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BIOMIMETIC MODEL REACTIONS OF CAVITY-BEARING PORPHYRINS*

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The importance of design and development of molecular assemblies in the laboratory simulation of a few biofunctions has been described. The biomimetic models comprise of a porphyrin unit with spatially oriented molecular cavities formed by cryptands, β-cyclodextrin and crown ether moieties. The structurally modified porphyrins serve as useful models for the study of cation transport and for the primary donor in the bacterial photosynthetic reaction-centre complex. The model compounds provide interesting systems for studying mechanistic features of photoinduced electron transfer reactions and for intramolecular interactions within the molecular super-structure.

The presence of a porphyrin unit in the porphyrin-crown ether molecular assemblies is shown to increase the lipophilicity of these molecules and exhibit enhanced selectivity and specificity for complexation of K^+ ions. The crown ether porphyrins function as efficient ionophores in the uncoupling of mitochondrial energy potential. This is ascribed to the energy-independent binding of the porphyrin-crown ethers to the outer membrane. The matello crown-porphyrins form noncovalent dimers on complexation with K^+, NH_4^+ and Ba^{2+} cations. These dimers have been characterised by magnetic resonance and optical spectral studies. The electro-chemical redox behaviour and EPR data of the 'super molecular' porphyrin dimers bear many similarities with the primary donor, P 870 of the purple photosynthetic bacterium.

The molecular voids present in these porphyrins are employed to house neutral organic molecules and lanthanide ions. It is demonstrated that the excited state of the porphyrin functions as an electron donor to the acceptors present in the molecular cavities. The efficiencies of the light-induced intramolecular radical-pair formation in these molecular assemblies are found to be much higher than those observed for intermolecular systems and closely analogous to the primary charge-separation reaction in the natural photosynthetic process.

Key Words: **Cavity-Bearing Porphyrins; Biomimetic Model Reactions**

INTRODUCTION

THE widespread occurrence of porphyrins and their metal derivatives in many proteins and enzymes has stimulated considerable interest in the chemistry of these molecules. Metalloporphyrins, chlorins and phlorins have lead to specific reactivity of haemoglobin, heme cytochromes, plant and bacterial photosynthesis.

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Development of molecular assemblies to accomplish some of the biofunctions has been one of the challenging problems. Among the various approaches, biomimetic methods afford an important and promising pathways. Biomimetism implies duplication of functions performed by molecular entities in biological systems either by modifying or isolating certain salient features pertinent to the real systems. Thus, development of biomimetic devices requires a preknowledge of structure and organisation of molecular entities and their *in vivo* mechanistic features. The porphyrin-based model compounds offer a distinct advantage in that these compounds are responsible for many biofunctions such as reversible oxygenation, facilitated electron transfer and photosynthetic electron transport. We describe here some of our efforts in the model reactions of the cationic transport system and the primary process in photosynthesis. In addition, we have devised methods to approach tetramer heme unit through interesting model compounds.

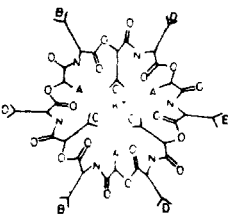
Biomimetic model systems require employment of molecular assemblies which bear close structural resemblances to the naturally occurring systems and exhibit properties similar to those of the natural systems. Many biofunctions necessitate cooperation of more than one molecular unit for specific reactions. Thus, it is often desirable to build molecular assemblies consisting of biomolecules with specific functional features. Development of such molecular systems offers multitude of possibilities to study intramolecular interactions, cooperative phenomena, host-guest recognition processes within a molecular framework and manifestation of specific reactions. The coexistence of more than one molecular entity within a given molecular structure is described in terms of supra molecules and a few such systems have been reported in literature.[1] In the present study, we report simple two molecular-unit systems comprising of porphyrins bearing crown ether molecular cavities and delineate some of the important properties of these molecular assemblies. The integral components of these supra molecular systems have specific functions. The porphyrin unit is important for the study of electron transport and reversible oxygenation reactions while the crown ethers are interesting abiological efficient ionophores. Our investigations on the porphyrin-crown ether assemblies have revealed important information on the cation transport phenomena in mitochondria and the nature of the primary donor in photosynthetic processes.

