Dimerization Effects on Spectroscopic Properties of Water-soluble Porphyrins in Aqueous and Micellar Media

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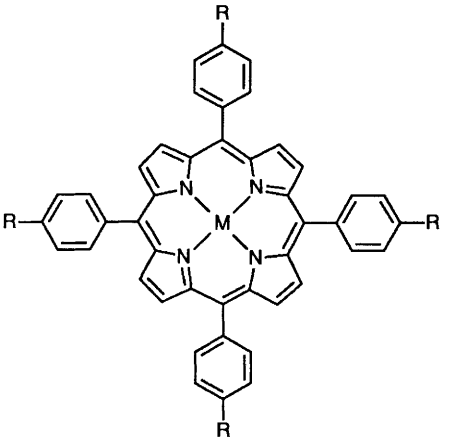
The effects of cation–crown ether induced dimerization on the optical and fluorescence spectra of free base 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (H_2tcpp^{4-}) and 5,10,15,20-tetrakis(4-sulphonatophenyl)porphyrin (H_2tpps^{4-}) and their metal derivatives (Cu^{2+}, Ni^{2+} and Zn^{2+}) have been studied in aqueous and micellar media. Dimerization induces a red shift of Q-bands in both optical and fluorescence spectra with quenching of fluorescence intensity. However, the Soret band experiences a blue shift in Cu^{2+} and Ni^{2+} derivatives, a red shift in Zn^{2+} derivatives and no shift in the free bases. The magnitude of these shifts depends on the structure of the metalloporphyrin as well as on the nature of the crown ether and cation present in solution. The formation constants for the dimer follow the order $Cu^{2+} \approx Ni^{2+} > H_2tcpp^{4-} > Zn^{2+}$. In micellar media the dimerization effect is observed only in anionic sodium dodecyl sulphate. In hexadecyltrimethylammonium bromide and Triton X-100, the porphyrins remain monomeric. An analysis of the data suggests that four cation–crown ether complexes are involved per dimer unit. The exciton formalism coupled with π–π interaction accounts for the observed shifts in Cu^{2+}, Ni^{2+} and free-base porphyrins while a satisfactory interpretation has to take charge-transfer contributions into account for Zn^{2+} derivatives.

Studies on aggregates of water-soluble porphyrins and metalloporphyrins are receiving attention in recent years in view of their similarities in structure and properties to those of chlorophyll aggregates involved in photosynthesis.[1–3] An additional interest in these systems is their use as photosensitizers mediating the photoproduction of H_2 and O_2 from water.[4–6] Previous studies on water-soluble porphyrins have shown the presence of a monomer–dimer equilibrium in the presence of electrolytes.[7–10] In order to understand the effect of dimerization on the physical and chemical properties of porphyrins, an intentional synthesis of porphyrins and phthalocyanines bearing appended crown ethers has been achieved. Addition of alkali-metal cations promotes dimerization in these systems and the dynamics of the dimerization process has recently been reported.[11–16] We have been interested in the aggregation properties of water-soluble porphyrins and our previous studies on these systems have shown that the presence of cations and crown ethers strongly promotes the equilibrium to dimer formation.[17] In continuation of our efforts towards an understanding of the above objectives, in the present study, we have investigated the effects of (*i*) the presence of different metal ions in the porphyrin cavity, (*ii*) the presence of different crown ethers of variable cavity size and (*iii*) the presence of organized media on the monomer–dimer equilibrium.

Two water-soluble porphyrins, 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (H_2tcpp^{4-}) and 5,10,15,20-tetrakis(4-sulphonatophenylporphyrin (H_2tpps^{4-}), and their divalent metal derivatives (Cu^{2+}, Ni^{2+} and Zn^{2+}) have been chosen to study the dimerization equilibrium. The crown ethers used were 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), 1,4,7,10,-13-pentaoxacyclopentadecane (15-crown-5) and 1,4,7,10-tetraoxacyclododecane (12-crown-4) and the surfactants chosen were anionic sodium dodecyl sulphate (sds), cationic cetyltrimethylammonium bromide [$NMe_3(C_{16}H_{33})Br$] and neutral Triton X-100 (TX-100).



		M	
(*i*)	$R = CO_2^-$,	2 H	H_2tcpp^{4-}
		Zn^{2+}	$[Zn(tcpp)]^{4-}$
		Cu^{2+}	$[Cu(tcpp)]^{4-}$
		Ni^{2+}	$[Ni(tcpp)]^{4-}$
(*ii*)	$R = SO_3^-$,	2 H	H_2tpps^{4-}
		Zn^{2+}	$[Zn(tpps)]^{4-}$
		Cu^{2+}	$[Cu(tpps)]^{4-}$
		Ni^{2+}	$[Ni(tpps)]^{4-}$

