A New Method for the Synthesis of Zinc Tetrakis-(3- methylpyridyloxy)-phthalocyanine and the Physical Properties of Dimers formed by Complexation of the Cationic Phthalocyanine with Anionic Porphyrins

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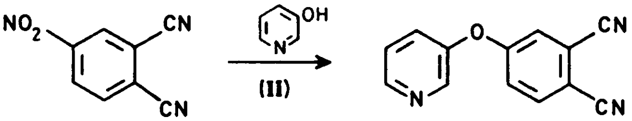
Face-to-face heterodimers have been obtained by pairing a cationic phthalocyanine with two different anionic, metal-free and manganese(III) porphyrins. Different behaviour has been observed for the spectroscopic and fluorescence properties of the dimers. For the manganese(III) porphyrin–phthalocyanine system, the intracyclic interaction is found to be weak. On the other hand, for the metal-free porphyrin–phthalocyanine system, a very strong interaction exists, which leads to a charge-separated species, (porphyrin)$^-$–(phthalocyanine)$^+$.

The most efficient primary electron donor in bacterial photosynthesis is a bacteriochlorophyll dimer, the special pair with two cofacial chromophores.[1] This has prompted numerous studies on cofacial,[2] hinged,[3] or singly linked and folded dimer porphyrins[4,5] or dimer phthalocyanine.[6] More recently, electrostatic porphyrin or phthalocyanine dimers formed by pairing cationic and anionic water-soluble compounds have been studied.[7,8] An intramolecular electron-transfer reaction has been proposed to explain the strong fluorescence quenching of the metal-free porphyrin by zinc or copper porphyrin in the corresponding zwitterionic dimers, but no direct charge separation has been found. By pairing oppositely charged phthalocyanine and porphyrin, which depending on the nature of the central metal and of the substituents have different redox properties, one should obtain peculiar redox properties which increase the charge transfer reaction efficiency.

We report here a new method for the synthesis of a cationic phthalocyanine, zinc tetrakis-(3-methylpyridyloxy)phthalocyanine, and its photophysical properties upon complexation with a metal-free and a manganese sulphonated porphyrin, in comparison with mixtures of non-charged compounds.

Synthesis of Tetrakis-(3-*methylpyridyloxy*)*phthalocyanine.*—The formation of substituted phthalonitriles remains the most difficult path in phthalocyanine synthesis. It has been recently shown that nucleophilic substitution reactions can easily occur for 4-nitrophthalonitrile (**I**).[9] The reaction of 3-hydroxypyridine (**II**) with (**I**) in alkaline media, gives (**III**) in good yield.



(**I**) (**II**) (**III**)

In the presence of zinc metal, the condensation of (**III**) gives zinc tetrakis-(3-pyridyloxy)phthalocyanine (**IV**) in 41% yield. This value is 1.5 times higher than that obtained from the reaction of 5-(3-pyridyloxy)-1,3-di-iminoisoindoline with a zinc salt.[10] It has been shown that the formation of the phthalocyanine macrocycle requires the presence of two neutral and two reduced phthalonitrile molecules.[11,12] In the case of metal complexes, it seems that the metal acts as a reducer towards the phthalonitrile, thus improving the yield of macrocycle. Moreover, the presence of the substituents on the phthalonitrile moieties induces an orientation effect during the formation of the macrocycle, as previously found for the tetra-t-butylphthalocyanine.[12] In the present case, the resulting phthalocyanine has the four pyridyloxy groups on the 2,9,17 and 24 positions (Figure 1a). N.m.r. spectroscopic data corroborate this structure.

The methylation of (**IV**) is achieved by reaction with methyl iodide in dimethylformamide. The quaternisation of (**IV**) yields 77% zinc tetrakis-(3-methylpyridyloxy)phthalocyanine, (**V**) (ZnPcTMPyr) which is soluble in water and polar organic solvents.

The tetrakis(sulphonatophenyl)metal-free porphyrin (H_2-TPPS) was from Ventron. The manganese porphyrin (MnTPPS) was synthesized by Harriman's method.[13] Zinc tetratolylporphyrin and zinc phthalocyanine were from Kodak.

Results and Discussion

Spectroscopic and Photophysical Properties of Zwitterionic Phthalocyanine–Porphyrin Dimers.—Spectroscopic properties. The electronic spectra of H_2TPPS, ZnTPP, and MnTPPS in Me_2SO are characterized by two types of bands. The most intense is the Soret band peaking respectively at 422, 428, and 467 nm for H_2TPPS, ZnTPP, and MnTPPS. The visible spectrum of MnTPPS has two maxima at 565 and 603 nm, characteristic of manganese (III) porphyrins.[14] The Q band of the metal-free porphyrin is split into four bands characteristic of a compound with D_{2h} symmetry. The molar extinction coefficient of the absorption maxima are reported in Table 1 and compared with literature values.

