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Supramolecular Assemblies of Porphyrins and Phthalocyanines Bearing Oppositely Charged Substituents. First Evidence of Heterotrimer Formation

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Received September 4, 1992

Mixtures of solutions of 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)porphyrins and 4,4′,4″,4‴-tetrasulfonated phthalocyanines in polar solvents are shown to contain well-defined supramolecular assemblies, consisting either of heterodimers or heterotrimers. The formation of these species is controlled by the affinity of the central metal ion of each chromophore for axially bound coordinating molecules. On the other hand, heteroaggregation has an influence on the axial reactivity of the chelated metals. Thus, copper and nickel phthalocyanines, which usually display no affinity for axial ligands, are able to bind strong donors such as pyridine or DMSO when involved in porphyrin–phthalocyanine heterodimers. Steric effects related to the position of the peripheral substituents have also been investigated.

1. Introduction

Coordination chemistry offers numerous examples of supramolecular assemblies bound by ion pair attraction in solution. In most cases, the properties of such complexes differ notably from those of the parent compounds. So-called ion pair charge-transfer (IPCT), or outer sphere charge-transfer (OSCT) transitions are frequently observed in these complexes[1] and have been successfully interpreted in the context of Marcus and Hush theories.[2] Organic molecules, on the other hand, are usually stable in an electrically neutral state. Nevertheless, a number of organic ions form stable ion pairs in solution, and IPCT type transitions have been observed in some cases. In the last few years, the photochemical properties of pairs of organic ions with methylviologen MV^{2+} (dimethyl-1,1-bipyridinium-4,4′) as the cation, have been particularly studied.[3] These complexes are usually highly photosensitive and yield the radical cation $MV^{\bullet+}$ upon light exposure. Ion pairs such as MV^{2+}/triphenylborate or MV^{2+}/benzylate have been used in photoelectrochemical cells.[4] The MV^{2+}/rose bengale couple has also been proposed as photosensitizer for the photoreduction of water.[5]

Stable ion pairs can also be obtained with tetrapyrrole macrocycles such as porphyrins and phthalocyanines grafted with ionic substituents of opposite charges. In this case, both the coulombic attraction between the charged substituents and the hydrophobic interaction of the aromatic macrocycles concur in holding the individual components together. It can therefore be expected that these compounds will form very stable complexes in polar solvents. In addition, their planar geometry allows close contact (and therefore extensive orbital overlap) in the face-to-face configuration. The formation of complexes of tetraanionic and tetracationic porphyrins with a 1:1 stoichiometry was first reported by Shimidzu[6] and then by Linschitz and colleagues.[7] The existence of similar complexes obtained from tetrasulfonated phthalocyanines and tetrakis(*N*-methylpyridinium-4-yl)porphyrins[8] or tetrakis(*N*-methylpyridinio)porphyrazines[9] has also been reported. In all cases, the complexes displayed optical properties (in particular absorption spectra) quite distinct from those of the parent species, indicating that an extensive orbital mixing was occurring upon pairing. The formation of low-lying charge-transfer states was suggested.[10] To this date, however, the photophysical properties of these complexes have attracted only very scarce attention.[11] As part of our continuous interest in the photophysical properties of supramolecular assemblies of porphyrins and phthalocyanines, we have undertaken an extensive study of the complexes obtained from tetrakis(*N*-methylpyridinium-4-yl)porphyrins and tetrasulfonated phthalocyanines (Figure 1), from the liquid[12] to the organized solid (Langmuir–Blodgett) phase.[13] We have addressed more specifically the following questions: (i) What type of assemblies do these molecules form in solution and why? (ii) What conformation do these complexes adopt in solution? (iii) What is the role of the nature of the central metal ions, of axial ligation, and of the solvent on the formation and stability of the heterocomplexes? (iv) Is it possible to control their photophysical properties through suitable chemical modifications of the parent species? (v) To what extent could these properties be modified when the complexes

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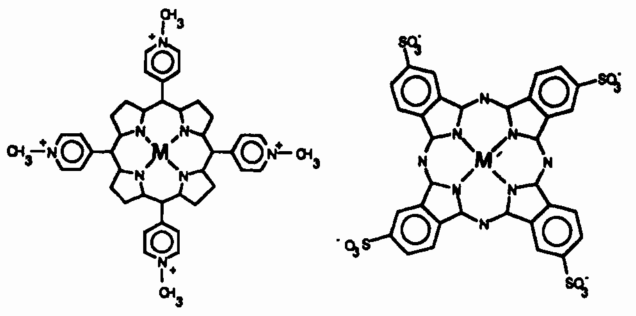

a: MTMPyP b: M'PcTS

Figure 1. Schematic representations of (a) tetrakis(*N*-methylpyridinium-4-yl) porphyrins with M = H_2 and Zn and (b) tetrasulfonated phthalocyanines with M' = H_2, Cu, Ni, and AlCl.

are transferred from the liquid to the solid state? (vi) Is it possible to extend the properties observed in solution to organized phases, in order to design new optically active materials? This paper presents our results concerning the three first questions. The others will be addressed elsewhere.[12,13]

2. Experimental Section

2.1. Materials. Free-base 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)porphine (H_2TMPyP) was purchased from Strem Chemicals as the tetraiodide salt and purified by ion exchange chromatography on a Dowex 2 (chloride) anion exchanger.[14] The zinc(II) (ZnTMPyP) and chloromanganese(III) (MnTMPyP) derivatives were obtained from the free-base by refluxing it with a 3-fold excess of the suitable acetate in water for 3 h. The crude products were concentrated and passed through a Dowex 2 ion exchange column. This last process was repeated at least three times. After precipitation in acetone, filtration and drying, microcrystalline powders of the zinc or manganese porphyrins were obtained in good yield. Their purity was checked by comparison of their UV-visible absorption spectra with literature data.[15] Samples of the zinc porphyrin were also obtained from Midcentury Chemicals. In most cases, their purity, as checked from their UV-visible spectra, was satisfactory, and they were used as such. One sample had to be purified by passing it twice on a Dowex 2 column.