Results and Discussion

The absorption spectra of H_2tcpp^{4-} in aqueous medium in the Q-band region are shown in Fig. 1(*a*). Addition of increasing amounts of K^+ ions to a solution containing H_2tccp^{4-} (4.81×10^{-5} mol dm^{-3}) and 18-crown-6 (5×10^{-2} mol dm^{-3}) causes: (*a*) reduction in absorbance and broadening of all the Q-bands and (*b*) a red shift of Q-bands with well defined isosbestic points. The magnitude of the intensity decrease and the red shift depends on the cation added and decreases in the order $K^+ \approx NH_4^+ > Na^+ \gg Li^+$ (Table 1). The addition of cations causes no absorption band shift in the Soret region. However, a decrease in absorbance and broadening of the Soret band was observed. These results suggest the existence of an equilibrium involving two species. Based on the findings of our earlier

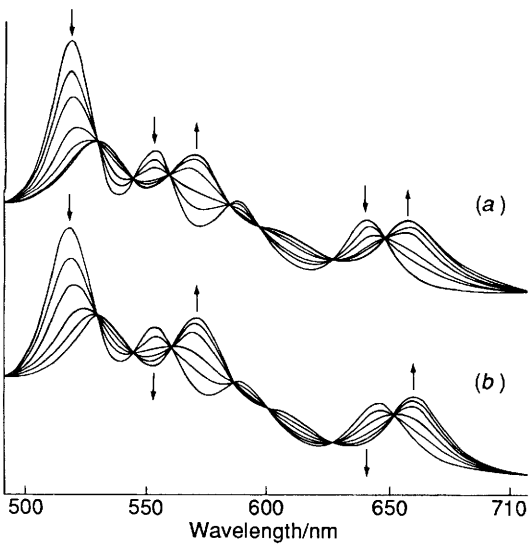


Fig. 1 Visible absorption spectra of H_2tcpp^{4-} in aqueous medium. (*a*) Effect of addition of increasing amounts of K^+ ions to a solution of H_2tcpp^{4-} [4.81×10^{-5} mol dm^{-3}] containing 18-crown-6 (0.05 mol dm^{-3}) at 25 °C; [K^+] = 4×10^{-3}, 9.3×10^{-3}, 2.3×10^{-2}, 6.3×10^{-2}, 1.7×10^{-1} and 1.9×10^{-1} mol dm^{-3}. Arrows indicate changes on increasing concentration of K^+. (*b*) Effect of temperature on spectra of H_2tcpp^{4-} [4.81×10^{-5} mol dm^{-3}] containing 18-crown-6 (0.05 mol dm^{-3}) and K^+ (1.9×10^{-1} mol dm^{-3}); T = 10, 20, 30, 40, 50 and 60 °C. Arrows indicate changes on decreasing temperature

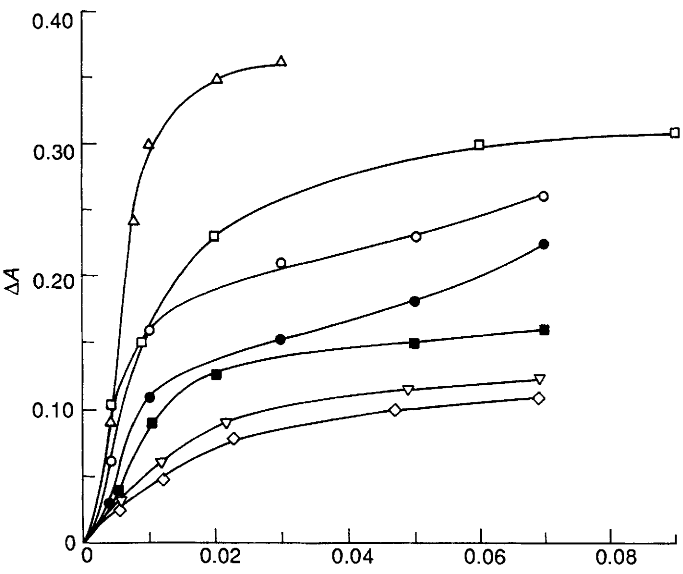


Fig. 2 Intensity changes of a prominent Q-band of $[Cu(tpps)]^{4-}$ (△), H_2tcpp (□), $[Cu(tcpp)]^{4-}$ (○), $[Ni(tcpp)]^{4-}$ (●), $[Ni(tpps)]^{4-}$ (■), $[Zn(tpps)]^{4-}$ (▽) and $[Zn(tcpp)]^{4-}$ (◇) [$\approx 5 \times 10^{-5}$ mol dm^{-3}] containing 18-crown-6 (0.05 mol dm^{-3}) and increasing amounts of K^+ ions in aqueous medium

Table 1 Dimerization induced absorption band red-shifts (nm) for free base porphyrins in the presence of cation–crown ether complexes *