The u.v.–visible electronic absorption spectrum of common metal phthalocyanines is characterized by two main bands, the Soret and Q bands. In contrast to the porphyrins, the most important absorption in the visible region corresponds to the Q band which peaks at *ca.* 675 nm depending on the nature of the metal and the solvent. This band has been attributed to the $a_{1u} \longrightarrow e_g$ transition of the ring. The double degeneracy is due to the D_{4h} symmetry of the macrocycle. The Soret band, much less intense, is attributed to the $a_{2u} \longrightarrow e_g$ transition of the ring.

In the present case, in contrast to ZnPc, the electronic spectrum of ZnPcTMPyr in Me_2SO shows two visible split Q_x and Q_y bands (664 and 695 nm), characteristic of a compound with D_{2h} symmetry.

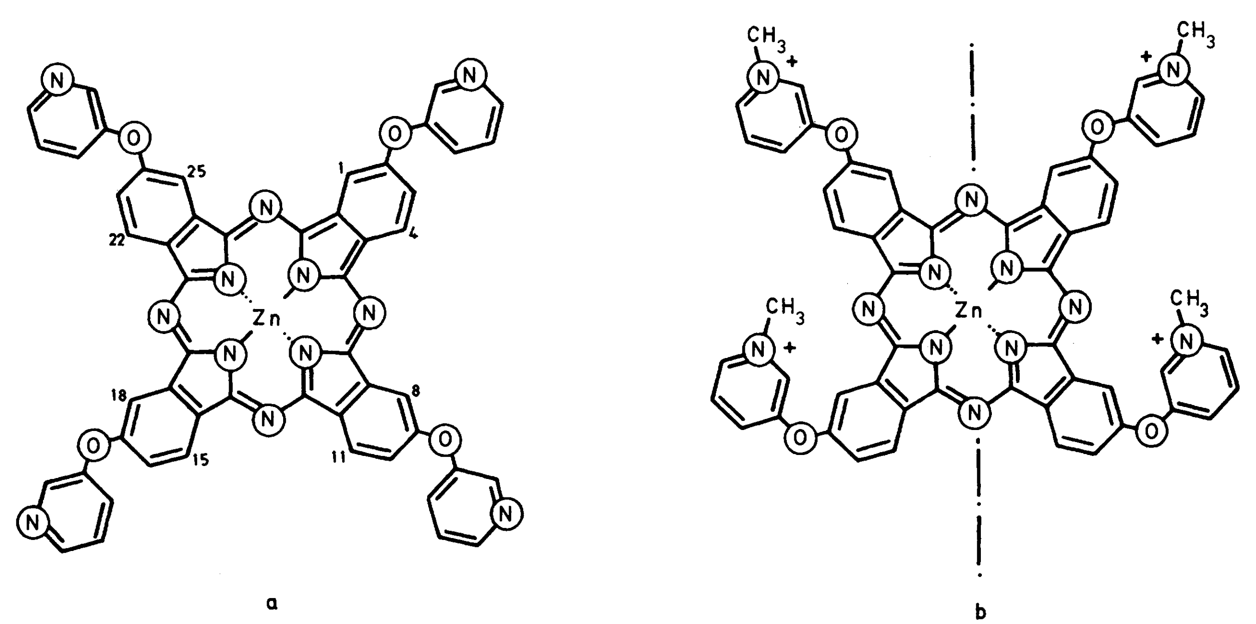


Figure 1. a, Zinc tetrakis-(3-pyridyloxy)phthalocyanine (**IV**) and b, zinc tetrakis-(3-methylpyridyloxy)phthalocyanine (**V**).

Table 1. U.v. and visible absorption maxima of porphyrins and phthalocyanines.

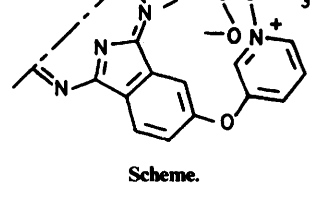
Compound	Solvent	$\lambda_{max.}$/nm	ε/dm^3 mol^{-1} cm^{-1}	Ref.
Mn^{III}TPPS	Me_2SO	467	1.03×10^5	This work
		565	0.97×10^4	
		603	0.80×10^4	
Mn^{III}TPPS	H_2O	469	0.95×10^5	*a*
		562	1.17×10^4	
		596	0.75×10^4	
Mn^{III}PTMPyr	H_2O	463	0.92×10^5	*a*
		560	1.10×10^4	
H_2TPPS	Me_2SO	422	2.92×10^5	This work
		515	1.35×10^4	
		550	0.68×10^4	
		588	0.39×10^4	
		644	0.37×10^4	
H_2TPPS	H_2O	412	5.3×10^5	*a*
		515	1.65×10^4	
		548	0.86×10^4	
		588	0.59×10^4	
H_2PTMPyr	H_2O	424	2.26×10^5	*a*
		520	1.45×10^4	
		558	0.92×10^4	
		584		
		638		
ZnPcTMPyr (D_{2h})	Me_2SO	342	3.84×10^5	This work
		664	5.5×10^4	
		695	6.0×10^4	
ZnPcTMPyr (D_{4h})	Me_2SO	340	6.67×10^4	This work
		676	1.5×10^5	
ZnPcTS	H_2O + Pyridine	360	1.25×10^5	*b*
		678	2.90×10^5	
ZnTPP	Me_2SO	428	6.90×10^5	This work
		561	2.81×10^4	
		601	1.66×10^4	
ZnPc	Me_2SO	344	7.1×10^4	This work
		672	2.0×10^5	

