

Mixed Aggregates of Phthalocyanines and Porphyrins Bearing Oppositely Charged Substituents

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Abstract

A number of metalloporphyrins bearing charged, peripheral substituents have been shown to associate with metallophthalocyanines with oppositely charged substituents. Job's plot analyses reveal that the aggregates contain equal numbers of phthalocyanines and porphyrins. The complexation is accompanied by significant changes in the near ultraviolet and visible spectra of the individual components. These spectral changes have been used to estimate equilibrium constants for the formation of the associated complexes. The nature of the interaction is discussed.

Introduction

A number of metalloproteins are known to contain assembled metalloporphyrin or -porphyrinoid units. Examples include proteins involved in photosynthesis. In these systems, it has been suggested that the 'light-gathering' antenna consists of aggregates of chlorophyll molecules forming a linear array [1]. Further, the reaction center from the purple photosynthetic bacterium *Rhodospseudomonas viridas* contains two closely associated bacteriochlorophyll *b* molecules (the 'special pair') [2]. The closest interaction is through a set of pyrrole rings which have an interplanar spacing of ~ 3 Å and Mg...Mg distance of ~ 7 Å. This interplanar spacing compares with the shortest interplanar spacing found in metalloporphyrin model compounds [3]. In addition, a number of heme proteins such as cytochrome *c*₃ are known to contain heme units in close proximity and show evidence of inter-heme magnetic coupling [4]. The arrangement of the porphyrin units in these molecules suggests that an interaction between the units is an essential feature in the electron transfer process. This idea is supported by the finding that thin films of cytochrome *c*₃ exhibit semiconduction properties [5].

An investigation of the interactions between assembled metalloporphyrinoids is of interest. Such

an investigation is amenable to modeling studies. Synthetic porphyrins and the structurally similar phthalocyanines share many of the characteristics of the naturally occurring porphyrin systems. In particular, these species exhibit spectral characteristics which have instigated numerous investigations of their photophysical and photochemical properties [6]. These large, planar, aromatic macrocycles have very intense $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the visible and near UV regions of the spectrum. Further, many water soluble metalloporphyrins and metallophthalocyanines are known to aggregate in solution. The degree of aggregation is dependent upon such factors as electrolyte concentration and solvent composition [7]. Recent solid-state studies on five-coordinate porphyrinato-iron(III) and -iron(II) complexes have demonstrated that dimer formation may involve spin-coupling of the metal centers [8].

Linschitz *et al.* [9] have recently shown that a spontaneous aggregation of porphyrins bearing cationic substituents with porphyrins bearing anionic substituents occurs in solution. This observation suggested to us that similar aggregates would be formed between porphyrins and phthalocyanines bearing oppositely charged substituents. During the course of our investigations, Gaspard *et al.* [10] reported preliminary findings on similar systems in dimethyl sulfoxide. The findings reported herein complement those of Gaspard. In addition, the nature of this electrostatically mediated interaction is addressed.

Experimental

Water soluble porphyrins [11] and phthalocyanines [12] were prepared by methods previously reported in the literature and were purified by repeated recrystallizations. The tetra(4-methylpyridyl)porphyrinatomanganese(III) cation was isolated as the chloride salt and the corresponding magnesium(II) cation was isolated as the perchlorate salt. The tetra(4-methylpyridyl)porphyrinato and tetrasulfophthalocyaninato ligands will hereafter be referred to as TMePyrP and TSP, respectively. Ab-

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sorption spectra and Job's plot data were obtained on a Hewlett-Packard 8451A Diode Array Spectrophotometer. Data analysis was facilitated using the spreadsheet program LOTUS 123. Job's plots were obtained from the reduction of photometric titration data.