Selected Biofunctions

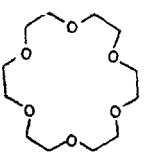
Cation Transport Systems

Several macrocyclic compounds are known to effect cation transport in mitochondria. The macrocyclic compounds relevant to the present study are crown ethers and porphyrins. These compounds provide useful tools for investigations of the ion transport mechanism. The molecular mechanism for cation translocation across biological membranes includes different types of processes.[2] The cation permeability can take place (*a*) by free ion diffusion through lipids (*b*) *via* mobile negatively charged pores (*c*) *via* fixed negatively charged pores (*d*) mobile neutral carriers (*e*) neutral (polar) pores and (*f*) by surface rate limiting reaction. The

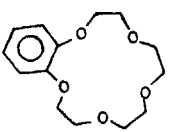
macrocyclic antibiotics that induce ion permeation in mitochondria belong to (*d*). Several antibiotics that fall under this class are devoid of charged groups and consist of oxygen atoms arranged in circular fashion which is energetically suitable to replace hydration cell around the cations through ion-dipole interactions. Cyclic polyethers bear a close structural resemblance to these antibiotics. The effect of some crown ethers on the ion transport in rat liver mitochondria has been examined by different workers.[3–5] It is shown that these ionophores induce the uptake of K^+ by mitochondria. This is followed by lowering of K^+ ion concentration in the outer medium, swelling of mitochondria, increased respiration and acidity. Among the crown ether ionophores, there exist three classes depending on the stoichiometry of the cation-crown ether complex (Fig. 1). They are (*i*) crown ethers with large hole size (30–crown–10) like valinomycin which can completely enclose the cation thereby excluding the contact with anions, solvents and membrane components, (*ii*) crown ethers, (e.g. benzo–15–crown–5) that form 1 : 2 complexes with K^+ and are less efficient as ionophores because of kinetic limitations and (*iii*)



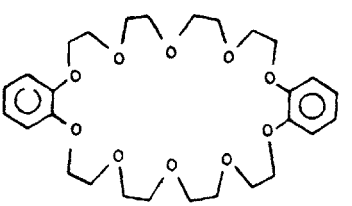
Valinomycin K^+ complex



18-Crown-6



Benzo 15-Crown-5



Dibenzo - 30-Crown - 10

FIG 1 Structures of crown ethers and valinomycin-K^+ complex : *A* = *L*-lactate, *B* = *L*-valine, *C* = *D*-hydroxy-isovalerate and *D* = *D*-valine.

crown ethers (e.g. 18-crown-6) that form 1 : 1 complex with K^+ and are still efficient for tranport since the enclosed cation is open to interact with solvents and anions. The ionophoric activity of the crown ethers and macrocyclic antibiotics has been studied in detail.

While the ionophoric behaviour of crown ethers has been well understood, studies on transport of porphyrins are only of recent origin and are essentially directed towards the understanding of heme synthesis inside the mitochondria.[6-9] Investigations on the transport and uptake of synthetic deutero and proto porphyrins across mitochondrial membranes reveal that the uptake is associated with the uncoupling and dissipation of mitochondrial energy potential, increased ion permeabillity and leakage of endogenous K^+ ions. Two possible mechanisms have been suggested. The transport can take place *via* passive energy-independent binding to the structures of outer compartment and/or *via* transmembrane K^+ gradient. The importance of cations on the porphyrin uptake is shown from the observation that only the porphyrin that entered mitochondria *via* the transmembrane K^+ gradient is able to get metallated by iron chelatase.

Reaction Centre Complexes in Photosystems

Natural photosynthesis provides one of the best known examples of light driven redox reactions using solar irradiance for the production of O_2 and fixation of CO_2. The photosynthetic apparatus located in the thylakoid membrane consists of an antenna for light harvesting and photosystems (PS) I and II wherein the reaction centres (RC) are located (Fig. 2). The pigment molecules, chlorophylls (Chl) are intimately associated with protein both in the antenna and RC complexes. The accepted dogma being that the incident light is harvested by antenna and is rapidly transducted to RC within a few nanoseconds.[10] In the RC, the excited state of the pigment is a strong reductant and an electron is lost to an acceptor strategically placed near by. The charge separation is accomplished rapidly through a series of electron acceptor-donor systems to prevent recombination losses. The recent cry-