High-purity samples of copper(II) 4,4',4'',4'''-tetrasulfonated phthalocyanines [Official name: tetrasodium (29*H*,31*H*-phthalocyanine-2,9,-16,23-tetrasulfonato(2-)-N^{29},N^{30},N^{31},N^{32})copper(II) (See Figure 1).] (CuPcTS) (as the sodium salt), obtained by condensation of 4-sulfophthalic acid,[16] were generously provided by Dr. S. Gaspard (Institut de Chimie des Substances, Naturelles, CNRS, Gif-sur-Yvette, France) and used as received. Chloroaluminium(III) 4,4',4'',4'''-tetrasulfonated phthalocyanine, obtained by the same method, was kindly supplied by Dr. R. Langlois (University of Sherbrooke, Quebec J1H5N4, Canada). The sample contained an appreciable amount of a nonabsorbing impurity, presumably NaCl, which was eliminated by passing it through a Dowex 50W cation exchange resin, evaporation of the colored fraction to dryness, washing the resulting solid thoroughly with 80% aqueous ethanol, and then with acetone, and drying it under reduced pressure. A sample of chloroaluminium tetrasulfonated phthalocyanine consisting in a mixture of isomers with the sulfonate groups in the 3- or 4-position (i.e. in a or b relative to the carbon atoms common to the pyrrole and benzo rings), was also purchased from Midcentury Chemicals. Nickel(II) 4,4',4'',4'''-tetrasulfonated phthalocyanine was purchased from Merck and dissolved in hot ethanol. After cooling, the insoluble material was filtered out and the remaining solution was evaporated to dryness. The resulting solid was dissolved in water, reprecipitated with acetone, filtered, washed with acetone and dried under reduced pressure. Thus, only the fraction which was soluble both in ethanol and in water was used. Free-base 4,4',4'',4'''-tetrasulfonated phthalocyanine (sodium salt) was purchased from Midcentury Chemicals, and treated in the same way as the nickel complex.

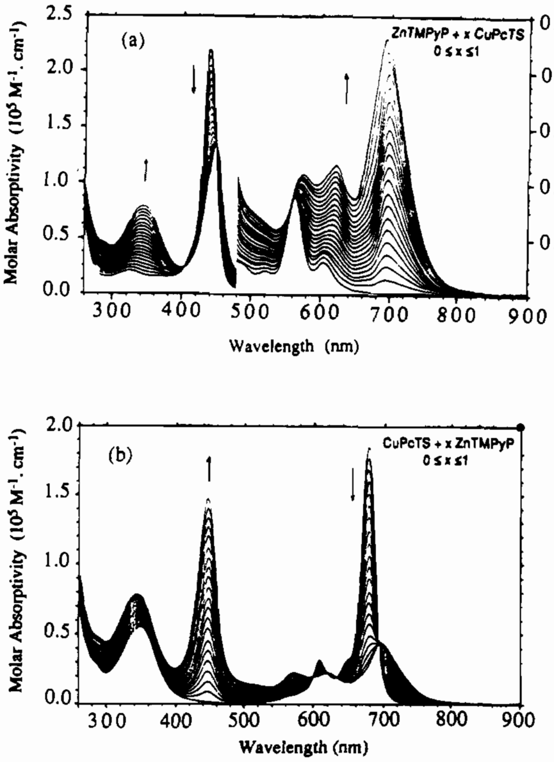

Figure 2. Spectral evolution of (a) a solution of 10^{-5} M ZnTMPyP in DMSO upon addition of small aliquots of 10^{-3} M CuPcTs. (b) a solution of 10^{-5} M CuPcTS in DMSO upon addition of small aliquots of 10^{-3} M ZnTMPyP.

2.2. Solvents. All the solvents used in this work were purchased from Merck (Uvasol spectroscopic grade) and used as received. Water was purified prior to using with a Millipore Milli-Q apparatus.

2.3. Spectroscopic Methods. Spectroscopic measurements were performed at room temperature in quartz cells (Suprasil quality, 1-cm optical pathlength). As the investigated compounds have a marked tendency to form strongly adhering films on glassware, the cells were systematically cleaned, first with sulfochromic acid, then with an alkaline detergent (TFD 4 in water), and finally with deionized water. UV-visible absorption spectra were measured on a Perkin-Elmer Lambda 5 spectrophotometer. Titrations were achieved by adding, with a micropipette, directly into the quartz cell, small aliquots (typically 5 μL) of a 10^{-3} M solution of phthalocyanine to 5 mL of a ca. 10^{-5} M solution of porphyrin, or the reverse. Dilution effects were thus rendered negligible, allowing the observation of fine isosbestic points. The added volumes were nevertheless taken into account in the construction of Job diagrams. Fluorimetric titrations were similarly performed by addition of small aliquots of a 10^{-4} M solution of phthalocyanine (or porphyrin) to 5 mL of a ca. 5.10^{-7} M solution of porphyrin (or phthalocyanine). Emission spectra were recorded on a SPEX Fluorolog-1 fluorimeter, automatically corrected for the fluctuations of the xenon lamp intensity and for the response of the photomultiplier. Excitation wavelengths were chosen so as to correspond to isosbestic points in the relevant absorption spectroscopic titration experiment. This provides an automatic normalization of the emission intensity to constant absorption. In all experiments, the maximal optical density over the fluorescence domain of both porphyrins and phthalocyanines was always less than 0.05 to avoid spectral distortion due to the inner-filter effect.

3. Results

3.1. MTMPyP/CuPcTS and MTMPyP/NiPcTs Complexes (M = H_2, Zn). Solutions in Dimethyl Sulfoxide. Heteroaggregation of oppositely charged porphyrins and phthalocyanines is most conveniently studied by spectroscopic methods. Figure 2a presents the spectral evolution of a solution of the zinc porphyrin ZnTMPyP in DMSO, upon titration with a solution of copper phthalocyanine CuPcTs. Similarly, the spectral evolution of a

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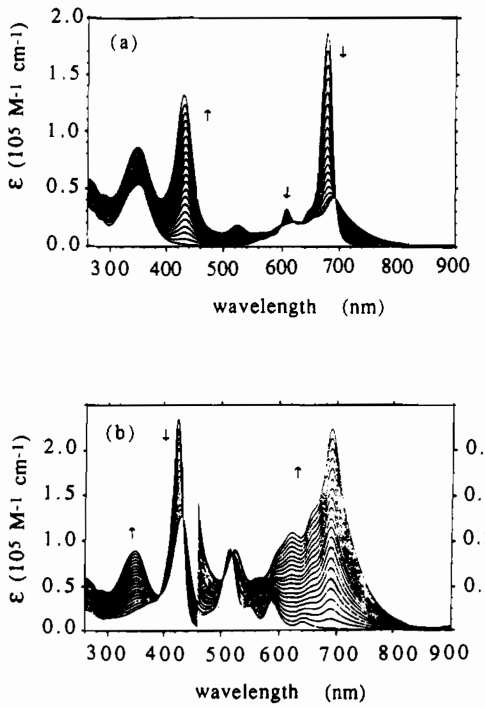

Figure 3. Spectral evolution of (a) a solution of 10^{-5} M H_2TMPyP in DMSO upon addition of small aliquots of 10^{-3} M CuPcTs. (b) a solution of 10^{-5} M CuPcTS in DMSO upon addition of small aliquots of 10^{-3} M H_2TMPyP.

solution of CuPcTS in DMSO upon addition of ZnTMPyP is shown in Figure 2b. In both cases, the reaction proceeds with sharp isosbestic points, and is completed when the (1:1) stoichiometry is reached. (Throughout the text, when the composition of a solution or the stoichiometry of a complex is indicated as *m*:*n*, the first number, *m*, refers to the prophyrin, and the second, *n*, to the phthalocyanine.) At this point, the resulting spectrum differs markedly from the sum of those of the reactants, revealing the formation of at least one new species, in which the chromophores interact strongly. Similar results, observed by Gaspard[8] and others,[9] were interpreted as evidences of the formation of heterodimers held face-to-face by electrostatic attraction, in equilibrium with the starting monomers. However, the existence of higher aggregates with the same overall stoichiometry could not be entirely ruled out.