		Q bands			
System	Medium	I	II	III	IV
H_2tcpp^{4-} + 18-crown-6 + K^+	Aqueous	20	—	16	13
H_2tcpp^{4-} + 18-crown-6 + NH_4^+	Aqueous	23	—	15	13
H_2tcpp^{4-} + 18-crown-6 + NH_4^+	sds	21	—	15	12
H_2tcpp^{4-} + 15-crown-5 + Na^+	sds	21	—	13	10
H_2tcpp^{4-} + 12-crown-4 + Li^+	sds	14	—	9	6
H_2tpps^{4-} + 18-crown-6 + K^+	Aqueous	22	18	13	9
H_2tpps^{4-} + 18-crown-6 + NH_4^+	sds	22	18	15	12
H_2tpps^{4-} + 15-crown-5 + Na^+	sds	19	10	10	7
H_2tpps^{4-} + 12-crown-4 + Li^+	sds	11	6	6	4

* Concentrations: porphyrin, $\approx 5 \times 10^{-5}$; crown ether, 0.05; cation, 0.19 mol dm^{-3}.

work,[17a,b] we conclude that the two species involved here are the monomer and dimer of H_2tcpp^{4-}. In the absence of cation and crown ether, under our experimental conditions, H_2tcpp^{4-} exists as a monomer and the addition of cation and crown ether strongly drives the equilibrium to the dimer. In the absence of cation the close approach of the two porphyrin monomers is not favoured due to repulsion of the negative charges on the periphery of the porphyrins. The added cation reduces this electrostatic repulsion by shielding the negative charges so facilitating the close approach of the two porphyrin rings to form a dimer through a π–π interaction. It is observed that the cation–crown ether complex is much more effective in driving the equilibrium to the dimer side than is the cation alone. This could be due to the exclusion of some water molecules from the solvation shell of the cation on complexation with the crown ether making the environment of the cation less polar and allowing the cation to approach the porphyrin more closely than can a completely solvated cation. The effect of temperature on the monomer–dimer equilibrium is apparent from Fig. 1(*b*). Evidently, small changes in temperature have a large effect on the extent of dimerization with lower temperatures favouring the formation of the dimer while higher temperatures shift the equilibrium towards the monomer.

Spectral titrations of crown ether–cation complexes with metalloporphyrins show a similar effect as for the free-base porphyrins. However the magnitude of intensity decrease and red shift were found to be dependent on the metal ion present in the porphyrin (Fig. 2). Well defined isosbestic points were observed in all the spectra and no shift in these were seen upon addition of higher concentrations of potassium ion. However, the shape of the curves in Fig. 2 reveal that the process of formation of the dimer involves more than one step. Two types of dimer can be visualized upon addition of cation–crown ether complex; a 'side-by-side' dimer of the type (tcpp)M–(cation–crown ether)–M(tcpp) involving only one cation–crown ether complex per dimer and a cofacial dimer which involves two or more cation–crown ether complexes per dimer. When K^+ ions are added to a solution of $[M(tcpp)]^{4-}$ (M = Ni^{2+}, Cu^{2+} or Zn^{2+}), the intensity decrease is sharp at lower concentrations of K^+ [< 0.025 mol dm^{-3}] probably indicating the formation of a side-by-side dimer with a very high formation constant. At higher concentration of K^+, a transformation of side-by-side dimer to a cofacial dimer occurs by encapsulating a second cation–crown ether complex. Since two more sites are still available in the cofacial dimer for saturation, it is possible that the encapsulation continues at higher concentrations until the two porphyrin units bind four cation–crown ether moieties in the metalloderivatives. However, Fig. 2 indicates a different stoichiometry for H_2tcpp^{4-}. We believe that in this instance the cofacial dimer involves only two cation–crown ether complexes per dimer probably because of the different symmetry of free H_2tcpp^{4-} from those of its metal derivatives.

An additional feature in the metalloderivatives is the shift of the Soret band. The complexes $[Cu(tcpp)]^{4-}$, $[Cu(tpps)]^{4-}$, $[Ni(tcpp)]^{4-}$ and $[Ni(tpps)]^{4-}$ show a blue shift of the Soret band on addition of 18-crown-6 and K^+ while $[Zn(tcpp)]^{4-}$ and $[Zn(tpps)]^{4-}$ show a red shift [Fig. 3(*a*)]. The Ni^{2+} and Cu^{2+} derivatives of both the porphyrins show a strong dimerization-induced shift while for the Zn^{2+} derivatives only a small shift is observed in the optical spectra (Table 2). It is known that the Ni^{2+} and Cu^{2+} derivatives have a planar structure with the four-co-ordinate metal ion at the centre of the