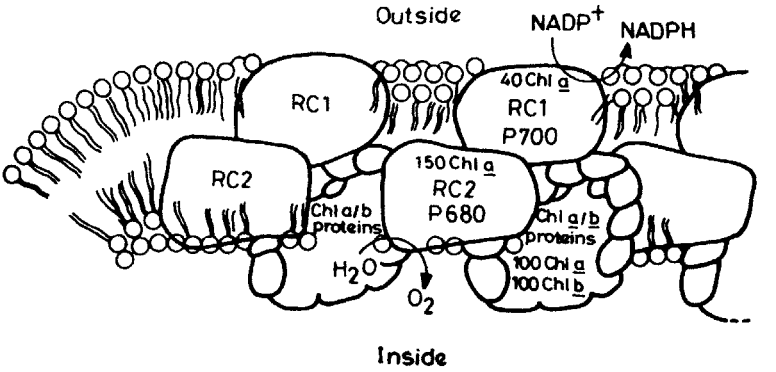


FIG 2 Thylakoid membrane depicting hypothetical positions of 'antenna' and 'reaction centre' proteins embedded in the membrane.

stallization of the RC protein from *Rhodolpseudomonas viridis*[11–13] and its EPR data revealed the orientation of the primary donor in the crystal in four magnetically nonequivalent sites. The solution EPR studies on the reaction centres of *Rhodospirillum rubrum* have provided a wealth of information concerning the dimeric nature of P870 cation radical.

Synthetic reaction centres to mimic charge-separation have been receiving increasing attention.[14–17] The cell free pigments, chlorophylls and its altered products, pyrochlorophillide, pheophorbide, pheophytin and porphyrins have been employed as model compounds to investigate the photophysical properties. Several dimeric porphyrins in which two porphyrin units are either joined by a single or more than one covalent linkage have been reported. The latter porphyrins can asssume two extreme configurations, face-to-face eclipsed or displaced structures. The advantage of using cofacial porphyrins is that the interplanar distance in these systems can be varied systematically. These dimeric porphyrins are shown to be excellent electrocatalysts for the conversion of molecular oxygen to water.[18–21] However, the utility of these dimers to duplicate the biofunctions of the RC-complex has not been realised. The possible reason for this lies in the rather restricted orientation of the two porphyrin planes and their interplanar distal separation.

Biomimetic Approach

The development of molecular assemblies to monitor the cation transport across biological membranes necessitates an ionophore with a receptor chromophore group which can signal the cation uptake and release during the transport process. Our earlier studies on the covalent attachment of crown ether to metal schiff-base chromophores have been found to be unsuitable since they did not exhibit any significant spectral change on cation complexation.[22] One of the approaches that offers interesting possbilities is to develop porphyrin crown ether assemblies. The porphyrins are very good chromophores and possess very interesting excited state properties. The choice of crown ethers is essentially dictated by their specificities for cation complexation. Moreover, the presence of crown ether entities in the porphyrin crown ether systems provides molecular voids to host the guest molecules. It is possible then to study the interaction between the excited state of the porphyrin and the guest molecules within the molecular framework. In what follows now, we shall describe a few molecular assemblies thus far been reported and their properties.

Lehn[1] has described several macropolycyclic structures consisting of dinucleating and polynucleating cryptands. The non-symmetrical macrotetracyclic porphyrin-cryptand system is worthy of mention (Fig 3). This system is expected to complex diammonium cation in a fashion similar to those of the dinucleating cryptates and offer opportunities to study the reactivities of co-bound organic substrates within a given molecular framework. Another interesting system involving porphyrin and β-cyclodextrin has been reported by Gonzales *et al.*[23] The molecular cavity

