl to this solution further shifts the oxidation potentials to 0.53 and 0.74 V, whereas NaCl marginally increases the potentials to the more anodic side. It is to be noted that addition of tetrabutylammonium chloride to preformed ZnTCP dimer exhibits two ring oxidation steps at the same potentials as those observed for the dimers formed in situ by adding KCl.

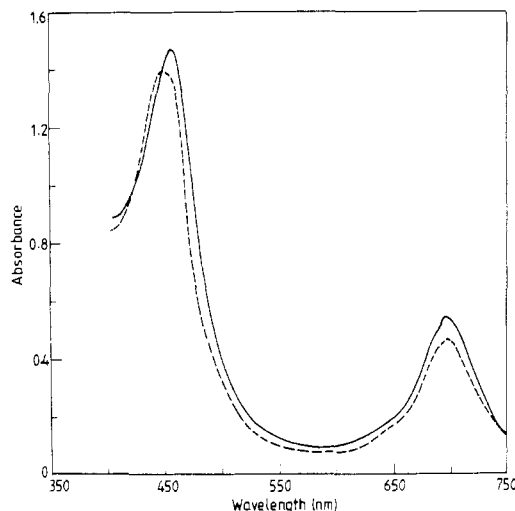
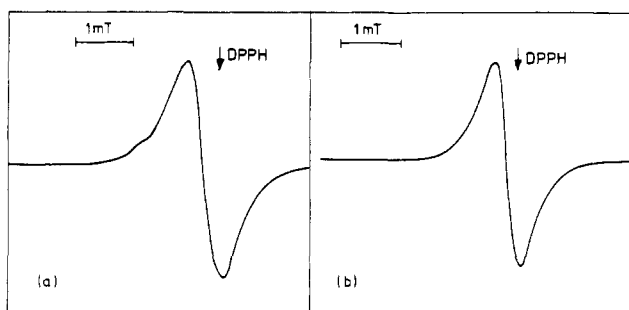
Table III. Optical Absorption and Emission Data for the Radical Cations of Monomeric and Dimeric Crown Porphyrins^a

radical cation	abs max, nm	emission max, nm
TCP	695, 457	740
(TCP) ₂ ^b	696, 450	weakly fluorescent ^c
ZnTCP	702, 454	718
(ZnTCP) ₂ ^b	700, 449	weakly fluorescent ^c

^a Measurements are made at 24 ± 1 °C in CH₃OH/CHCl₃ (1:1, v/v). ^b Radical cations of (TCP)₂ and (ZnTCP)₂ are produced on addition of KCl to the monocation radicals of respective monomers. ^c Very weak fluorescence is observed, blue-shifted (~50 nm) with respect to the emission maxima of the monomer cation radical.

obtained for the noncovalently linked crown porphyrin dimers justify the description of supermolecules. The extent of the splitting of the HOMO of the monomer unit on supermolecule formation depends on the magnitudes of interplanar separation and the angle to which one of the π planes is rotated with respect to the other in the dimer. Previous results on EPR data of Cu(II) and VO²⁺ crown porphyrin dimers² indicate that the interplanar separation is not significantly different (3.8 ± 0.2 Å) while the angle of rotation could be different and lie in the range 10–40°. It is known that a change in the angle of rotation between the two π planes in the supermolecular dimers formed between two naphthalene/anthracene moieties alters the total energy of the system.¹¹ We believe that the extent of lowering of the ring oxidation potentials of the porphyrin dimers relative to those of the corresponding monomers originates from the variations in the angle of rotation of the two porphyrin planes. These variations in the rotational angles do not arise from the electronic/inductive effects operating due to the coordination by the metal ions. This is ascertained from the absence of any correlation between the electronegativity of the metal ions and the ring oxidation potentials of the respective dimers. The rotation of the porphyrin π planes with respect to each other is purely a geometric constraint imposed by the *meso*-aryl groups bearing the crown ether cavity. It is known that the presence of different metal ions in the porphyrin results in different dihedral angles between the porphyrin π plane and the *meso*-aryl ring.¹² These differences could be reflected in different extents to which the porphyrin plane has to be rotated to achieve a stable configuration, thus providing a favorable disposition of the oxygen atoms around K⁺. It is worth mentioning here that, in all the metalcrown porphyrin dimers reported in this study, the redox chemistry originates from the π -electronic manifold and there is no metal–metal interaction.