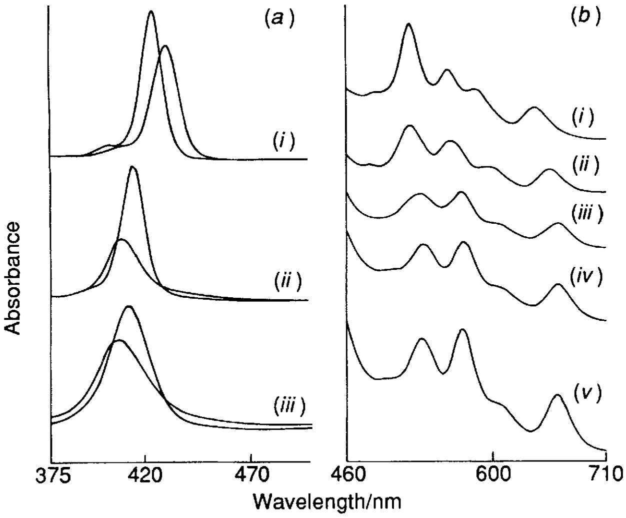


Fig. 3 Visible absorption spectra of free base and metalloporphyrins under different conditions in 0.1 mol dm^{-3} sds solution containing Tris (30 mmol dm^{-3}). (*a*) Comparison spectra of monomer and dimer of (*i*) $[Zn(tcpp)]^{4-}$, (*ii*) $[Cu(tcpp)]^{4-}$ and (*iii*) $[Ni(tcpp)]^{4-}$ in the Soret region at 25 °C. Spectra with reduced absorbance values correspond to dimer. (*b*) Optical spectra in the Q-band region of (*i*) H_2tcpp^{4-}, (*ii*) H_2tcpp^{4-} + 12-crown-4 + Li^+, (*iii*) H_2tcpp^{4-} + 15-crown-5 + Na^+, (*iv*) H_2tcpp^{4-} + 18-crown-6 + K^+ and (*v*) H_2tcpp^{4-} + 18-crown-6 + NH_4^+ at 5 °C (5 × 10^{-5} mol dm^3 porphyrin, 0.05 mol dm^{-3} crown ether, 0.1 mol dm^{-3} cation)

Table 2 Dimerization induced absorption band shifts[a] (nm) and the exciton coupling parameter (cm^{-1}) for metalloporphyrins in the presence of cation–18-crown-6 complexes

System[b]	Medium	Q-band(s) I	Q-band(s) II	Soret band	V
$[Cu(tcpp)]^{4-} + K^+$	Aqueous	12	12	−8	1856
$[Cu(tcpp)]^{4-} + NH_4^+$	sds	14	13	−6	1727
$[Ni(tcpp)]^{4-} + K^+$	Aqueous	8	—	−9	2659
$[Ni(tcpp)]^{4-} + NH_4^+$	sds	7	—	−7	1986
$[Zn(tcpp)]^{4-} + K^+$	Aqueous	1	1	+1	—
$[Zn(tcpp)]^{4-} + NH_4^+$	sds	11	9	+7	—
$[Cu(tpps)]^{4-} + K^+$	Aqueous	11	12	−4	2924
$[Cu(tpps)]^{4-} + NH_4^+$	sds	10	12	−6	2726
$[Ni(tpps)]^{4-} + K^+$	Aqueous	8	—	−5	4308[c]
$[Ni(tpps)]^{4-} + NH_4^+$	sds	7	—	−3	4124[c]
$[Zn(tpps)]^{4-} + K^+$	Aqueous	2	2	+1	—
$[Zn(tpps)]^{4-} + NH_4^+$	sds	9	6	+7	—

[a] A positive value indicates a red shift. [b] In the presence of 0.05 mol dm^{-3} 18-crown-6; *ca.* 5 × 10^{-5} mol dm^{-3} metalloporphyrin, 0.19 mol dm^{-3} cation. [c] The Soret bands were too broad in these cases to calculate the half band width thereby increasing Δλ values.

porphyrin core* whereas in the Zn^{2+} complexes the metal is out of the plane of the porphyrin core and an axial water molecule is incorporated in the co-ordination sphere.[7,8] The planar nature of the Ni^{2+} and Cu^{2+} derivatives allows the close approach of the two porphyrin rings leading to a stronger π–π interaction and resulting in a large red shift of the Q-bands. The presence of axial ligands in Zn^{2+} derivatives however hinders the close approach of the two rings with the consequent reduced π–π interaction resulting in only a small red shift of the Q-bands in aqueous medium. In fact literature data suggest that the Zn^{2+} derivatives do not actually dimerize in aqueous solutions in the presence of an electrolyte.[7,8]

A comparison of optical spectra of H_2tcpp^{4-} and its metal derivatives (5 × 10^{-5} mol dm^{-3}) in aqueous medium and in 0.1 mol dm^{-3} sds solution containing 30 mol dm^{-3} Tris [tris(hydroxymethyl)methylamine] shows small decreases in molar absorption values and slight blue shifts (4–5 nm) of Soret bands in 0.1 mol dm^{-3} sds.† This indicates that in 0.1 mol dm^{-3} sds the porphyrins show a tendency to aggregate due probably to the presence of free Na^+ ions in sds solution. Addition of cations and crown ether produces similar effects on the optical bands of the porphyrins as found in the aqueous solutions [Fig. 3(*b*)] indicating that the equilibrium is shifted to dimer formation. This observation suggests that H_2tcpp^{4-} and its metal derivatives does not reside at the hydrophobic region of the sds micelle. On the other hand addition of crown ethers and cations did not produce any appreciable changes in the spectra of the porphyrins in $NMe_3(C_{16}H_{33})Br$ or TX-100 solutions suggesting that the porphyrin derivatives remain monomeric in these micelles. This could be due to the solubilization of the porphyrin derivatives into the micelles due to the electrostatic interaction of negatively charged porphyrins with cationic $NMe_3(C_{16}H_{33})Br$ while strong hydrophobic interactions could be responsible in neutral TX-100. These results parallel the findings of Kadish *et al.*[19] on H_2tpps^{4-} and its metal derivatives in micellar media.