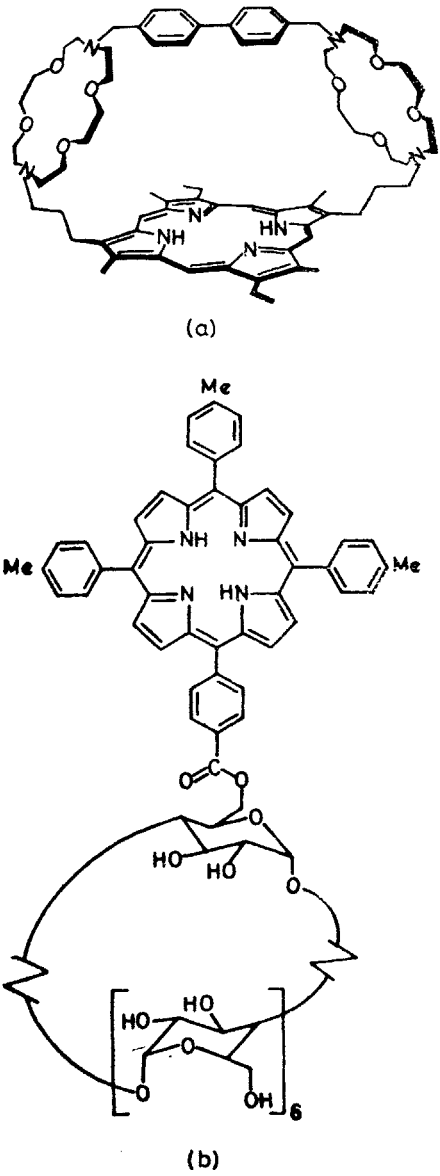
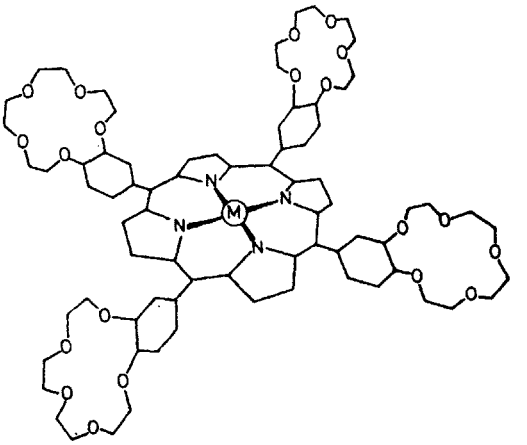


FIG 3 Structures of (*a*) mixed tritopic macrotetracyclic receptor and (*b*) β-cyclodextrin linked porphyrin.

formed by the cyclodextrin entity in the porphyrin periphery has been used to host various acceptors, quinones and nitrobenzenes (Fig. 3). These compounds have been used to mimic the light induced electron transfer process in the RC-complex. It is found that these compounds exhibit intramolecular photochemical electron transfer from the excited porphyrin centre to the guest acceptors housed in the cyclodextrin cavity. The efficiency of photo-induced electron transfer in these

systems is found to be much better than in the inter molecular systems comprising of solvent separated excited donor and acceptors. Another example of cavity bearing porphyrins is benzo-18-crown-6 appended to the *meso* positions of 5, 10, 15, 20-tetraphenylporphyrin (H_2TPP).[24] No detailed studies are, however, available.

One of the best characterized crown porphyrins is that reported by Thanabal and Krishnan.[25–26] The novel *meso*-tetrakis (benzo-15-crown-5) porphyrin (TCP) and its various metal [*M* = Mn(III), VO(II), Co(II), Ni(II), Cu(II), Zn(II), Ag(II), Pd(II) and Pt(II)] derivatives, (MTCP) (Fig. 4) are shown to exhibit many interest-



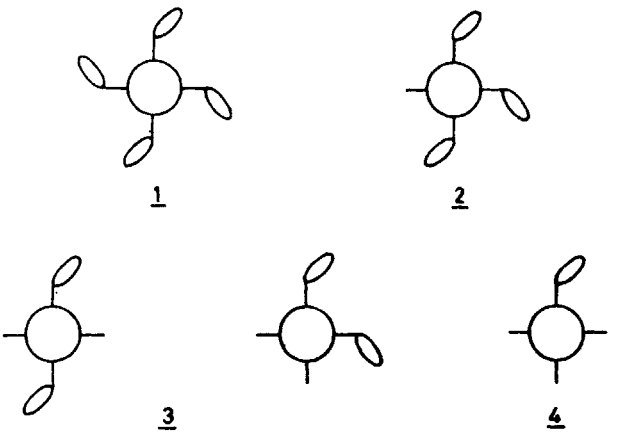


FIG 4 Structure of tetrakis (benzo-15-crown-5) porphyrin. The partially substituted porphyrins are shown. The full circle represents the porphyrin (N_4) plane while the ellipse and the line denote the substituents benzo-15-crown-5 cavity and phenyl ring in the *meso* positions respectively. 2 is *Tris* crown porphyrin, (*Tris*CP) while 3 has both *trans* and *cis* Biscrown porphyrin, (BCP). 4 is monocrown porphyrin (MCP).