In a typical experiment, a 10 ml aliquot of a 50% ethanol/water (*v/v*) solution of one component was titrated with a similar solution of the second component. The concentration of the solutions was between 10^{-6} and 10^{-5} M in either metalloporphyrin or metallophthalocyanine. The conditions were chosen so that self-aggregation of the individual components was minimized. The titration was monitored by circulating the resultant solution through a 1.00 cm flow cell. Absorption data was collected at a number of wavelengths after each addition of titrant. Absorption spectra were recorded periodically during the titration. Data manipulation was performed in a manner similar to that described in the literature [13], *i.e.* the observed absorbances were corrected for dilution as follows

$$Y = A_{\text{obs}} - C_{\text{Pc}}\epsilon_{\text{Pc}} - C_{\text{P}}\epsilon_{\text{P}}$$

where C_{Pc} and C_{P} are the concentrations and ϵ_{Pc} and ϵ_{P} are the molar absorptivities of the phthalocyanine and porphyrin, respectively. The molar absorptivities for the metalloporphyrins and metallophthalocyanines were determined under the conditions employed for the photometric titrations.

Results and Conclusions

Figure 1 shows the absorbance spectra of $\text{Ni}(\text{TSP})^{4-}$ and $\text{Mn}(\text{TMePyrP})^{5+}$. The spectra exhibit the characteristic Soret band of the porphyrin and the Q band of the phthalocyanine. Figure 1 also contains the spectra of a 1:1 mixture of the porphyrin and the phthalocyanine. The spectrum of the mixture exhibits several noteworthy features. The Q band and

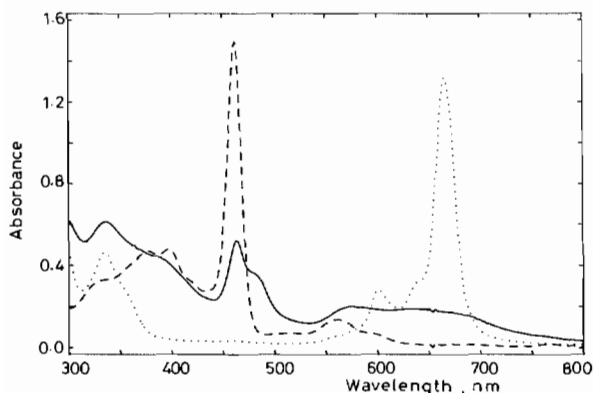


Fig. 1. Absorbance spectra of 10^{-5} M $\text{Ni}(\text{TSP})^{4-}$,; 10^{-5} M $\text{Mn}(\text{TMePyrP})^{5+}$, - - -; and a 10^{-5} M solution of each component, —; in 50% (*v/v*) ethanol.

the Soret band are very much reduced in intensity. Further, absorption bands red-shifted from the porphyrin Soret band and the phthalocyanine Q band are observed. For comparison, an absorption spectrum calculated using the Beer–Lambert law and difference spectrum is shown in Fig. 2. Figure 3 displays the spectral changes observed during the course of a photometric titration. Similar results were obtained in all cases examined. These observations suggest marked perturbations in the frontier molecular orbitals of the two precursors. Absorption band broadening and shifting are indicative of aggregate formation in porphyrin and phthalocyanine systems (*vide infra*). This suggests that the spectral changes observed in our systems are a result of porphyrin–phthalocyanine association.

A decrease in intensity and broadening of the Soret band has been observed upon the formation of aggregates of manganese crown-ether porphyrins [14] and also of water soluble iron porphyrins [15]. Similar broadening of the Q band accompanies aggre-

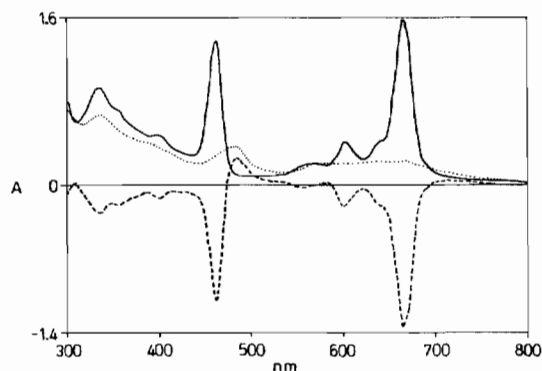


Fig. 2. Absorbance spectrum of a 1:1 mixture of $\text{Ni}(\text{TSP})^{4-}$ and $\text{Mn}(\text{TMePyrP})^{5+}$,; spectrum calculated using the Beer–Lambert law, —; and the difference spectrum, - - -.