A comparison of the dimerization-induced shifts in aqueous media with that of 0.1 mol dm^{-3} sds solution indicate that the magnitude of shifts for H_2tcpp^{4-} and its Cu^{2+} and Ni^{2+} derivatives are similar. However, for Zn^{2+} derivatives, the magnitude of shifts are larger in 0.1 mol dm^{-3} sds solution relative to that found in aqueous solution. This suggests an enhanced dimerization of Zn^{2+} derivatives in 0.1 mol dm^{-3} sds. Recently, a similar effect of enhanced aggregation was observed for $[Zn(tpps)]^{4-}$ in 0.1 mol dm^{-3} sds.[19] Further work is in progress to probe into the reasons for this enhanced aggregation which is found only for the Zn^{2+} derivatives.

The room-temperature fluorescence spectrum of H_2tcpp^{4-} in the presence and absence of 18-crown-6 and K^+ ions in aqueous and micellar media is shown in Fig. 4. The free base porphyrin H_2tcpp^{4-} exhibits two emission bands at 644 and 702 nm both in aqueous and sds media. The following changes were noted upon addition of K^+ and 18-crown-6. The band at 644 nm is red shifted to 681 nm and the band originally at 702 nm appears as a small shoulder at 750 nm. Furthermore, the intensity of these bands is reduced by a factor of two. The fluorescence excitation spectra reflect the cation–crown ether effects on the absorption spectra. Similar effects were observed for Zn^{2+} derivatives but the magnitude of shifts was much reduced. The emission data are listed in Table 3.

Effect of Cations and Crown Ethers.—In order to see whether different cations had different effects on dimer formation, optical spectra of solutions containing the same amount of H_2tcpp^{4-} [5 × 10^{-5} mol dm^{-3}] and 0.1 mol dm^{-3} LiCl, NaCl, KCl or NH_4Cl were recorded. It was found that in the absence of crown ether only a relatively small variation in the amount of dimer formed was observed on changing the cation. However, in the presence of added crown ether, substantial differences can be seen in the spectra with respect to the magnitude of red shifts and intensity decrease depending on which cation is added. For example, when 18-crown-6 was present, the magnitude of red shifts decreased in the order $K^+ \approx NH_4^+ > Na^+ \gg Li^+$; for 15-crown-5, the order is $K^+ \approx NH_4^+ \approx Na^+ > Li^+$ while for 12-crown-4, Li^+ gives rise to shifts comparable to those

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* The observation of only one Soret band both for $[Ni(tcpp)]^{4-}$ and $[Ni(tpps)]^{4-}$ suggests that they are four-co-ordinate. However $[Ni(tmpyp)]^{4+}$ [tmpyp = 5,10,15,20-tetra(methylpyridinio)porphyrinate] shows two Soret bands indicating the existence of both four- and six-co-ordinate derivatives.

† The critical micelle concentrations for sds, $NMe_3(C_{16}H_{33})Br$ and TX-100 in neutral aqueous solutions at 25 °C are 8.1 × 10^{-3}, 9.2 × 10^{-4} mol dm^{-3} and 0.54% v/v (≈3 × 10^{-4} mol dm^{-3}) respectively.[18]

Table 3 Emission data of free-base and metalloporphyrin monomers and dimers *

Porphyrin	Medium	$Q_{(0-0)}$/nm	$Q_{(0-1)}$/nm	$I_{(0-0)}/I_{(0-1)}$
H_2tcpp^{4-}	Aqueous	644	702	2.01
	sds	649	710	2.17
	$NMe_3(C_{16}H_{33})Br$	649	710	2.41
$[\{H_2(tcpp)\}_2]^{8-}$	Aqueous	681	751	4.00
	sds	680	750	3.65
	$NMe_3(C_{16}H_{33})Br$	651	716	2.37
$[Zn(tcpp)]^{4-}$	Aqueous	610	659	1.76
	sds	610	660	1.34
	$NMe_3(C_{16}H_{33})Br$	613	664	2.35
$[\{Zn(tcpp)\}_2]^{8-}$	Aqueous	614	662	1.82
	sds	614	663	2.11
	$NMe_3(C_{16}H_{33})Br$	613	664	2.31
$[Zn(tpps)]^{4-}$	Aqueous	605	652	1.66
	sds	607	658	1.34
$[\{Zn(tpps)\}_2]^{8-}$	Aqueous	608	659	1.33
	sds	614	661	1.53

* Dimers were generated by addition of K^+ and 18-crown-6. Concentrations: H_2tcpp^{4-}, 2.4 × 10^{-5}; $[Zn(tcpp)]^{4-}$, $[Zn(tpps)]^{4-}$, 2 × 10^{-5}; 18-crown-6, 0.05; cation, 0.19 mol dm^{-3}.