Titration of CuPcTS with the free-base porphyrin H_2TMPyP in DMSO proceeds in a similar way (Figure 3). However, in this case the spectral evolution does not stop at the 1:1 stoichiometry. Instead, a new set of isosbestic points appears, which is observed up to the 1:2 stoichiometry (Table I). As this observation is inconsistent with the formation of a dimeric species only, one may assume that a trimeric species, in which two phthalocyanines are associated with one porphyrin, is also formed according to Scheme I, where P represents the porphyrin, and Pc the phthalocyanine. This assumption is further supported by the differential absorption spectra shown in Figure 4b,c. These spectra were measured in the following conditions: a 1:10 mixture of H_2TMPyP and CuPcTS was placed in the sample cell and the spectrum was recorded with the reference cell containing either a 0:9 solution (Figure 4b) or a 0:8 solution (Figure 4c) of phthalocyanine. In the first case, a huge depression is observed in the 680-nm region of the spectrum, which corresponds to the Q band of the uncomplexed phthalocyanine. No depression is observed in the second case. If reaction 1 (Scheme I) was the only one that occurred, the sample cell should contain at least 9 equiv of uncomplexed phthalocyanine, and a positive absorption should be observed throughout the whole spectrum. On the other hand, if reaction 2 also occurs, then the equivalent number of uncomplexed phthalocyanines present in the reference cell must be between eight and nine, and the absorption in the 680-nm region will be negative in the first case, and positive in the second, as is indeed the case. Following a similar reasoning, the spectrum displayed in Figure 4a suggests that the trimer P_2Pc (i.e. two porphyrins associated with one phthalocyanine) is not formed.

Scheme I

$$\mathrm{P} + \mathrm{Pc} \rightarrow \mathrm{PPc} \qquad (1)$$

$$\mathrm{PPc} + \mathrm{Pc} \rightarrow \mathrm{PPc}_2 \qquad (2)$$

The data from the spectroscopic titration experiments have been analyzed using Job's method.[17] This method relies on the fact that the optical density of a mixture of chromophores which do not react on each other is the sum of the absorptions due to each chromophore separately. Correlatively, departures from additivity as the composition of the solution is continuously varied can be interpreted as evidence of the formation of a complex. In Job's method, the stoichiometry of this complex can be deduced from the composition at which the deviation from additivity is a maximum. [As was stressed in Job's original paper[17a] and in later systematic studies performed by other workers,[17b] this is generally not true if more than one complex is formed in the conditions of the experiment. However, in cases where no more than two different complexes are formed and the formation constants for the successive complexations are large, Job's method still provides useful information (see supplementary material).] In practice, the absorptions measured at a given wavelength for mixtures with various ratios of porphyrin and phthalocyanine have been used to calculate the expression

$$F(x) = \mathrm{d}(x) - (\epsilon_{\mathrm{Pc}} - \epsilon_{\mathrm{P}})x - \epsilon_{\mathrm{P}} \qquad (3)$$

where $x = [\mathrm{Pc}]/([\mathrm{P}] + [\mathrm{Pc}])$ is the mole fraction of phthalocyanine Pc (ignoring the molecules of solvent), ϵ_{Pc} and ϵ_{P} are the molar absorptivities of the phthalocyanine and of the porphyrin respectively, and $\mathrm{d}(x)$ is the actual optical density of the solution divided by the total concentration of chromophores. Thus, $F(x)$ represents the deviation from additivity of the absorption of a mixture of x mol·dm^{-3} of phthalocyanine and $(1 - x)$ mol·dm^{-3} of porphyrin, in molar absorption units. Job diagrams are obtained by plotting $F(x)$ as x is continuously varied. The diagram obtained in the ZnTMPyP/CuPcTS case at wavelength λ = 680 nm is shown in Figure 5. It consists roughly of two straight lines intersecting at x = 0.5, as is typically the case when only a 1:1 complex is formed. Similar diagrams are obtained when the spectral variations at other wavelengths (e.g. 360 and 440 nm) are used. In contrast, the diagrams obtained for the couple H_2-TMPyP/CuPcTS (Figure 6) present three regimes: for x smaller than 0.5, $F(x)$ varies linearly with x, as in the preceding case; for x greater than 0.5, the evolution comprizes two distinct linear stages, with an intersection for x = 0.67. For this couple, therefore, two different species are formed in solution, one with a 1:1 stoichiometry and another one with a 1:2 stoichiometry, in accordance with the proposed scheme (Scheme I). The formation equilibrium constants for these complexes, as well as the molar absorptivities, can be graphically assessed from the preceding diagrams. The detailed procedures and their derivation are given as supplementary material. Formation constants are listed in Table I.

The preceding observations have been confirmed by titration experiments followed by fluorescence spectroscopy. The fluorescence of both ZnTMPyP and H_2TMPyP is severely quenched upon addition of CuPcTS. Figures 7 and 8 show the progressive decrease of the emission intensity of these two porphyrins as a

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Table I. Structural, Physical, and Optical Properties of Porphyrin–Phthalocyanine Mixed Systems[a]