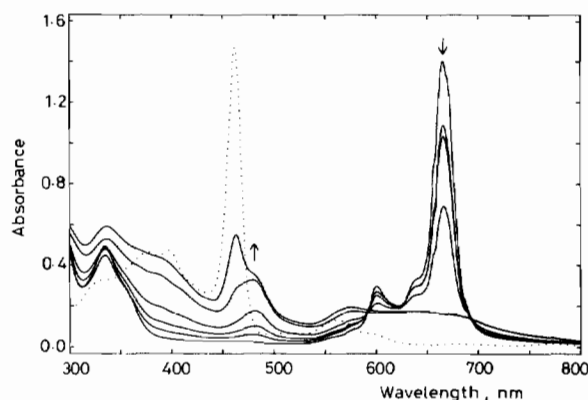


Fig. 3. Spectral changes accompanying the spectrophotometric titration of 10^{-5} M $\text{Ni}(\text{TSP})^{4-}$ with 10^{-5} M $\text{Mn}(\text{TMePyrP})^{5+}$. $\text{Mn}/\text{Ni} = 0, 0.1, 0.2, 0.4, 0.8, 1.0$. The spectrum of $\text{Mn}(\text{TMePyrP})^{5+}$ alone is shown for comparison,

gation of various M(TSP) species [7]. A blue shift and broadening of the Soret band or Q band is observed when porphyrins [16] or phthalocyanines [17, 18a] are covalently linked in such a way that the macrocycles are cofacial. This shift to higher energy has been attributed to exciton coupling [18, 19] and through-space $\pi-\pi$ interactions [17]. In contrast, red shifts in the absorption bands of bacteriochlorophylls *c*, *d* and *e* occur upon dimerization [20]. A broadening of the Soret band with no shift is observed for the *strati*-bisporphyrins of Kagan *et al.* [21] when compared to the monomeric precursors. Obviously, the extent of any exciton coupling or through-space $\pi-\pi$ interaction which may exist is dependent upon the individual characteristics of the macrocycles which are involved and upon their relative orientations with respect to one another [19]. The red shift observed may thus be a result of the lower symmetry expected of a phthalocyanine-porphyrin complex compared to a self aggregate (with D_n symmetry).

Job's plots were constructed to ascertain the stoichiometries of the aggregates. Table I lists the porphyrin-phthalocyanine combinations examined.

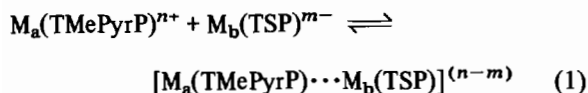
TABLE I. Formation Constants^a

M(TMePyrP)/M(TSP)	K
Mg/Co	1.3×10^5
Mg/Ni	2.0×10^5
Mn/Co	2.1×10^5
Mn/Ni	3.0×10^5

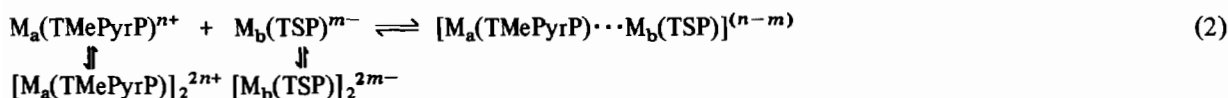
^aIn 50% (v/v) ethanol.

In all cases, the formation of a 1:1 complex is suggested. However, the existence of higher order aggregates containing equal numbers of phthalocyanines and porphyrins cannot be ruled out. Figure 4 displays an example of Job's plot. Each combination was examined at a number of wavelengths, with particular attention focused on the Soret and Q bands and the two bands associated with the aggregate.