It is worthwhile to consider the optical spectra of the dimers and their oxidized radicals to derive information concerning their electronic structures. The molecular exciton formalism¹³ for these dimers demands a red-shift of the Q bands of the porphyrins (Table II), assuming a coplanar and rotated arrangement of transition dipoles (of the individual porphyrins). The exciton coupling parameters of the dimers calculated by using the expression of Kasha¹⁴ are given in Table II. It is found that there exists no correlation between the first ring oxidation potential of the dimers and the Q_{0,0} band of the dimers or with the calculated exciton coupling parameters. The absence of correlation suggests that the excited states of the dimers are indeed different. It is of interest to note that besides TCP and MTCPs, the protonated and deprotonated TCP, [TCPH₄]²⁺ and [TCP]²⁻, also form dimers

**Figure 5.** Optical absorption spectra of TCP⁺ (—) in CH₂Cl₂/CH₃OH (1:1) and on addition of KCl (---). TCP⁺ is produced by addition of Br₂ to TCP (~0.05 mM) solution in CH₂Cl₂/CH₃OH (1:1).**Figure 6.** EPR spectra of (a) ZnTCP⁺ and (b) ZnTCP⁺ after addition of KCl in CH₂Cl₂/CH₃OH (1:1) at 140 K. Instrument settings: microwave frequency, 9.046 GHz; microwave power, 2 mW. ZnTCP⁺ is produced by addition of Fe(ClO₄)₃ to ZnTCP in CH₂Cl₂/CH₃OH (1:1) solvent mixture. The observed *g* values are (a) 2.0032 and (b) 2.0030.

as revealed from the red-shifted Q bands and blue-shifted Soret bands, the shifts being relative to the corresponding bands in the monomeric units.¹⁵ The first electron-transfer step for [TCPH₄]²⁺ occurs beyond 1.6 V (SCE) in CH₂Cl₂ while that for [TCP]²⁻ is observed at 0.5 V in THF (Table I). The ring oxidation potentials of the dimeric analogues of these compounds, however, could not be observed in the potential range 0.0–1.3 V. The ability of these species to form dimers shows that the Coulombic repulsions do not inhibit dimer formation and the driving force is reckoned as that due to the cation complexation.

Turning our attention to the optical spectra of the oxidized products, it is observed that addition of KCl to the monomeric cation radicals of TCP and ZnTCP results in the formation of dimers. Optical absorption and emission data on the cation radicals of both the monomers and the dimers are given in Table III. Chemically oxidized species of TCP or ZnTCP display absorption bands in the red region relative to those of the corresponding cations of TPP and ZnTPP in CH₃OH/CHCl₃ (1:1 v/v). It is interesting to note that addition of KCl to these monomeric crown porphyrin radicals results in the decrease of absorbance values with concomitant shifts in the absorption bands (Figure 5). Also, the oxidized dimers are found to be weakly fluorescent. This indicates the enhancement of the excited-triplet-state yield. Attempts to oxidize the preformed dimeric TCP and ZnTCP by Br₂ leads to the spectral changes, which are not

- (11) (a) Ferguson, F.; Man, A. W. H.; Morris, J. M. *Aust. J. Chem.* **1973**, *26*, 91–102, 103–110. (b) Chandross, E. A.; Ferguson, F.; McRae, E. G. *J. Chem. Phys.* **1966**, *45*, 3546–3552.
- (12) Scheidt, R. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 3, Part A, Chapter 9, pp 463–511.
- (13) (a) Kasha, M.; Rawls, H. R.; Et-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371–392. (b) Tinoco, I. *Radiat. Res.* **1963**, *20*, 133.
- (14) The exciton coupling parameter *V* is calculated by using Kasha's formula, $V = (e^2\mu^2/R^3)G$, where μ and R are the dipole moment and the perpendicular distance between two porphyrin planes, respectively. G is the geometric factor, which is close to unity in this case. μ^2 is calculated by using the formula $\mu^2 = (\epsilon_{\max}/2500M)(\Delta\lambda/\lambda_{\max})$, where M is the degeneracy ($M = 1$) and $\Delta\lambda$ is the band width at half-maximum. ϵ_{\max} is the molar absorptivity at the wavelength maximum λ_{\max} .

- (15) [TCPH₄]²⁺, formed on addition of molar equivalents of CF₃COOH (or HCl) to a solution of TCP in CH₃OH/CHCl₃ (1:1 v/v), has absorption bands at 695 and 457 nm ($E_{1/2}$ in CHCl₃ >1.6 V). Addition of KCl decreases the optical densities of the bands and is accompanied by a ~16 nm blue-shift of the Soret band. Similar spectral changes are observed for [TCP²⁻]₂ obtained by addition of KCl to [TCP]²⁻.

commensurate with those observed on addition of KCl to Br₂-oxidized porphyrins. This may be due to the presence of a number of oxidized species in equilibrium and/or further reactions involving the radicals.¹⁶