system	solvent	complexes abs	complexes fluo	isob points (nm) P by Pc	isob points (nm) Pc by P	K_{ass}(abs)	K_{ass} (fluo)
ZnPTMPyr^{4+}/CuPcTS^{4-}	DMSO	P/Pc	P/Pc	404, 448, 560	600, 618,632, 694	$K_d = 4.0 \times 10^7$ M^{-1}	$K_d = 3.6 \times 10^7$ M^{-1}
	H_2O	impossible	P_2/Pc			not determined	not determined
			P/Pc	382, 454, 551, 573	575, 700		
	H_2O–dioxane	P_2/Pc		380, 454, 549, 576	634, 702	not determined	not determined
		P/Pc		390, 448			
		P/Pc_2			342, 358, 593, 694	$K_d = 4.0 \times 10^7$ M^{-1}	$K_d = 3.6 \times 10^7$ M^{-1}
	H_2O–pyridine	P/Pc	P/Pc	399.3, 460, 571	598, 699		
H_2PTMPyr^{4+}/CuPcTS^{4-}	DMSO	P/Pc	P/Pc	392.6, 434.2, 505.4, 519	598, 622, 634, 693.3	$K_d = 2.3 \times 10^{10}$ M^{-1}	$K_d = 2.3 \times 10^{10}$ M^{-1}
		P/Pc_2	P/Pc_2			$K_T = 4.8 \times 10^{17}$ M^{-2}	$K_T = 5.1 \times 10^{17}$ M^{-2}
ZnPTMPyr^{4+}/H_2PcTS^{4-}	DMSO	P_2/Pc				$K_T = 7.2 \times 10^{17}$ M^{-2}	$K_T = 6.8 \times 10^{17}$ M^{-2}
		P/Pc	P/Pc	416, 445, 558	605, 630, 716	$K_d = 4 \times 10^{10}$ M^{-1}	$K_d = 3.8 \times 10^{10}$ M^{-1}
ZnPTMPyr^{4+}/NiPcTS^{4-}	DMSO	P/Pc	P/Pc	401.5, 446.7, 557.3	595, 613.5, 626.6, 686		
ZnPTMPyr^{4+}/AlPcTS^{4-}	DMSO	P/Pc	P/Pc				$K_d = 5.5 \times 10^7$ M^{-1}
(Langlois's sample)	H_2O		P_2/Pc				
		P/Pc	P/Pc	378, 436, 542, 557	608, 626, 638, 696		
			P/Pc_2				
H_2PTMPyr^{4+}/NiPcTS^{4-}	DMSO	P/Pc		385.4, 433.7, 504, 520.1	592, 622, 692	$K_d = 1.2 \times 10^{10}$ M^{-1}	
		P/Pc_2				$K_T = 9 \times 10^{16}$ M^{-2}	

[a] NiPcTS in DMSO: ϵ(675.5 nm) = 177 500 M^{-1}·cm^{-1}, ϵ(336.8) = 48 300 M^{-1}·cm^{-1}. H_2PcTS in DMSO: ϵ(694 nm) = 117 500 M^{-1}·cm^{-1}, ϵ(673.8 nm) = 117 500 M^{-1}·cm^{-1}, ϵ(342.7 nm) = 48 300 M^{-1}·cm^{-1}. K_d = (PPc)/(P)(Pc) and K_T = (PPc_2)/(P)(Pc)^2 or (P_2Pc)/(P)^2(Pc).

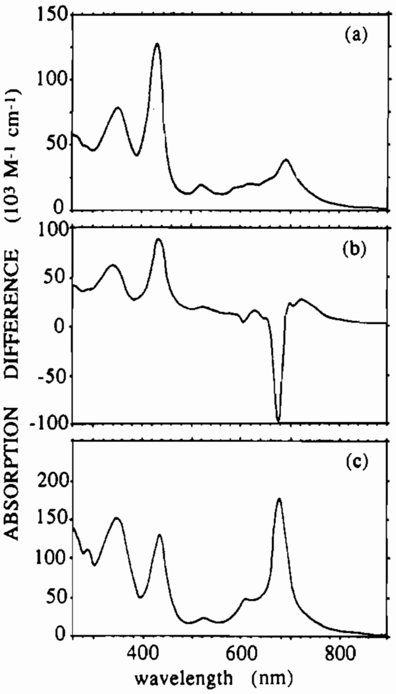

Figure 4. Differential absorption spectra under different conditions: (a) sample cell = mixture of H_2TMPyP/CuPcTS 10/1 in DMSO, reference cell – 9/0; (b) sample cell = mixture of H_2TMPyP/CuPcTS 1/10 in DMSO, reference cell = 0/9; (c) sample cell = mixture of H_2TMPyP/CuPcTS 1/10 in DMSO, reference cell = 0/8.

function of the equivalent number of CuPcTS added in solution. Since CuPcTS is not fluorescent, the observed emission at any point of the curve is the sum of those of the reaction product(s) and of the uncomplexed porphyrin, provided that no long-range quenching occurs. Considering the low concentrations used in our experiments, this seemed particularly unlikely. Nevertheless, we checked that the fluorescence of a 10^{-6} M solution of the uncharged (but otherwise analogous) 5,10,15,20-tetraphenylporphine in DMSO was unquenched by the addition of 2 equiv of CuPcTS. In the case of ZnTMPyP, the fluorescence intensity decreases linearly as the amount of CuPcTS increases, until the 1:1 stoichiometry is nearly reached, and then remains approximately constant, at about 10% of its initial value. In the case of H_2PcTS, the fluorescence intensity also decreases linearly with the amount of CuPcTS added from 0 to 1 equiv. In addition, a second linear regime, with a significantly smaller slope, is observed

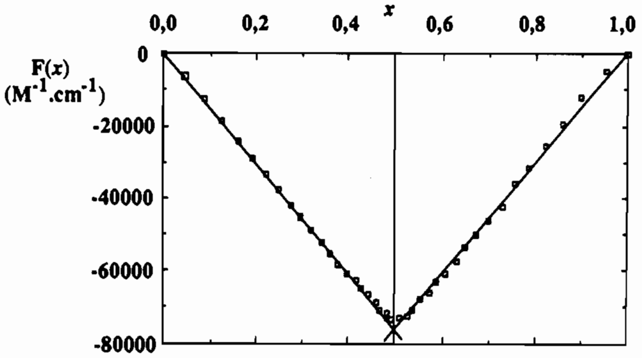

Figure 5. Job diagram for the ZnTMPyP/CuPcTS system in DMSO. λ = 680 nm.

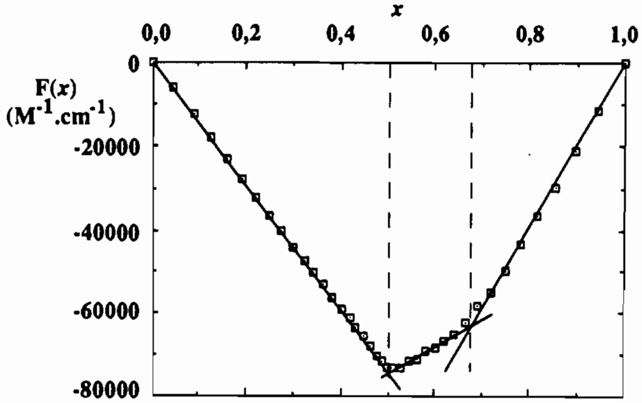

Figure 6. Job diagram for the H_2TMPyPCuPcTS system in DMSO. λ = 680 nm.