[a] K. Kalyanasundaram and M. Neumann-Spallard, *J. Phys. Chem.*, 1982, **86**, 5163. [b] A. Harriman and M. C. Richoux, *J. Chem. Soc., Faraday Trans. 2*, 1980, 1618.

Heating the ZnPcTMPyr solution provokes a spectral evolution from D_{2h} symmetry to D_{4h} (Figure 2). The same effect is observed on vigorously bubbling gases (Ar,O_2) through the solution. This spectral evolution was found to be irreversible and especially fast for dilute solutions (in Me_2SO or $HCONMe_2$). All these results argue against the hypothesis of either metal loss during methylation or of the presence of aggregates in the medium. The D_{2h} symmetry is due to a change in the electron density of the two opposite aza bridges of the macrocycle because of their interaction with the two proximate 9,17 pyridinium groups (Figure 1b).[15] The disappearance of such an interaction upon heating, bubbling, or diluting the solution gives back D_{4h} symmetry.

An n.m.r. study supports this hypothesis. The n.m.r. spectrum of ZnPcTMPyr in Me_2SO shows two groups of signals (Figure 5b). The first between δ 8 and 10 corresponds to the 28 aromatic protons. The second one between δ 4 and 5 is attributed to the 12 protons of the *N*-methyl groups. The integral measurements of the second group indicate the existence of two types of methyl groups in equal proportion. Moreover, from the integral of the $HCONMe_2$ signal (at δ 3.7), it can be established that each N^+–CH_3 group can be solvated by six or seven $HCONMe_2$ molecules.

Because of the binding mode of the substituents on the 2,9,17, and 24 positions, only the 9 and 17 substituents can more easily interact with the aza bridges of the macrocycle. This labile motion interaction can be hindered by the presence of the residual $HCONMe_2$ molecules. It is possible to insert a $HCONMe_2$ molecule between the nitrogen of the macrocycle and a pyridinium nitrogen as found with the help of molecular models (Scheme).



Scheme.

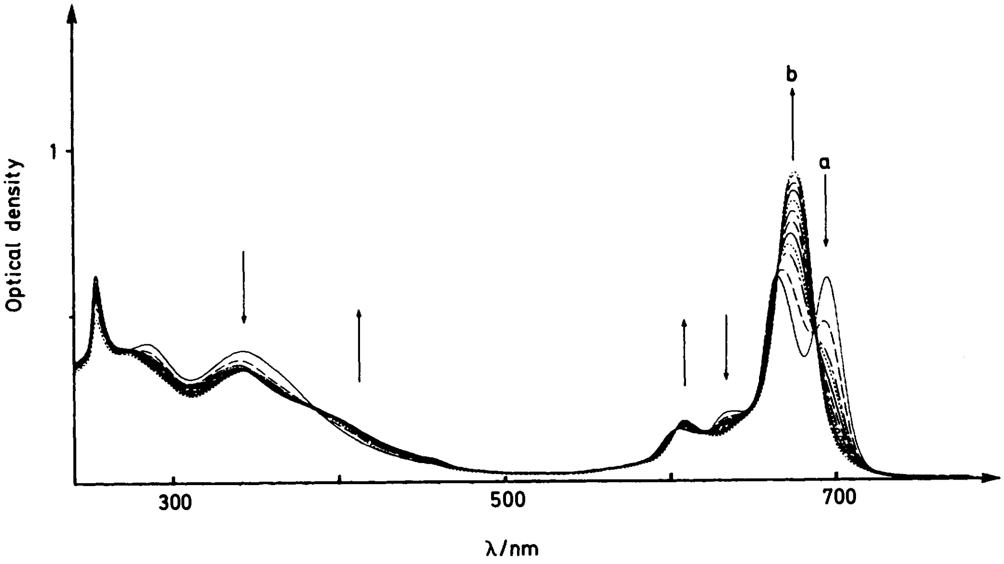


Figure 2. Spectral evolution of ZnPcTMPyr in Me_2SO upon heating: a, D_{2h} form; b, D_{4h} form.