The EPR spectra of the oxidized radical ions are often helpful in arriving at the unpaired electron densities in the same orbital extending over various centers of the molecule. Such information can be derived from the hyperfine splitting spacings observed in the EPR spectra. Stable monocation radicals of metal-free and Zn(II) derivatives of porphyrins can be produced by chemical or electrochemical methods. Green solutions of ZnTCP⁺ (~0.1 mM) produced by reacting together equimolar amounts of Br₂ or Fe(ClO₄)₃ and ZnTCP in CH₃OH/CHCl₃ (1:1 v/v) exhibit EPR parameters similar to those of ZnTPP⁺.¹⁷ Addition of KCl to these solutions has very little influence on the spectral features (Figure 6). We are not able to obtain a good EPR spectrum for chemically oxidized preformed dimers. However, it is observed that the EPR spectra of ZnTCP⁺ and (ZnTCP)₂⁺ obtained by controlled-potential electrolysis of ~0.1 mM solutions of ZnTCP and (ZnTCP)₂, respectively, exhibit strikingly similar $\Delta H_{p,p}$ values with a small change in the *g* parameters.¹⁸ In all these cases, we were unable to observe the hyperfine couplings in the EPR spectra. The similarities in the EPR spectral parameters of monocation and dication radicals of the dimers compared with those for the monocation radicals of the corresponding monomers suggest that the odd electron in the dimeric radical cation may not be shared on both the rings unlike in the oxidized primary donor, P₈₆₅⁺, of the purple photosynthetic bacterium where the electron is delocalized over the two bacteriochlorophyll rings of

the special-pair (BChl)₂ dimer.¹⁹ The localization of the charge on one of the porphyrin rings of the crown porphyrin dimer may be attributed to the diminished contribution of the charge-resonance term to the stability of the monocation radicals of these dimers.²⁰

It is of interest to note that the magnitude of the difference between the first ring oxidation potential of the monomer to that of the dimeric crown porphyrin system is comparable to that found for the reaction center complex of the bacteriochlorophyll system.²¹ Despite this similarity, the weakly fluorescent behavior of crown porphyrin dimers is in contrast to the special-pair (BChl)₂ dimer. This particular feature along with the observation of localized charge in the cation radical of crown porphyrin dimer seems to arise from the structural constraints, though supermolecular formalism is found to be adequate for the description of noncovalent dimers reported in this study and the "special-pair" (BChl)₂ dimer of the bacteriochlorophyll system.

Acknowledgment. G.B.M. thanks the Council of Scientific and Industrial Research, New Delhi, for a fellowship.

Registry No. MgTCP, 97374-52-2; VO(TCP), 81642-65-1; Ni(TCP), 97374-53-3; Cu(TCP), 81293-80-3; Zn(TCP), 97374-54-4; Mn^{III}TCP, 81315-54-0; (MgTCP)₂, 97430-79-0; [VO(TCP)]₂, 82521-41-3; (NiTCP)₂, 97430-81-4; (CuTCP)₂, 97430-78-9; (ZnTCP)₂, 97430-82-5; (Mn^{III}TCP)₂, 97430-80-3; ZnTCP⁺, 97374-56-6; (ZnTCP)₂⁺, 97430-83-6; [TCPH₄]²⁺, 97374-57-7; [TCP]₂²⁺, 97374-58-8; (TCP)₂, 97374-55-5; TCP⁺, 97374-59-9; TCP, 81294-37-3; NaCl, 7647-14-5; KCl, 7447-40-7.

- (16) As the second oxidation potential of ZnTCP dimer is within the reach of oxidizing power of Br₂ or Fe(ClO₄)₃, it is possible that both mono and dication radicals are formed upon adding these oxidizing agents to preformed dimers. Reactions of these radicals among each other and with methanol (Dolphin, D.; Felton, R. H.; Borg, D. C.; Fajer, J. *J. Am. Chem. Soc.* **1970**, *92*, 743-744) possibly lead to ill-defined absorption spectra.
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- (18) The EPR parameters of the radical cations are calculated as follows: ZnTCP⁺, *g* = 2.0027, $\Delta H_{p,p}$ = 0.4 mT; (ZnTCP)₂⁺, *g* = 2.0023, $\Delta H_{p,p}$ = 0.4 mT.

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- (21) It is known that P₈₆₅ is oxidized about 200 mV less positive than BChl-a in vitro (Prince, R. R.; Dulton, P. L. In "The Photosynthetic Bacteria"; Clayton, R. C., Sistrom, W. R., Eds.; Plenum Press: New York, 1978; pp 439-453). Interestingly, in the studies of special-pair models, the oxidation potential of a given chlorophyll has never become less positive by more than ~75 mV on covalent dimerization of the chlorophyll (Waiselewski, M. R. In "Frontiers of Biological Energetics"; Dulton, P. L., Leigh, J. S., Scarpa, A., Eds.; Academic Press: New York, 1978; Vol. 1, pp 63-72).