up to 2 equiv. Thereafter, no further evolution occurs, the final fluorescence intensity being only 5% of the initial value. This behavior is fully consistent with Scheme I: the first linear regime in Figure 8 corresponds to reaction 1 in this scheme. The linearity of the evolution shows that complex formation predominates over dissociation in the equilibrium. Thus, after the first equivalent, the heterodimer is almost quantitatively formed. The second regime then corresponds to reaction 2. As for Job's diagrams, the equilibrium constants are easily determined from the distance between the experimental curve and the intersection of the lines extrapolated from the linear parts of the graph in Figures 7 and 8 (see supplementary material). These values, which are listed

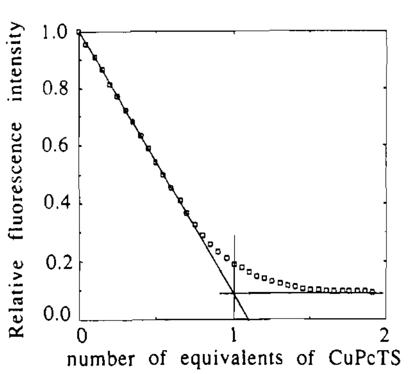

Figure 7. Evolution of the ZnTMPyP fluorescence upon addition of small aliquots of CuPcTS. Solvent = DMSO.

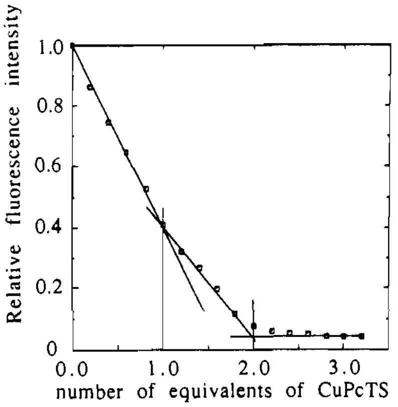

Figure 8. Evolution of the H_2TMPyP fluorescence upon addition of small aliquots of CuPcTS. Solvent = DMSO.

in Table I, are in excellent agreement with those obtained with Job's method.

Replacing phthalocyanine CuPcTS by NiPcTS in the preceding experiments produced completely similar results. As in the case of copper phthalocyanine, we found that NiPcTS forms only a 1:1 complex with ZnTMPyP in DMSO, whereas it forms both the 1:1 and the 1:2 complex with H_2TMPyP. The formation constants of these complexes are also listed in Table I.

Solutions in Water. Although metallotetrapyridiniumylporphyrins usually exist as monomers in aqueous solutions below 10^{-3} M, the free-base H_2TMPyP has been shown to form mainly dimers at concentrations above 10^{-7} M.[15c,18] Tetrasulfonated phthalocyanines are also generally known to self-aggregate in water.[19] Thus, although spectroscopic titration experiments, both in absorption and emission, clearly show the formation of mixed complexes between H_2TMPyP and CuPcTS (or NiPcTS), we were unable to determine their stoichiometry without ambiguity because of competing self-aggregation processes. The zinc porphyrin ZnTMyP, however, is essentially monomeric in water at concentrations up to 10^{-3} M. As a result, the spectral evolution upon mixing with either CuPcTS or NiPcTS is much simpler. Figure 9 shows the spectral evolution of a solution of CuPcTS in water, upon addition of ZnTMPyP. The starting spectrum displays the blue-shifted Q-band of aggregated phthalocyanine (620 nm), due to exciton coupling, in addition to the "normal" Q band of the monomer at ca. 680 nm. These features are strongly altered upon addition of the porphyrin. Two well-defined isosbestic points are observed up to 1 equiv. The resulting spectrum at this point is similar to the spectrum of the same mixture in DMSO (Figure 2), although the lowest energy transition is slightly red-shifted (710 nm instead of 695 nm) and less intense (especially as compared with the two bands at ca. 575 and 620 nm). Job's method could not be used in this case, because of the complication due o self-aggregation of the starting phthalocyanine. However, fluorescence titrations revealed the formation of at least two complexes: a mixed dimer (1:1) and the trimer consisting in two porphyrins and one phthalocyanine (2:1). Interestingly, this last species was observed neither with H_2TMPyP nor with ZnTMPyP in DMSO solutions.

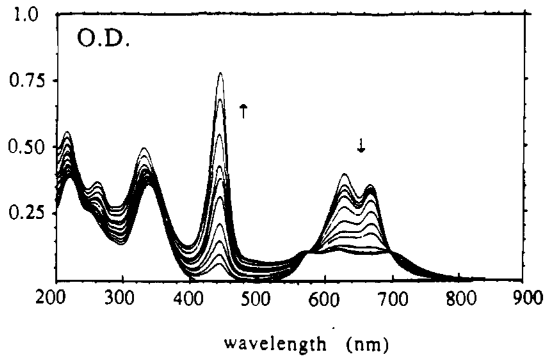

Figure 9. Spectral evolution of a solution of 6×10^{-6} M CuPcTS upon addition of small aliquots of 6×10^{-4} M ZnTMPyP in water.

Table II. Spectroscopic Properties of ZNTMPyP in Various Solvents

solvent	λ (nm)	ε (10^5 M^{-1}·cm^{-1})
H_2O	436.0	2.04
	562.5	0.206
	604.9	0.076
H_2O + dioxane	435.6	2.05
	561.9	0.194
	604.7	0.076
H_2O + pyridine	441.6	2.20
	567.7	0.175
	610.8	0.081

Solutions in H_2O–Pyridine and H_2O–Dioxane Mixtures. Addition of organic solvents to aqueous solutions of tetrasulfonated phthalocyanine is known to prevent self aggregation.[19a,d] Accordingly, we found that addition of either pyridine or dioxane to an aqueous solution of CuPcTS promotes the monomeric form at the expense of the dimer. For a ca. 10^{-5} M solution, the monomer is nearly quantitatively obtained for a pyridine or dioxane content of about 10% volume or 1.24 M. In both cases, the resulting spectra are almost identical. The Q-band peaks at 676 nm ($\epsilon = 1.96 \times 10^5$ M^{-1}·cm^{-1}) when pyridine is used, and at 675 nm ($\epsilon = 2.05 \times 10^5$ M^{-1}·cm^{-1}) in the case of dioxane. On the contrary, the absorption spectrum of ZnTMPyP in a water-pyridine mixture (20% volume) differs significantly from the corresponding spectrum in either pure water or the water-dioxane (20% volume) mixture (Table II). This difference can be attributed to the formation of a monopyridinate, wherein a pyridine molecule is axially coordinated to the Zn(II) ion.[20]

The spectroscopic titration experiments previously described for the ZnTMPyP/CuPcTS couple in DMSO have been repeated