ing spectral features on complexation with cations. It is demonstrated that cations, K^+, Ba^{2+} and NH_4^+, which require two benzo-15-crown-5 cavities for complexation, induce dimerization of crown ether porphyrins (CP). The dimer formation is evidenced from the dramatic changes in the optical and magnetic resonance features of CPs. More importantly, the K^+ complexation of TCP and its metal derivatives result in the red shift of the visible absorption bands followed by a blue shift of the soret absorption band of the CPs. In addition, the K^+ complexation completely quenches the fluorescence emission of CPs. The authors have employed these features not only to monitor the dimer formation but also to obtain the values of dimerization constants of these CPs. The cation induced dimerization can be represented by

$$2MTCP + 4C^+ \rightleftharpoons [(MTCP)_2C_4]^{4+},$$

where C^+ represents any one of the cations K^+, NH_4^+, Ba^{2+}. The dimerization constant (K) can be written as

$$K = \frac{[(MTCP)_2\ C_4)^{4+}]}{[MTCP]^2\ [C^+]^4}$$

The K-values for a few representative porphyrins are given in Table I. It is realised that tetracrown substituted porphyrins form much stabler cation complexes relative to the less substituted crown porphyrins. Further, the complexation is highly specific for K^+ ion. The interesting possibility of employing these chromophoric crown ether porphyrins as ionophores for K^+ ion has been explored.

Crown Ether Porphyrins as Ionophores

It is recognized that an efficient ionophore should be highly selective and specific for a given cation. These crown ether porphyrins though are capable to complex Na^+ and K^+ ions, the dramatic spectral change is observed only when

TABLE I

The cation-induced dimerisation constants (log K) of crown porphyrins and their metalloderivatives

Porphyrin	log K			Ref. No.
	K^+	NH_4^+	Ba^{2+}	
TCP	26.0±1.4	16.0±1.1	14.0±1.7	25
VOTCP	27.6±2.5	16.4±1.6	20.7±2.0	26
VO*Tris*CP	15.8±1.8	11.2±1.5	14.0±1.7	26
*Cis*VOBCP	12.7±1.2	*a*	*a*	26
CoTCP	23.0±1.6	*a*	*a*	37
CuTCP	24.0±1.0	15.0±1.9	13.0±1.7	25
ZnTCP	26.4±2.2	14.0±1.8	14.0±1.5	37
AgTCP	27.0±1.0	*a*	*a*	36
PdTCP	27.5±1.2	*a*	*a*	36
PtTCP	26.5±1.3	*a*	*a*	36
Mn(III) TCPCl	19.0±1.8	*a*	*a*	36

[a]Quantitative evaluation of dimerisation constants is rendered difficult.

they are complexed with K^+ ions owing to the dimerization process. It is shown that Na^+ only forms 1 : 1 complexes with CPs with no perceptible changes in the spectral features of CPs. This particular aspect is exploited by Dasgupta *et al.*[27] in employing the CPs as ionophores in the respirating rat liver mitochondria.

The intracellular K^+ ion uptake by the crown ether porphyrins has clearly been demonstrated by the oxygen uptake measurements which are expressed in terms of respiratory coefficient index (RCI). Interestingly, the presence of porphyrin entity in the crown ether moiety enhance the ionophoric behaviour relative to the free crown ether (Fig. 5) and the uncoupling of the mitochondrial oxygen potential