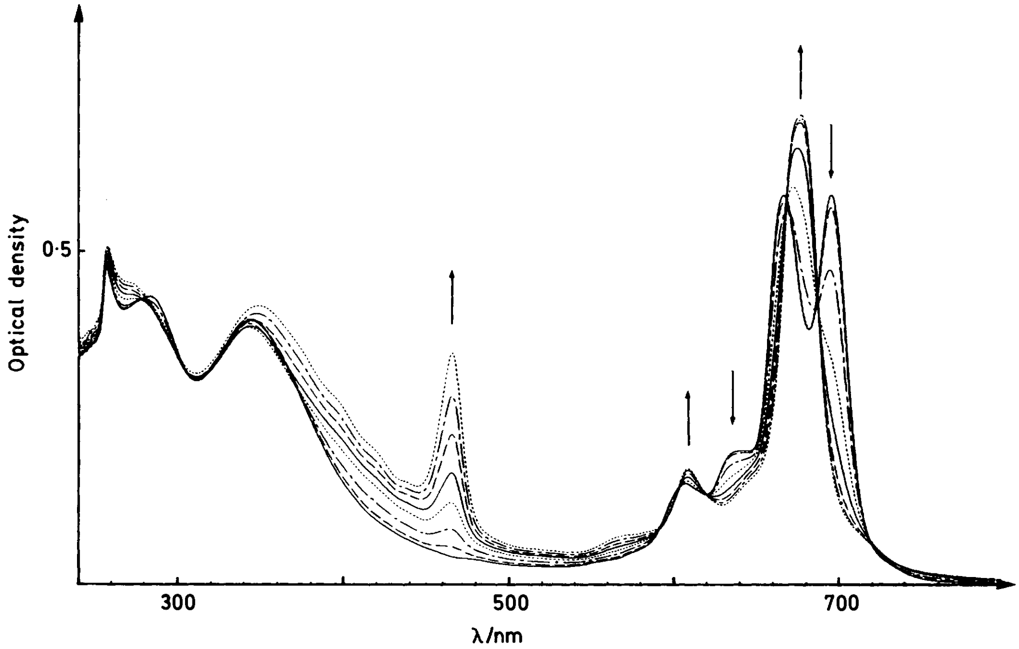


Figure 3. Spectral evolution of ZnPcTMPyr in Me_2SO upon addition of Mn^{III}TPPS.

Under these conditions, the well defined peak at δ 4.5 (6 H) is attributed to the completely free N^+–CH_3 groups in the 2 and 24 positions. For the 9 and 17 N^+–CH_3 groups, the existence of three little peaks (total 6 H) is consistent with the hypothesis of a stacked position of the N^+–CH_3 groups in interaction with the aza bridges of the macrocycle *via* a $HCONMe_2$ molecule.

Progressive heating or mechanical disturbance by bubbling gas through the solution destroys this interaction and modifies the solvation of the N^+–CH_3 group (Figure 6c).

In order to remove the residual $HCONMe_2$, the compound was purified by successive precipitation with acetone.

Solutions of the purified ZnPcTMPyr in Me_2SO give rise to Figure 6d composed of two close peaks at δ *ca.* 4.4 (each 6 H). Heating the solution no longer changes the shape of the spectrum, thus indicating the existence of two magnetically different groups. This is consistent with 2,9,17,24 substitution previously reported for tetra-t-butylphthalocyanine.[12]

The molar extinction coefficient values have been determined for both the D_{2h} and D_{4h} compounds. They are respectively $5.5 \pm 0.1 \times 10^4$ at 664 nm and $6.0 \pm 0.1\ 10^4\ dm^3\ mol^{-1}\ cm^{-1}$ at 695 nm for the D_{2h} form and $1.5 \pm 0.1 \times 10^5\ dm^3\ mol^{-1}\ cm^{-1}$ at 676 nm for the D_{4h} compound.

Another way to induce spectral evolution from D_{2h} towards D_{4h} symmetry consists of disrupting the intracyclic interactions by engaging the four pyridinium substituents in electrostatic bonds with a negatively charged substituted macrocycle. This is obtained by progressively adding to ZnPcTMPyr (D_{2h}) a tetrasulphonated manganese(III) porphyrin axially co-ordinated with an acetate ligand (Figure 3). The interaction between the pyridinium and the sulphonate groups is stronger than the intracyclic interaction and the D_{4h} symmetry of the ZnPcTMPyr macrocycle is progressively recovered. Complete evolution is obtained for an equimolar mixture.