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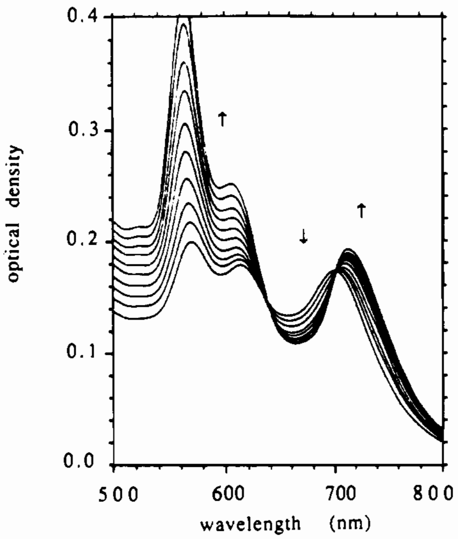

Figure 10. Spectral evolution of a 1/1 mixture of 10^{-5} M ZnTMPyP/CuPcTS in water/dioxane 80/20 (v/v) upon addition of small aliquots of 10^{-3} M ZnTMPyP.

in both water–pyridine (20% volume) and water–dioxane (20% volume) mixtures. In the first case, the results are entirely similar to those obtained with DMSO as the solvent: only the heterodimer is formed. In the water–dioxane medium, on the other hand, a completely different behavior is observed:

(i) The series of absorption spectra obtained after addition of progressive amounts of porphyrin to a solution of the phthalocyanine exhibits four perfectly defined isosbestic points (at 342, 358, 593, and 694 nm) up to the 1:2 stoichiometry, which disappear upon further addition of porphyrin.

(ii) Similarly, the series of spectra obtained after addition of progressive amounts of phthalocyanine to a solution of the porphyrin exhibits four isosbestic points (at 380, 454, 549, and 576 nm) up to the 2:1 stoichiometry; only two isosbestic points are observed (at 390 and 448 nm) from 0.5 to 1 equiv of phthalocyanine.

(iii) When successive aliquots of ZnTMPyP are added to a 1:1 solution of ZnTMPyP and CuPcTS, the spectral evolution displayed in Figure 10 is observed: the dimer absorption at 700 nm, is red-shifted by ca. 15 nm; two isosbestic points are present at 634 and 702 nm, which are lost after addition of 1 equiv of porphyrin.

All these observations suggest that not only the dimer ZnPCuPc but also the two trimers ZnP(CuPc)$_2$ and (ZnP)$_2$CuPc are formed in the water–dioxane medium. Job's methodology is not very useful in this case: the diagrams present a somewhat tormented aspect, due to the many different equilibria involved in this system. However, these diagrams display singularities around the $^1/_3$ and $^2/_3$ mole fractions that are compatible with the existence of the two aforementioned trimers (Figure 11). Confirmation of the existence of at least the (ZnP)$_2$CuPc species is obtained from the fluorescence titration experiment.

Solutions in DMSO-MeOH Mixtures. Figure 12 shows the visible part of the absorption spectrum of a 1:1 solution of H$_2$-TMPyP and CuPcTS in pure DMSO and in the presence of an increasing proportion of methanol. The same evolution is observed when either water, ethanol or dioxane is used instead of methanol. The presence of at least two isosbestic points (at 596 and 726 nm in the case of MeOH) indicates that an interconversion reaction between two distinct species takes place. The nature of this reaction will be discussed below.

3.2. ZnTMPyP/H$_2$PcTS Complexes. As its metallo derivatives, H$_2$PcTS exists in DMSO as a monomer. Its absorption spectrum displays the Q-band splitting typical for tetrapyrrolic macrocycles with D_{2h} symmetry. Upon addition of ZnTMPyP, the absorption spectrum is modified along the same general trends as observed with CuPcTS or NiPcTS (Figure 13): the split Q-band collapses, while a lesser, red-shifted band arises. Interestingly, the splitting is conserved in this process. Incidentally, this confirms that the redmost absorption in the spectra of the 1:1 species corresponds to an excitation which is essentially localized on the phthalocyanine moiety. Other absorptions occur in the lower wavelength part of the spectrum. Three isosbestic points are present at 608, 624, and 716 nm. Job's plots clearly show the formation of two complexes, namely the dimer ZnP–H$_2$Pc and

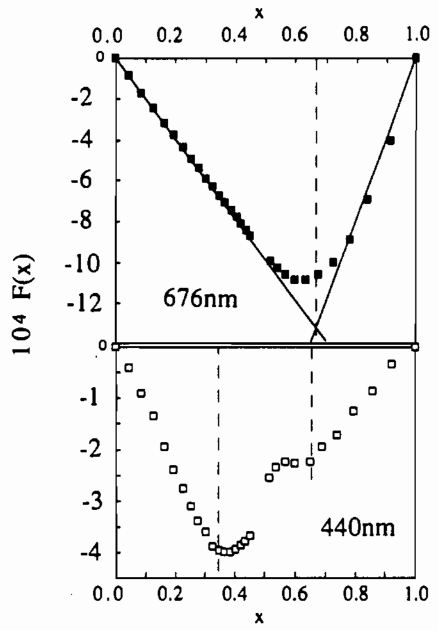

Figure 11. Job diagram for ZnTMPyP/CuPcTS in water/dioxane 80/20 (v/v).

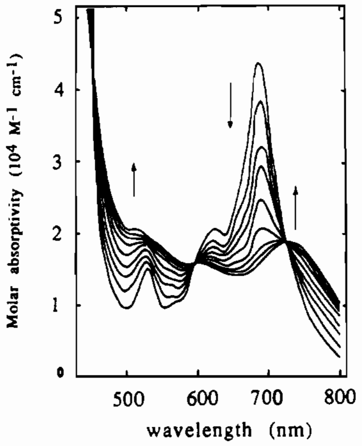

Figure 12. Effect of the ligation power of the solvent on the absorption spectrum of a 1/1 H$_2$TMPyP/CuPcTS dimer, starting from pure DMSO and increasing the proportion of MeOH.

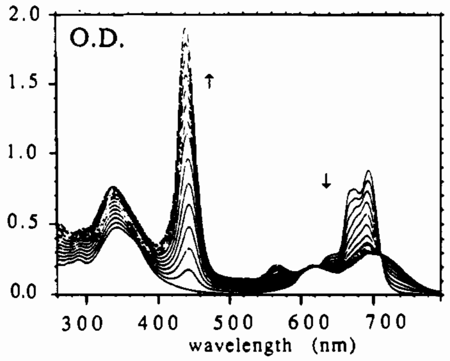

Figure 13. Spectral evolution of a solution of 9.4 × 10^{-6} M H$_2$PcTS in DMSO upon addition of small aliquots of 10^{-3} M ZnTMPyP.

the trimer $(ZnP)_2H_2Pc$. The formation of these two species is also evident from fluorescence titration experiments (Table I). In all three cases, the fluorescence due to the porphyrin (bands at 629 and 669 nm) decreases regularly up to 1 equiv thereafter remaining stationary, whereas a new band appears around 700 nm, corresponding to an emission from the phthalocyanine moiety.