Table 4 Formation constants of porphyrin dimers induced by cation-crown ether complex in aqueous medium at 25 °C

Porphyrin	log *K*	log K^a
H_2tcpp^{4-}	11.0 ± 1.5	4.66
$[Cu(tcpp)]^{4-}$	12.5 ± 1.8	5.23
$[Ni(tcpp)]^{4-}$	12.8 ± 1.8	5.20
$[Cu(tpps)]^{4-}$	12.9 ± 1.8	4.61, 4.83
$[Ni(tpps)]^{4-}$	12.2 ± 1.5	—
$[Zn(tcpp)]^{4-}$	10.0 ± 1.0[b]	*c*
$[Zn(tpps)]^{4-}$	10.0 ± 1.0[b]	*c*

[a] These values are taken from refs. 7 and 8. [b] In 0.1 mol dm^{-3} sds solution. [c] Under the conditions described in refs. 7 and 8, dimerization does not occur.

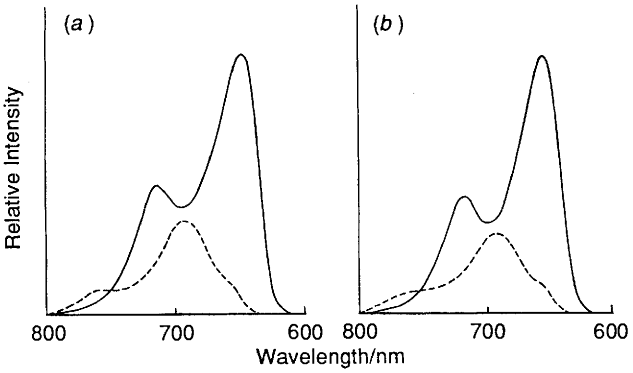

Fig. 4 Fluorescence spectra of H_2tcpp^{4-} (2.4 × 10^{-5} mol dm^{-3}) (——) and H_2tcpp^{4-} + 18-crown-6 + NH_4^+ (· · · ·) in (*a*) aqueous medium and (*b*) 0.1 mol dm^{-3} sds solution containing Tris (30 mmol dm^{-3}) at 25 °C

observed for Na^+ in presence of 15-crown-5 (Table 1). Similar effects were observed for several crown-ether linked porphyrins and phthalocyanines upon complexation with alkali-metal cations.[11b,13,14] Selectivity towards the different cations varies with crown ether ring size and maximum effects were observed when the size of the crown ether cavity and the ionic radii of the metal ions match. Apparently, in the absence of crown ethers, the role of cations is to shield the negative charges in the periphery of the porphyrins that oppose dimerization.[1a] However, in the presence of crown ethers, one has to relate the observed effects to the stability and structure of the cation–crown ether complexes formed since the crown ethers have different affinity for different cations dependong on their cavity size.[20] A study of the literature reveals that the stability constants (log *K*) for K^+ and NH_4^+ binding with 18-crown-6 are 2.06 and 1.1, respectively while it is <0.3 for Na^+ and no detectable complex formation is found for Li^+ with 18-crown-6.[21] On the other hand, 15-crown-5 has much larger affinity for Na^+ compared to 18-crown-6 while 12-crown-4 and 14-crown-4 have larger affinity for Li^+ ions.[20] This is thought to be due to the different ionic sizes of cations and the differing sizes of the holes in the crown ethers.* Thus, the magnitude of dimerization induced shifts follows the same order of formation constants for the cation–crown complexes,[21] and that the amount of dimer formed depends on the stability of the cation–crown ether complexes. Also, it is seen from Table 1 that the dimerization induced shift for the Li^+–12-crown-4 complex is smaller than those observed for the K^+–18-crown-6 complex indicating that the shielding power of the Li^+ complex is not as effective as that of the K^+ complex. This could be due to the small size of the Li^+ complex relative to the K^+ complex and as well as to the large solvation energy of Li^+ compared to K^+. It is also observed that the magnitude of red shifts observed when only cations are present is much less than when both cation and crown ether are present; in the presence of 0.1 mol dm^{-3} KCl, the Q-bands of H_2tcpp^{4-} experience a shift of 10, 4 and 2 nm, respectively while in the presence of the K^+–18-crown-6 complex the same bands experience a shift of 20, 16 and 13 nm, respectively. This observation indicates that the involvement of crown ether forces the dimer into a conformation which allows for increased π–π interaction between the two porphyrin rings.[11a,b]