The absorption spectrum of an equimolar mixture of

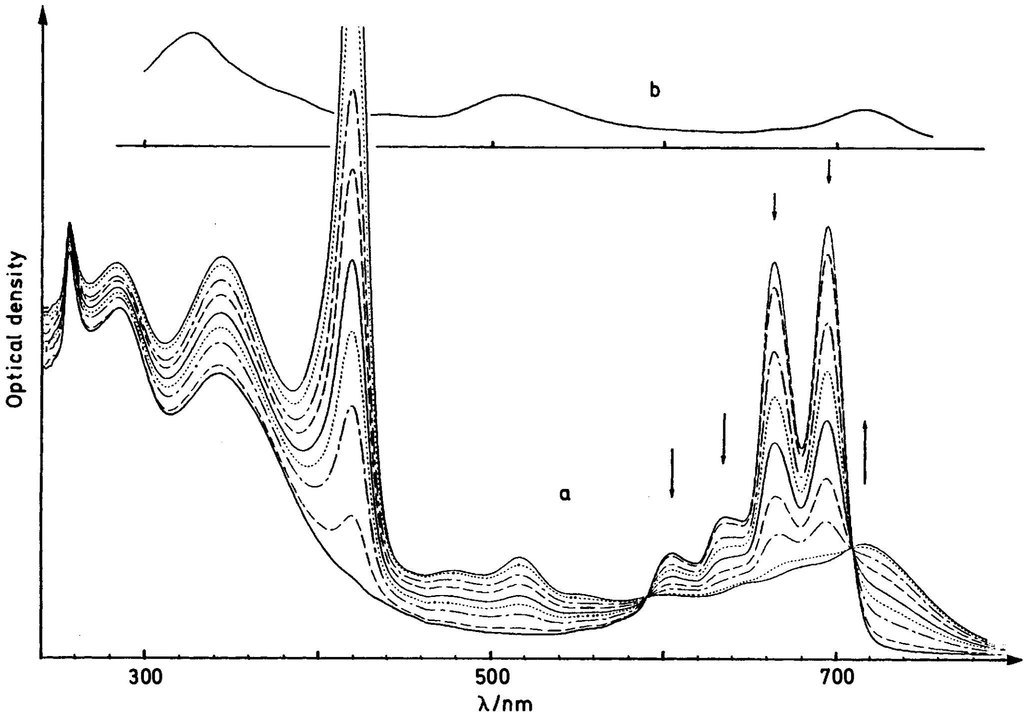


Figure 4. a, Spectral evolution of ZnPcTMPyr in Me_2SO upon addition of H_2TPPS. b, Electronic absorption spectrum of electrochemically obtained $ZnPcBu^{t+}$ in Me_2SO.

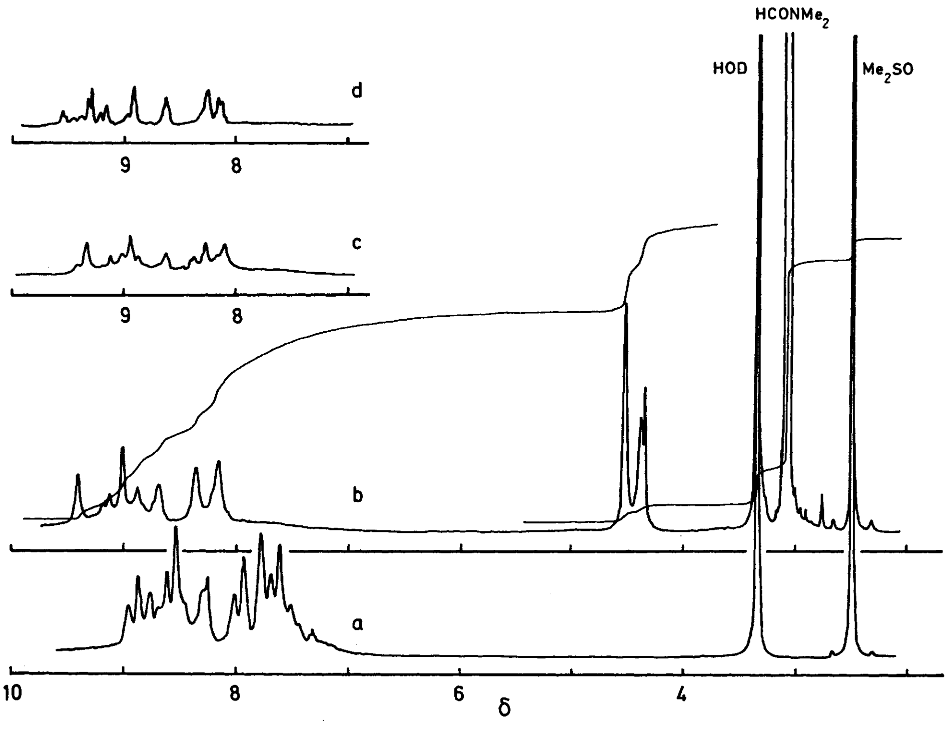


Figure 5. N.m.r. spectra of phthalocyanines in Me_2SO: a, (**IV**); b, (**V**); c, (**V**) after heating; d, after further recrystallisation with acetone.