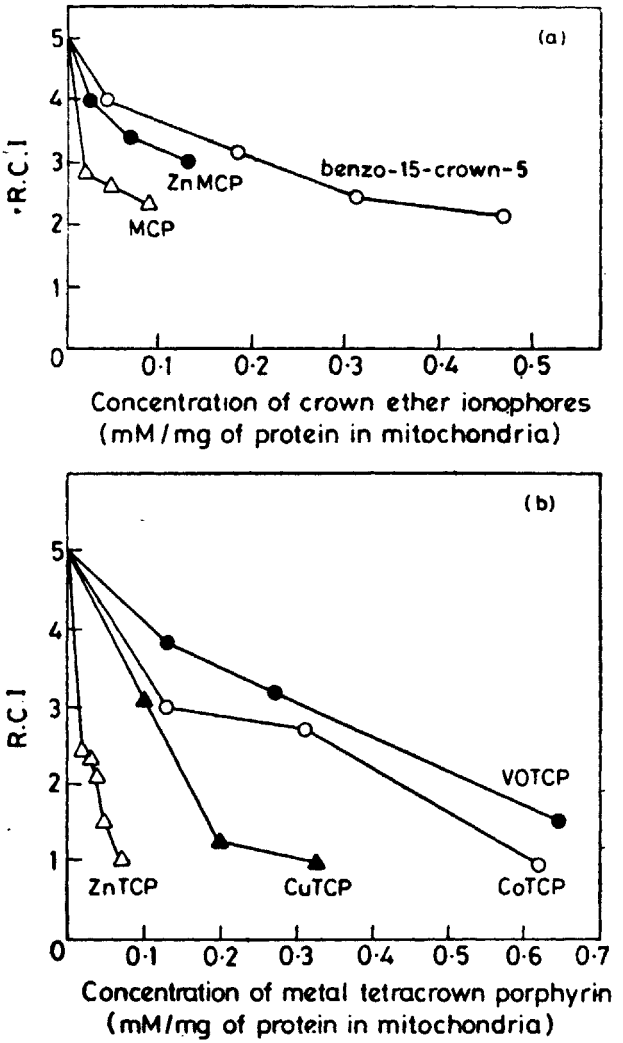


FIG 5 (*a*) Variation of RCI values of the ionophore, benzo-15-crown-5 in different environments. (*b*) Variation of RCI values as a function of central metal ion in the tetracrown porphyrin VOTCP(●), CoTCP(○), CuTCP(▲) and ZnTCP(Δ).

increases with the number of crown ether entities. The influence of central metal ions (in MTCPs) on the lowering of the RCI values has shown to follow the order Zn > Co > Cu > VO. A possible reasoning for this can be traced to the different permeation rates of MTCPs depending on their binding to the outer membrane wall and the dependence of metal ions on the relative ease of intracellular K^+ ion uptake. The reduced RCI values can be viewed as an inhibitory effect upon the oxidative phosphorylation reactions in the mitochondria. It is not clear whether the central metal ion can influence this part of the reaction or through the energy-independent binding to the outer compartment.

These studies point out that the presence of porphyrin moiety increases the lipophilicity of crown ethers thereby enhancing the permeation rates. The non-fluorescent behaviour of K^+ ion complexes of CPs provides a convenient tool to monitor the intracellular K^+ ion uptake by these porphyrins. It is pertinent to mention here that the dissociation of the cation-induced dimers inside the mitochondria is found to be not significant as evidenced by the lowering of the RCI values. It appears that the passive diffusion of CPs through membrane wall is the likely mechanism for the ionophoric behaviour.

Crown Ether Porphyrin Dimers as Models for RC Complex

Various formulations of porphyrin and chlorophyll dimer have been proposed as models for the reaction centre in the "special pair" bacteriochlorophyll complex.[14–16] The available data on the EPR[28–29] and electrochemical redox potential[30] of the primary donor in bacteriochlorophyll system indicate that the P865 is oxidized about 200mV less positive than bacteriochlorophyll *in vitro* and the odd electron in the dimeric radical ion is delocalized over the two chlorophyll rings. The singly linked[31] and doubly linked porphyrin dimers[32,33] do not exhibit and of the properties observed in the natural system. A possible reason for this behaviour can be traced to the non-favourable oriententation of the porphyrin planes due to the presence of rigid covalent linkage. The noncovalent dimers formed by the CPs form attractive models for the 'special pair' chlorophyll.

In a recent study, Bhaskar Maiya and Krishnan[34] investigated the redox and EPR behaviour of the 'super molecular' non-covalent dimers formed by the TCP and its metal derivatives. It is found that the first ring oxidation of the dimers occurs at a less anodic potential relative to the monomeric species (Table II). The magnitude of lowering of this potential is comparable to that observed for the *in vivo* bacteriochlorophyll system. Despite this resemblance in the redox behaviour of the crown porphyrin dimers, the EPR data of the oxidized dimers reveal that the odd electron is more or less localized on one of the porphyrin rings in contrast to that observed for the primary donor $P865^+$ of the purple photosynthetic bacterium. It may be pointed out that these 'super molecular crown porphyrin dimers are nearly fluorescent owing to the eclipsed conformation which promotes the interaction between the lone-pair orbitals of nitrogens of one of the porphyrin planes with the π-system of the other (*vide* infra).