Evaluation of Dimer Formation Constants (*K*) *in the Presence of Crown Ethers*.—The progressive decrease in absorbance of a prominent Q-band on increasing addition of cation–crown ether complex is made use of to evaluate the extent of dimer formation using a method described previously.[11b] The cation–crown ether induced dimerization can be represented by equation (1) where P stands for porphyrin molecule, C^+

$$2P + nC^+ \overset{K}{\rightleftharpoons} (P_2C_n)^{n+} \qquad (1)$$

represents the cation–crown ether complex and *n* is the number of cation–crown ether complexes incorporated. The value of *n* was varied from 1 to 4, the upper limit chosen since there are four negative groups in the periphery of porphyrin. The method

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* The cavity sizes of 18-crown-6, 15-crown-5 and 14-crown-4 are 2.6–3.2, 1.7–2.2 and 1.2–1.5 Å respectively. The ionic sizes of Na^+, K^+, NH_4^+ and Li^+ are 1.94, 2.66, 2.86 and 1.36 Å respectively.

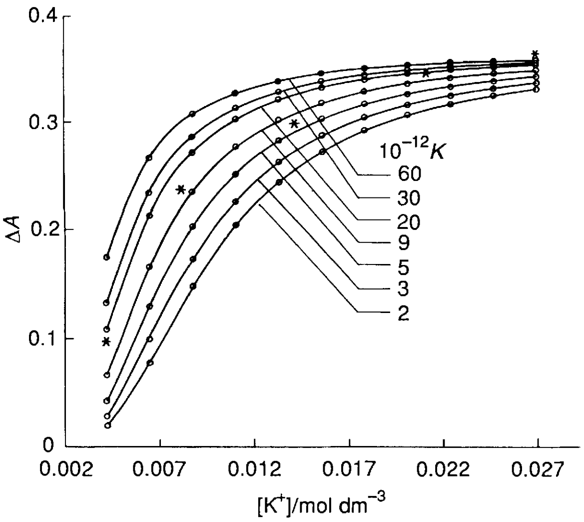

Fig. 5 Difference in absorbance values ΔA *vs.* concentration of K^+ ions added for various assumed values of K for dimerization of $[Cu(tpps)]^{4-}$ (for $n = 4$, see text); (○) theoretical, (*) experimental

adopted here assumes different values of K and computes the theoretical values of x, the amount of dimer formed and ΔA, the decrease in absorbance at each concentration of cation added using experimentally known parameters such as the porphyrin concentration, the concentrations of cations added, the decrease in absorbance at each cation concentration added and the molar absorption values of monomer and dimer (the absorption values for the dimer being calculated from the spectrum run at 5 °C). The details of the method are given in ref. 11*b*. A computer program was devised to carry out the calculations using the Newton–Raphson iterative method. Theoretical plots of ΔA *vs.* concentration of the cation added for various values of K were constructed. The experimental points were then mapped into this plot, and the best fit chosen for the overall formation constant of the dimer. Calculations were performed varying the value of n from 1 to 4 and in all the cases the best fit was observed when $n = 4$ suggesting that four cation–crown ether complexes are involved per dimer. A representative plot for the K^+–18-crown-6 induced dimer of $[Cu(tpps)]^{4-}$ for $n = 4$ is given in Fig. 5. The values of K are in Table 4.

Table 4 also shows a comparison of the values of K evaluated in the present study for the dimerization process and those reported in literature for dimers formed by concentration effects in the presence of electrolyte.[7,8] In our case the magnitudes of the overall formation constants are very much larger compared to reported values for the same systems in the absence of crown ethers. The following explanation is offered for this observation: (*a*) since crown ethers have very large affinity for cations and since the amount of dimer formed depends on the stability of the cation–crown ether complex, we tend to believe that the formation constants (K) reported here represent a composite of the dimer formation constant and the cation–crown ether complex stability although it is difficult to estimate the individual contribution of these two effects to the overall formation constant. However the results indicate the high selectivity of cation–crown ether complexes to shift the equilibrium to formation of the dimer. (*b*) The dimers formed here are discrete and the dimerization process differs from aggregation promoted by concentration effects in the presence of electrolyte.[7,8] Despite the difference in magnitude between dimer formation studied here and in the absence of crown ethers,[7,8] the general trend of stabilities follows the same order in both instances.

Origin of Absorption and Emission Band Shifts.—A knowledge of the dimer structure is essential to account for the spectral shifts. Our previous ESR and ENDOR (electron nuclear double resonance) studies on the cation-induced dimerization of crown-ether linked porphyrins and of cation–crown ether induced dimers of water-soluble porphyrins have established the face-to-face orientation of the two porphyrin rings with cation–crown ether complex sandwiched between the negatively charged groups.[17] Additional support for this conclusion comes from the observation that many covalently linked diporphyrins[22–24] and porphyrin crown dimers[11] of well defined geometry exhibit spectral shifts of similar magnitude to those in the present study.