MnTPPS and ZnPcTMPyr is not very different from that corresponding to the sum of the two monomer spectra. Minor changes are observed, such as a small decrease in the intensity of both the porphyrin Soret band and the phthalocyanine Q band, with a slight blue shift (5 nm) for the latter.

By comparison with a mixture of non-charged porphyrin (ZnTPP) and phthalocyanine (ZnPc), for which the electronic absorption spectrum of an equimolar mixture is identical with the sum of the corresponding monomer spectra, this indicates that a weak interaction occurs between the two macrocycles, because of the face-to-face structure of the complex.

Completely different behaviour is observed upon addition of H_2TTPS to a ZnPcTMPyr solution. A drastic decrease in the intensity of the Q_x and Q_y bands of the phthalocyanine occurs

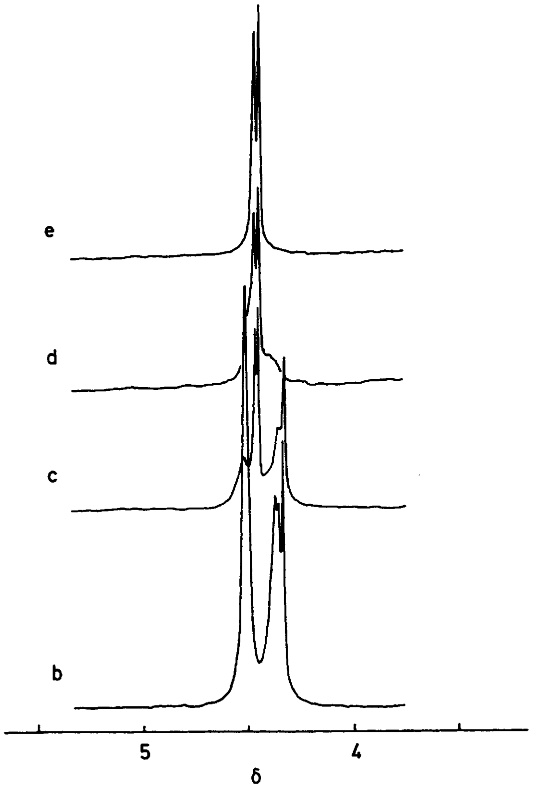


Figure 6. N.m.r. spectral evolution of ZnPcTMPyr in Me_2SO: b, starting material with D_{2h} symmetry; c, obtained upon heating; d, after recrystallisation; e, spectrum d at high temperature.

Table 2. Excited state and redox potential values of porphyrins and phthalocyanine.

Compound	E_{S_1}/eV	E_{T_1}/eV	$E_{\frac{1}{2}}$(ox.)/eV	$E_{\frac{1}{2}}$(red.)/eV
H_2TPPS	1.91	1.44	+1.05	−1.02
Mn^{III}TPPS	2.21	1.78*	> +1	−0.25
ZnPcTMPy	1.83	1.13	+0.86	−0.40

Solvent = Me_2SO.

* From the phosphorescence wavelength maximum of Mn^{III}TPPyr in ethanol, A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, 1979, 1543.

and a new band, peaking at 720 nm appears in the red region (Figure 4). The same reaction occurs on mixing H_2TPPS with the D_{4h} phthalocyanine species.

The face-to-face structure of the complexes favours π–π intermacrocyclic interaction and a charge-transfer reaction occurs in the present case. The phthalocyanine Q band disappears in favour of a new band at 720 nm (Figure 4) corresponding to the radical cation $ZnPcTMPyr^+$. The face-to-face structure of the electrostatic complexes is also consistent with their fluorescence properties.

Fluorescence properties. The fluorescence maxima of the different porphyrins and phthalocyanines are reported in Figure 7. Because of the low energy levels of the phthalocyanine excited states by comparison with those of the porphyrins, one would expect efficient energy transfer to occur, as found for the covalently linked, folded porphyrin–phthalocyanine dimer.[6] However, no energy transfer from the porphyrin moiety to the phthalocyanine occurs in either case. The emission spectra and intensity of ZnTPP and ZnPc monomers remain unchanged in the equimolar mixture indicating that no interaction occurs between the two chromophores. On the contrary, all the emissions from the 'electrostatic' heterodimers are quenched with respect to the monomer fluorescence as shown in Figure 8. For the H_2TPPS–ZnPcTMPyr system, the drastic fluoresence quenching (95% decrease) of both the chromophores is consistent with the existence of an efficient charge transfer reaction in the ground state. For the MnTPPS–ZnPcTMPyr system, only a 43% decrease in the intensity of the phthalocyanine fluorescence is observed. All these results are consistent with the face-to-face nature of the 'electrostatic' complexes.