3.3. ZnTMPyP/ClAlPcTS Complexes. The coordination chemistry of aluminum phthalocyanines is particularly rich. Al^{III} can axially bind one or two ligands.[21] As $AlCl_3$ is used in the synthesis of tetrasulfonated Al-phthalocyanines, one obtains the chloro-Al-phthalocyanine. In water, it is commonly believed that ClAlPcTS is totally in the monomeric form, presumably due to the presence of a weakly bound axial ligand (Cl^- and/or two H_2O or OH^- ligands) which prevent self-aggregation.[22] A freshly prepared water solution of the compound effectively exhibits the same spectrum as DMSO solutions. However, the same solution kept in the dark for many weeks evolutes with time, and the spectrum shows a depletion and blue shift of the phthalocyanine Q band, which indicates that self-aggregation occurs.

The study of the ZnTMPyP/ClAlPcTS system fortuily allowed us to carry out the influence of the position of the SO_3^- groups in the phthalocyanine benzene ring on the complexation process. Two distinct samples were used. The first one, synthesized according to Weber and Bush's method,[16] was a gift from Dr. Langlois. This method gives a mixture of isomers in which the four SO_3^- are grafted either on positions 2 or 3, 9 or 10, 16 or 17, and 23 or 24 (see figure 14). Those isomers are commonly designed as the 4,4′,4″,4‴-tetrasulfonated phthalocyanine by analogy with the 4-sulfophthalic acid from which they issued. The second sample came from Midcentury Chemicals. The HPLC analysis of this sample showed the presence of multiple isomers presumably obtained by direct treatment of ClAlPc with sulfuric acid. The analysis of the fragments resulting from the degradation of the Midcentury sample by fuming nitric acid, using Ali's procedure,[23] showed two sharp peaks corresponding respectively to 3-sulfophthalamide and 4-sulfophthalamide and a very tiny one corresponding to the nonsubstituted phthalamide (Figure 14). This result indicated that the Midcentury product is highly sulfonated and contains approximately 50% of the sulfonate groups on the 3,3′,3″, or 3‴ position and 50% on the 4, 4′, 4″, or 4‴ position.

Complexation of each phthalocyanine sample with ZnTMPyP gave very different results. Heterodimerization efficiently occurred with the sample consisting in pure 4,4′,4″,4‴-tetrasulfonated phthalocyanine, and the 1:1 complex presented a spectrum closely similar to those reported for ZnTMPyP/CuPcTS and $ZnTMPyP/H_2PcTS$ (Figure 15a). On the contrary, heterodimerization only partially occurred with the Midcentury sample (Figure 15b). This discrepancy will be discussed in the next section.

4. Discussion

The experimental data reported in the preceding section indicate that the nature of the complexes obtained in solution depend on the solvent (or cosolvent), and also on the presence of a metal ion in the porphyrin and/or in the phthalocyanine. This dependence can be adequately rationalized by taking into account the possibilities of axial coordination on both macrocycles, and by making the following assumptions:

(i) Complexation occurs only when the macrocycles can adopt a close-contact, face-to-face mutual configuration, in order to optimize π–π interactions between aromatic cores.

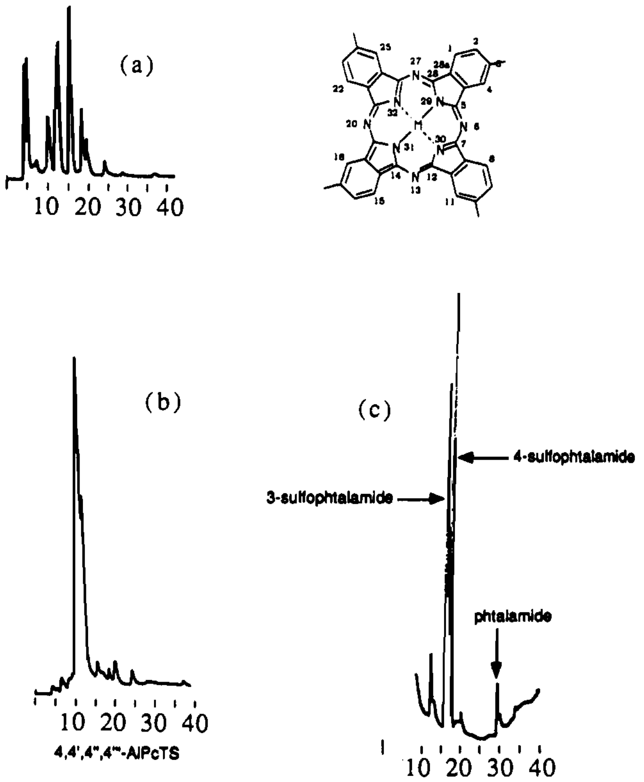

Figure 14. HPLC chromatograms of (a) a sample of ClAlPcTS from Midcentury Chemicals (b) a sample of 4,4′,4″,4‴-tetrasulfonated ClAlPcTS given by Dr. Langlois, and (c) phthalamides obtained by treatment of the Midcentury sample with nitric acid. Elution time is given in minutes.

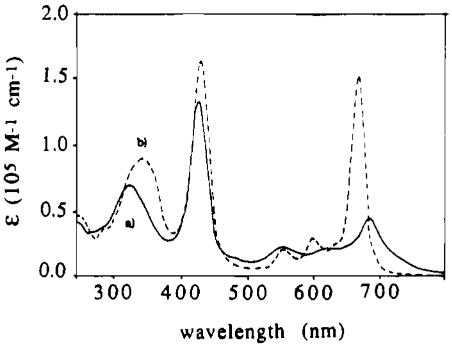

Figure 15. Spectra of a 1/1 mixture of 10^{-5} M ZnTMPyP/ClAlPcTS in water (a) with the 4,4′,4″,4‴ tetrasulfonated ClAlPcTS given by Dr. Langlois; (b) with a mixture (50/50) of 3,3′,3′m,3‴- and 4,4′,4″,4‴-ClAlPcTS from Midcentury Chemicals.

(ii) Heterotrimers are of the "sandwich" type, with two porphyrins separated by a phthalocyanine, or the reverse, in order to optimize coulombic interactions between the charged substituents.