The dimerization-induced blue shift observed for Soret bands of $[Cu(tcpp)]^{4-}$, $[Cu(tpps)]^{4-}$, $[Ni(tcpp)]^{4-}$ and $[Ni(tpps)]^{4-}$ and the fluorescence quenching are in accordance with the predictions of exciton theory.[25] The exciton coupling parameters calculated from the available spectral data (Table 2) are of comparable magnitude to those observed for several diporphyrins[24] and dimers of metal crowned phthalocyanines.[13]

Experimentally, it is found that both H_2tcpp^{4-} and H_2tpps^{4-} do not give rise to Soret band shifts. There are of course a range of configurations for which the exciton theory predicts only a small or zero Soret band shift.* So this experimental finding can be accounted for within the framework of exciton formalism. This finding is also experimentally supported by the fact that many diporphyrins which have well defined structure such as the dimer of 5,10,15,20-tetraphenylporphyrin $[\{H_2tpp\}_2]$ synthesized by Kagan *et al.*[23] do not show a Soret band shift relative to the monomer. However, the Q-bands and emission bands do show a large red shift on dimerization as observed in the present study. Interestingly, a recent report by Firman *et al.*[26] on the induced dimerization of H_2tpps^{4-} by a polyammonium macrocycle indicates a blue shift of the Soret band of H_2tpps^{4-} upon dimerization. Evidently, relatively minor changes in dimer geometry can have a profound effect on spectral characteristics.

However, the exciton formalism does not explain the large red shifts of Q-bands observed both in optical and fluorescence spectra upon dimerization. In these systems, the bonding between the dimer constituents is due, at least in part, to attraction between the porphyrin rings. The absence of any covalent links allows the rings to assemble in such a way as to promote the interaction between π-molecular orbitals of chromophores resulting in strong π–π interactions. The strength of this interaction may be reflected in the magnitude of red shifts of the Q-bands. This kind of interaction has been suggested as a substantial source of red shifts found between absorption bands for *in vitro* and *in vivo* chlorophyll a.[27a] A theoretical account of the nature of such π–π interactions has appeared recently.[27]

The Zn^{2+} derivatives of both the porphyrins H_2tcpp^{4-} and H_2tpps^{4-} surprisingly show a red shift of the Soret band upon dimerization [Fig. 3(*a*)]. A purely excitonic interaction cannot account for this observation.[25] In the absence of excitonic interaction, one has to invoke a charge-transfer mechanism to explain the observed shifts. A complete charge transfer is ruled out based on our earlier studies on photoexcited triplets of the Zn(tpps) dimer.[17c] This study indicated that the observed changes in the zero-field splitting parameter D and the associated changes in the kinetic decay parameters would fit a model of a delocalized triplet state with some charge transfer contribution. We believe that an excitonic interaction with some charge transfer contribution could explain the observed red shift

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* The exciton splitting for oblique transition dipoles can be given by $E = 2|M|^2/r^3(\cos\alpha + 3\cos^2\theta)$, where θ and α define the orientation of one porphyrin relative to other with respect to the axis through the centres of the dimer constituents. From this equation it is clear that for parallel planes the maximum splitting will be found when the x and y axes of each chromophore have the same orientation and no shift will be found when the axes are orthogonal. For details, see ref. 25*a*.

in the Soret region. However, the question as to why zinc porphyrins behave differently from those of Ni^{2+} and Cu^{2+} derivatives is not clearly understood at this time. It is possible that the non-planar structure of zinc porphyrin causes rearrangement of energy levels leading to availability of low-lying charge-transfer states. Cyclic voltammetric studies on monomer and dimers of Zn^{2+} porphyrin derivatives are underway to verify the availability of such low-lying charge-transfer states.

Experimental

The porphyrins H_2tcpp^{4-} and H_2tpps^{4-} (as its sodium salt) were obtained from Strem Chemicals, USA and were used as supplied. The metal derivatives (Zn^{2+}, Cu^{2+} and Ni^{2+}) were prepared and purified following published procedures.[7,28] Crown ethers, sodium dodecyl sulphate, $NMe_3(C_{16}H_{33})Br$ and TX-100 were obtained from Aldrich Chemicals, USA. All metal salts were of Analar grade.

Double-distilled water was used for all the studies. For spectroscopic studies the aqueous medium contains 30% sucrose and 30 mmol dm^{-3} Tris–HCl buffer and the pH was adjusted to 9.6 using a digital pH meter. Micellar solutions were prepared by adding appropriate amounts of surfactants to water and allowing mixtures to stir for *ca.* 20 min; 30 mmol dm^{-3} Tris–HCl was then added and stirring was continued for another 10 min. The required amount of solid porphyrin was then added continuing stirring for an additional 20 min.

Electronic spectra were recorded on a Shimadzu UV-160 spectrophotometer fitted with an adjustable temperature unit. Fluorescence spectra were recorded on a Spex Romalog system with Spex Photon Counting and Spectra Physics model 165 Ar-ion laser (514.5 nm) as the excitation source.

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