TABLE II

The first ring oxidatials of the K^+ ion induced dimers[a] and selected optical spectral data of the dimers

Compounds	$E_{1/2}$ V	$\Delta E^b_{1/2}$ V	$\Delta\lambda^c_{cm-1}$	V^d_{cm-1}
$(TCP)_2$	0.70	0.20	270	162
$Mg(TCP)_2$	0.50	0.07	430	2830
$[VO(TCP)]_2$	0.87	0.13	510	3640
$(NiTCP)_2$	0.90	0.11	260	1580
$(CuTCP)_2$	0.84	0.12	300	2160
$(ZnTCP)_2$	0.55	0.15	260	1540

a Potentials are with respect to SCE.
b Difference between the formal electrode potentials of the first oxidation of the monomer and the dimer.
c Difference between the energies of the absorption maxima corresponding to the *Q*-bands of the monomer and dimer.
d Exciton coupling parameter calculated at the observed absorption maxima.

The EPR data on the crown porphyrin dimers of Cu(II), VO(II), Ag(II) and Co(II) have proved detailed structural features of these dimers. Attempts have been made to estimate the interplanar distances in the cation-induced dimers (MTCPs) from the position of low field signal and $2D$-values. The values thus obtained for the various MTCP dimers are given in Table III. It is observed that the interplanar distance does not depend on the nature of the metal ion and is independent of the number of appended crown ether moieties in the porphyrin periphery. This has been rationalised in terms of steric features of benzo-15-crown-5

TABLE III

EPR data for selected K^+ ion induced dimers of metallocrown porphyrins

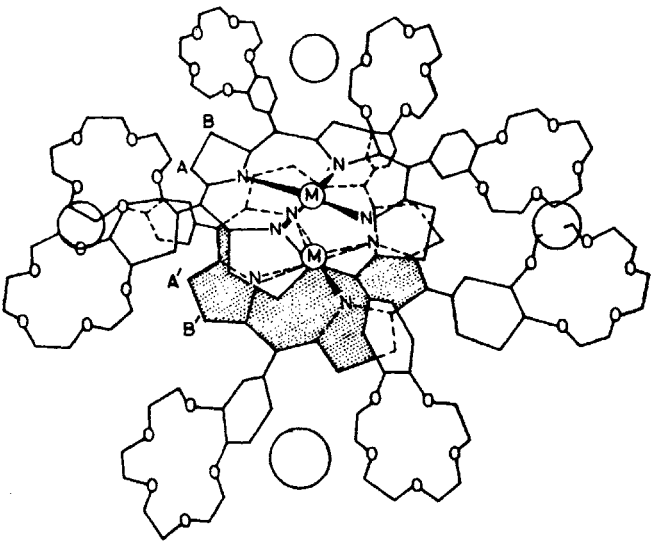
Dimers	$g_\parallel$	$g_\perp$	$D_\parallel$ gauss	$D_\perp$ gauss	RM–M[a] Å
$(CuTCP)_2$	2.190	2.060	380	380	4.31 4.23
$(CuTrisCP)_2$	2.176	2.048	372	368	4.33 4.26
$(cisCuBCP)_2$	2.181	2.064	366	356	4.36 4.32
$(transCuBCP)_2$	2.185	2.058	370	362	4.35 4.29
$(VOTCP)_2$	1.967	1.987	268.5	261	4.70 4.73
$(AgTCP)_2$	1.960	1.730			3.90

[a]The first entry corresponds to parallel region and the second to perpendicular region.

moieties.[26] An eclipsed conformation has been proposed (Fig. 6) for these dimers based on the spectral data.[25,26]

An ENDOR study[35] on the dimerization of CuTCP has provided confirmatory evidence for the proposed structure. The magnitude of the effect of intermolecular dipole-dipole coupling on the in-plane proton hyperfine components is consistent with Cu-Cu separation of 4.20Å. It is shown that the interaction between two MTCPs originates from exciton coupling rather than any metal-metal interaction. This is demonstrated in the larger magnitude of the exciton coupling parameter(V) (Table III) relative to the weakly interacting covalently linked chlorophyll dimers.[38]

It is known that the optical absorption spectral features of the reaction centre complex are quite different from that observed for isolated pigments.[39,40] The long



M = 2H, VO, Co, Zn, Ag (II), Pd (II) and Pt (II)
Cu (II)

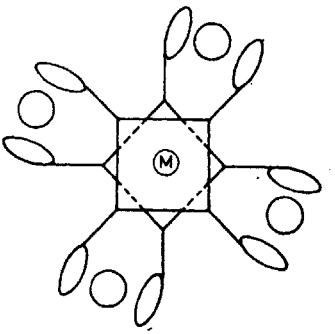


FIG 6 Structure of the cation induced metallo tetra-crown porphyrin dimers. Rotation of the porphyrin planes in the dimer is depicted.