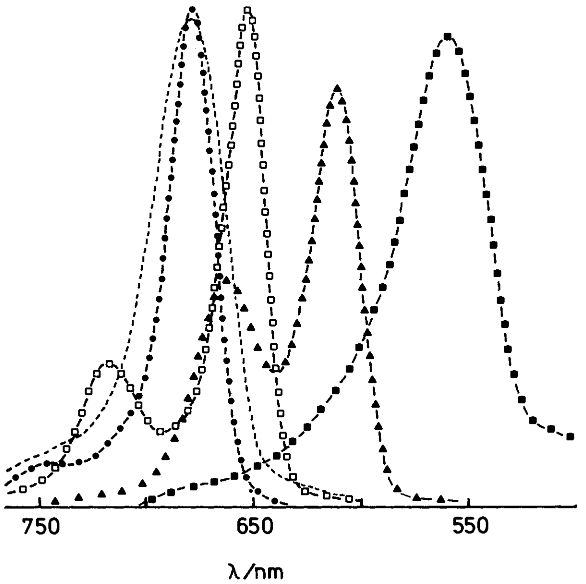


Figure 7. Fluorescence spectra of: ■, MnTPPS, λ_{exc} 467 nm; ▲, ZnTPP, λ_{exc} 420 nm; □, H_2TPPS, λ_{exc} 420 nm; ●, ZnPc, λ_{exc} 625 nm; ----, ZnPcTMPyr, λ_{exc} 625 nm, solvent Me_2SO.

Similar results have been reported for 1:1 porphyrin cation–anion (P^+–P^-) aggregates or covalently linked metal porphyrins.[7,8] In all cases, a decrease and broadening of the porphyrin Soret band is observed and the fluorescence of each chromophore is appreciably quenched but no charge separation leading to P^+–P^- species has been reported. Fluorescence quenching has been explained in terms of the existence, at room temperature, of low lying charge transfer states in certain dimers, which depend on the redox properties of each moiety. The partial fluorescence quenching in the MnTPPS–ZnPcTMPyr system can also be explained in terms of the existence of low lying charge transfer states as seen from the redox potential values of the two chromophores. However, as they also exist in the H_2TPPS–ZnPcTMPyr system and because of the difference in their behaviour, we are tempted to believe that electron affinity and moreover the proximity of the two macrocycles (in terms of molecular orbital overlapping) might be the most important parameters in the charge separation efficiency. The presence of the acetate ligand in the Mn^{III}TPPS compound could increase the intermacrocycle distance, and thus decrease their interaction.

Conclusions.—The spectroscopic and photophysic properties of face-to-face heterodimers formed upon pairing a cationic phthalocyanine with anionic porphyrins allow the importance of not only the redox properties of the compounds, but also their electron affinity and the effect of intermacrocycle distance on the charge separation efficiency to be estimated.

A ground state $(H_2TPPS)^-$–$(ZnPcTMPyr)^+$ species is obtained for 1:1 H_2TPPS–ZnPcTMPyr, whereas for Mn^{III}TPPS, only a weak interaction occurs. This difference might be due to the presence of an axial ligand on the

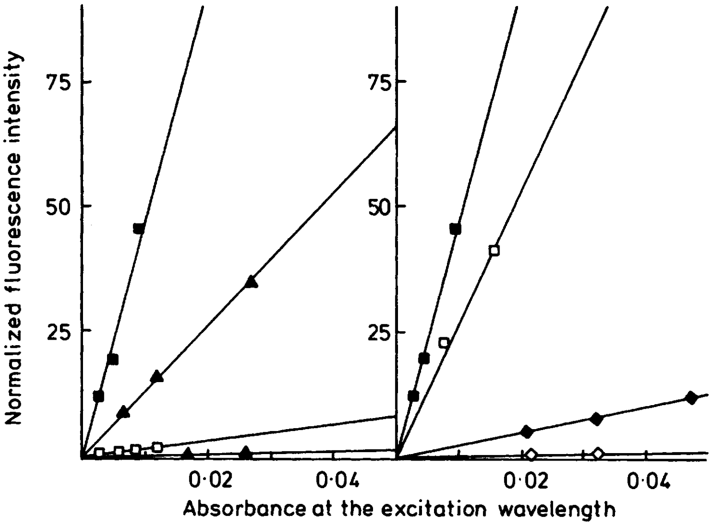


Figure 8. Normalized fluorescence intensity as a function of the absorbance at the excitation wavelength: a, H_2TPPS–ZnPcTMPyr system; λ_{exc} 625 nm; ■, ZnPcTMPyr monomer, λ_F 680 nm; □, ZnPcTMPyr in 1:1 dimer, λ_F 683 nm; ▲, H_2TPPS monomer, λ_F 653 nm; △, H_2TPPS in 1:1 dimer, λ_F 653 nm; b, MnTPPS–ZnPcTMPyr system; λ_{exc} 625 nm; ■, ZnPcTMPyr monomer, λ_F 680 nm; □, ZnPcTMPyr in 1:1 dimer, λ_F 683 nm; λ_{exc} 467 nm; ◆, MnTPPS monomer, λ_F 560 nm; ◇, MnTPPS in 1:1 dimer, λ_F 560 nm, solvent Me_2SO.