We have estimated the formation constants for the equilibrium (1)



using the Soret or Q band absorbances observed under conditions of low aggregate concentration. The results are listed in Table I. The similarity in the



values suggests that the interaction is primarily electrostatic and that the central metal ions do not play an important role in determining the nature and strength of the interaction. These values are about an order of magnitude smaller than the range reported by Gaspard [10b] for similar systems in dimethylsulfoxide. This discrepancy may be attributed to the different solvent system employed.

The nature of the interaction is apparently two fold: there is an attraction between peripheral substituents of opposite charge and a hydrophobic interaction between the macrocycle cores. Addition of electrolyte disrupts the aggregate. The effect of ionic strength on the absorption spectra of the Mn(TMePyrP)···Co(TSP) system is shown in Fig. 5. The absorption spectrum reverts to that expected for monomeric Mn(TMePyrP)Cl⁴⁺ in the Soret region. However, the Q band region reveals that the Co(TSP)⁴⁻ is dimerized under conditions of high ionic strength. (The case for metallotetrasulfophthalocyanine dimerization is well documented [7].) This implies that the tetraarylporphyrin···phthalocyanine hydrophobic interaction is weaker than the phthalocyanine···phthalocyanine interaction in the solvent system employed. Consider the equilibria (2). Under conditions of low ionic strength, the charge attraction between the cationic porphyrin and anionic phthalocyanine predominates. As the charge attraction is reduced with increasing ionic strength, the hydrophobic interaction predominates and the equilibrium is shifted toward phthalocyanine dimerization. The bulky aryl groups on the porphyrin result in a weaker interaction between porphyrin and phthalocyanine than between phthalocyanines. Although Mg(TMePyrP)⁴⁺ appears to aggregate in the solvent system employed for these experiments, we have

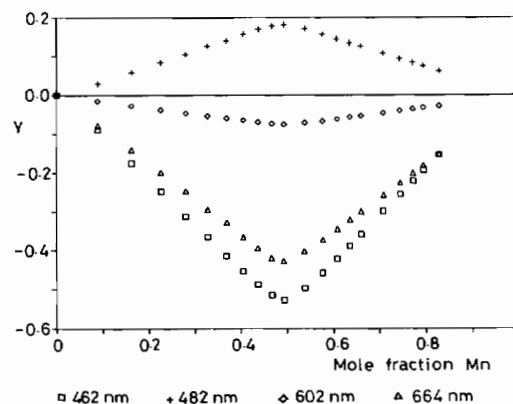


Fig. 4. Job's plot for Mn(TMePyrP)⁵⁺···Co(TSP)⁴⁻ aggregation at the indicated wavelengths.

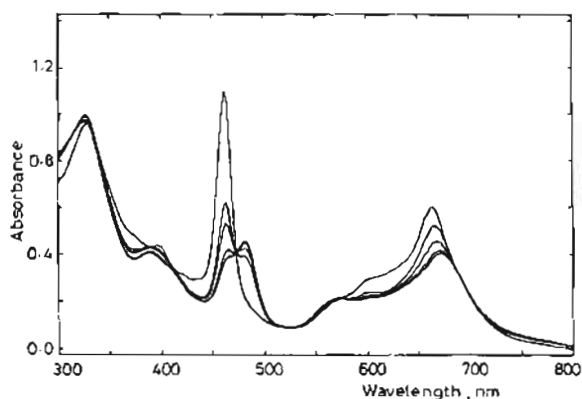


Fig. 5. Effect of added electrolyte on the absorbance spectrum of a 1:1 mixture of $\text{Co}(\text{TSP})^{4-}$ and $\text{Mn}(\text{TMePyrP})^{5+}$. $[\text{NaClO}_4] = 0, 0.005, 0.01$ and 0.09 M.

observed no evidence for $\text{Mn}(\text{TMePyrP})\text{Cl}^{4+}$ aggregation in 50% (v/v) ethanol. However, an apparently weak, electrolyte dependent association between manganese porphyrin units has been observed in dimethylformamide [22].

How the formation of these aggregates affects the electro- and photochemistry of these species is yet to be determined. Work in these areas is in progress.

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