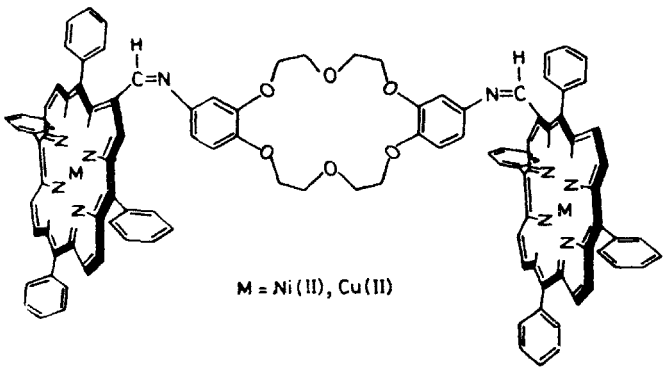


FIG 7 Structure of *Bis*-porphyrin schiff-base of dibenzo-18-crown-6.

wavelength absorption band of chlorophyll molecule at 668nm is found to be red shifted in the *in vivo* reaction centre complex P700. The spectral behaviour of the synthetic reaction centres thus far reported do not match this large red shift observed in the *in vivo* system. An interesting *bis*-porphyrin system (Fig. 7) has been developed by Bhaskar Maiya and Krishnan[41] wherein a dibenzo-18-crown-6 moiety is linked to two porphyrin units through two schiff-base linkages. The protonation studies of these schiff-base porphyrins reveal large red shift of the visible absorption band at 580nm to 620nm in the protonated form. The magnitudes of the red shifts are akin to that observed in the natural system. However, the electrochemical redox behaviour of the schiff-base porphyrins are not consistent with the reported values for the reaction-centre complex.[30]

Host-Guest Interactions in Crown Porphyrins

The presence of molecular voids in the peripheral positions of the porphyrin provides a convenient method to study intramolecular interactions between the porphyrin and the guest molecule housed in the cavity. Blondeal *et al.*[42] employed the crown porphyrins developed by Thanabal and Krishnan[25] to study photoexcited electron transfer reactions. It is known that trivalent lanthanide Eu^{3+} forms a stabler complex with benzo-15-crown-5 relative to Eu^{2+}. It is found that irradiation of a Eu^{3+} complex of Zn(II) crown porphyrin leads to the reduction of Eu^{3+} to Eu^{2+} ion. The electron transfer arises from the excited triplet state of Zn(II) porphyrin to Eu^{3+} housed very near the porphyrin centre. This provides one of the very few examples of intramolecular photoexcited electron transfer reactions. The Schiff-base *bis*porphyrin system[41] offers multide of such possibilities.

CONCLUSIONS

A few porphyrins bearing molecular cavities have been reported. The molecular voids are formed by β-cyclodextrin molecules, crown ether entities and cryptand molecules. These molecular assemblies form very interesting systems for studying the mechanistic aspects of intramolecular photochemical electron transfer reactions. The proximity of the molecular cavity to the porphyrin unit permits a detailed

elucidation of the distal and orientation factors in governing the light-induced electron transfer reactions between the excited state of the porphyrin and the acceptor housed in the host cavity. A few reactions thus far reported have been successful and we expect this area of research to be continuing and a fruitful one. The interesting aspect of dimer formation of these porphyrin molecular assemblies through cation complexation furnishes novel methods to accomplish non-covalent dimers. The latter exhibits remarkable properties possibly due to the favourable orientation of porphyrin planes in the dimers. The schiff-base bisporphyrin forms an attractive model towards achieving a 'tetramer' heme moiety. It is known that Cs^+ ion forms a 1 : 2 complex with dibenzo-18-crown-6 and it is expected that Cs^+ ion complexation of the schiff-base porphyrin leads to a dimer with four porphyrin units. It is hoped that in the near future many of these aspects would be investigated. The molecular assemblies form better biomimetic models than the individual molecular entities owing to their spatial orientation.

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