manganese which increases the intermacrocycle distance and thus weakens the interaction.

Preliminary investigations of a light driven oxidation–reduction of the MnTPPS–ZnPcTMPyr system already give promising results, as both oxidised Mn^{IV} and reduced Mn^{II} are found to exist.[16] As the role of manganese in the evolution of O_2 in the photochemical reaction centre of porphyrins is known, the face-to-face heterodimers or oligomers are very promising systems for the elaboration of artifical photosynthetic systems for the light-to-chemical energy conversion.

Experimental

The u.v.–visible electronic spectra of porphyrin and phthalocyanine monomers, and of their mixtures were recorded with a Perkin-Elmer 5 spectrometer. The solvent used, dimethyl sulphoxide (Merck), was spectroscopic grade. The concentrations of the solutions were varied from 5×10^{-8} to 5×10^{-6} mol dm^3.

Fluorimetry.—Fluorescence spectra were recorded at room temperature with an LS5 Perkin-Elmer fluorimeter equipped with a red sensitive R928 photomultiplier. Very dilute solutions of ZnPcTMPyr, H_2TPPS, MnTPPS, ZnTPP, and ZnPc in Me_2SO, and of their mixtures were used in order to avoid spectral distortions due to the inner filter effect and emission reabsorption. The optical density of each solution was less than 0.05 for a 1 cm pathlength cell. The air-saturated solutions were excited at 420 and 625 nm for the H_2TPPS–ZnPcTMPyr and ZnTPP–ZnPc systems and at 467 and 625 nm for MnTPPS–ZnPcTMPyr. The fluorescence spectra were recorded at 500–800 nm.

N.M.R. Study.—The n.m.r. spectra of dilute solutions of phthalocyanine (10^{-3} mol dm^3) were recorded with a Bruker AM 200 apparatus. The chemical shifts were calibrated by the solvent (Me_2SO) peak.

Materials.—All the materials obtained from commercial sources are of analytical or spectroscopic grade. The organic solvents were dried and distilled before use.

4-(3-Pyridyloxy)phthalonitrile (**III**). A solution of 4-nitrophthalonitrile (**I**) (0.4 g) and 3-hydroxypyridine (**II**) (0.45 g) plus an excess of dried potassium carbonate in anhydrous $HCONMe_2$ (20 ml) was stirred under argon for 24 h. The product (**III**) (380 mg, 74%) was crystallised from ethanol–water, m.p. 126 °C, $\nu_{max.}$(Nujol) 2 230 cm^{-1} (C≡N). The bands due to the NO_2 groups disappeared.

Zinc tetrakis-(3-pyridyloxy)phthalocyanine (**IV**). A mixture of (**III**) (80 mg) with an excess of powdered zinc was heated at 130 °C for 4 days in the presence of a few grains of ammonium molybdate. The resulting mixture was no longer pasty and a green product was obtained which is soluble in Me_2SO. After filtration to remove residual zinc, the solvent was evaporated and the product (140 mg, 41%) washed with acetone and then dried under vacuum at 78 °C, $\lambda_{max.}$(Me_2SO) 678 nm (ε 1.8×10^5 dm^3 mol^{-1} cm^{-1}) (Found: C, 63.2; H, 3.05; N, 17.25. $C_xH_yN_aO_bZn{\cdot}2H_2O$ requires C, 63.3; H, 3.3; N, 17.0%).

Zinc tetrakis-(3-methylpyridyloxy)phthalocyanine (**V**). A $HCONMe_2$ solution of (**IV**) (70 mg) in the presence of an excess of methyl iodide was refluxed for 24 h. After evaporation of the solvent, the resulting grey product was washed with acetone to obtain a colourless filtrate. The product (77%) is grey green (87 mg) and contains 24–26 mol $HCONMe_2$. After heating in Me_2SO and recrystallisation with acetone, the resulting product is practically free of $HCONMe_2$.

Manganese(III) *tetrakis(sulphonatotolyl)porphyrin*.The Mn^{II} porphyrin was synthesized by Harriman's method.[13] The ligand is the acetate group and the counter-ion is Na^+.

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