4.1. Axial Coordination on the Porphyrin Moiety. To our knowledge, there is no definite evidence in the literature, of axial ligation by water on zinc porphyrins. (Even if such ligation occurs, it is certainly very labile.) However, axial coordination by stronger ligands on zinc porphyrins has been known for a long time. The formation and the structure of monopyridinates is especially well-documented.[20] These complexes adopt a square-pyramidal geometry, with the zinc ion slightly displaced out of the mean plane of the porphyrin toward the pyridine ligand. The approach of a phthalocyanine macrocycle onto the corresponding "face" of the porphyrin ring is thus strongly hindered. In neat water or in the water–dioxane mixture, on the other hand, both faces of the porphyrin are readily accessible by phthalocyanine macrocycles. Thus, steric hindrance resulting from axial coordination

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on the porphyrin moiety explains why the 1:2 complex exists in water or in water–dioxane solutions, but not in water–pyridine solutions. It may be noted that, in these last two cases, the dielectric constant of the medium is decreased by approximately the same amount with respect to neat water,[24] so that coulombic interactions between the different charged species are essentially the same in the two media. This clearly indicates that the difference of behavior originates in the first sphere of coordination.

DMSO is a strongly coordinating solvent, with a high donor number: $DN_{SbCl_5} = 29.8$ on Gutmann's scale.[25] It has both a "hard" site (the oxygen atom), and a "soft" one (the sulfur atom) and is thus able to coordinate most transition metal ions. ZnTMPyP will therefore exist as a five-coordinate square-pyramidal species in DMSO solutions, with only one face accessible by the phthalocyanine. H_2TMPyP, on the other hand, remains square-planar, with both faces available. Hence, the formation of a 1:2 heterotrimer is allowed in the latter case (and effectively observed), but is hindered in the former case.

4.2. Axial Coordination on the Phthalocyanine Moiety. Axial coordination on the phthalocyanine moiety may also be invoked to explain why the 2:1 complex does not exist in DMSO or in the water–pyridine mixture, whereas it is observed in neat water or in the water–dioxane mixture. To our knowledge, axial ligation on either copper or nickel phthalocyanines has never been reported in the literature (though there are several exemples of axially coordinated nickel porphyrins[20a,26,27]). On the contrary, these species are generally deemed to exist only as tetra-coordinate square-planar compounds.[21] However, the following points should be noted:

(i) The most frequent geometry for Cu(II) complexes is the pseudooctahedral one, with a tetragonal distortion arising from the Jahn–Teller effect; in some cases, this effect is strong enough to yield the square–planar, four-coordinate species, but the intermediate five-coordinate square-pyramidal geometry is also frequently observed.[28]

(ii) Occurrences of axial coordination, especially by nitrogenous bases such as pyridine, pyrimidine, picoline, imidazole, ...) have been established for various copper and nickel porphyrins.[20a,27,29]

We propose here that copper phthalocyanine is able to axially bind strongly donor ligands, at least when it is involved in a heterodimer with a porphyrin. This proposition is supported by the following experimental evidences:

(i) Whereas the 2:1 heterotrimer is readily observed both in neat water and in the water–dioxane mixture, it is observed neither in DMSO nor in the water–DMSO mixture.

(ii) Isosbestic points are observed in the visible absorption spectrum when methanol or water is progressively added to a 1:1 solution of H_2TMPyP/CuPcTS in DMSO; the spectral evolution agrees with the interconversion reaction between the heterodimer axially coordinated (on the copper atom by necessity) by a DMSO molecule on one hand and the uncoordinated heterodimer on the other hand.

(iii) When the possibility of axial coordination on the phthalocyanine is suppressed, i.e. when free-base phthalocyanine is used, the existence of the 2:1 trimer in DMSO is clearly evidenced both by absorption and by fluorescence emission measurements.

As the behavior of NiPcTS is completely similar to that of CuPcTS with respects to the formation of the 2:1 trimer in coordinating solvents, we conclude that, similar to CuPcTS, axial coordination on the Ni phthalocyanine is rendered possible by the formation of a heterodimer with a porphyrin. This may be rationalized considering the electronic configuration of the metal ion in these complexes.

The electronic structures of several metallophthalocyanines have been calculated by several methods some years ago. PEEL calculations[30] have shown that the electronic configuration of the copper ion in copper phthalocyanine can be represented as $(3d)^{9,143}(4s)^{0,536}(4p)^{0,474}$. Hence, there is a net charge of +0.848 on the copper atom, which may thus behave as a weak Lewis acid and accept a σ-donor extra ligand. However, the energetic repartition of the essentially metal-centered orbitals is $2eg(d_{xz}, d_{yz}) < 1b_{2g}(d_{xy}) < 2a_{1g}(d_{z^2}) < 2b_{1g}(d_{x^2-y^2})$. The d_{z^2} orbital is fully occupied (1.954 electron), and lies 0.19 au (~42000 cm^{-1}) above the $d_{x^2-y^2}$ orbital, which is only half occupied (1.288 electron). The high energy difference between these two orbitals, which is mainly due to the small radius of the macrocycle cavity, results in the square–planar coordination being strongly stabilized with respect to the square-pyramidal or to the octahedral ones. However, in the case of a face-to face porphyrin–phthalocyanine dimer, it is clear that the energy of the copper ion d_{z^2} orbital will be raised because of its strong interaction with the porphyrin electronic distribution. On the other hand, van der Waals interactions between stacked tetrapyrrolic macrocycles often results in a distortion (ruffling or doming) of their structure, which helps to relax the strong repulsion between the $d_{x^2-y^2}$ orbital of the central metal ion and the coordinating nitrogen atoms.

The energy levels of the nickel phthalocyanine have also been calculated theoretically.[21,31] For example, Schäffer et al.,[31] using the extended Hückel method, have determined the following order for the energies of the metal-centered (d) orbitals: $b_{2g}(d_{xy}) < e_g(d_{xz}, d_{yz}) < a_{1g}(d_{z^2}) \ll b_{1g}(d_{x^2-y^2})$. The energetic gap between orbitals $a_{1g}(d_{z^2})$ and $b_{1g}(d_{x^2-y^2})$ depends strongly on the Ni–N distance: It falls from 3.84 to 2.52 eV when the distance increases from 1.83 (phthalocyanine) to 1.96 Å (tetraazaporphyrin). Schäffer et al. have proposed the following explanation for the reported absence of axial coordination in the case of nickel phthalocyanines: according to their calculations, the adduction of two axial pyridine ligands forming an elongated pseudooctahedral complex increases the energy of the d_{z^2} orbital by 2.75 eV, versus only about 0.13 eV for the $d_{x^2-y^2}$ orbital. Consequently, the axially coordinated complex should be paramamagnetic (high-spin Ni(II)), whereas the uncoordinated one is diamagnetic. However, high-spin Ni(II) complexes normally have Ni–N distances greater than 2.0 Å. According to Schäffer et al., the porphyrin macrocycle may expand to accomodate the larger Ni(II) high-spin ion, whereas the more rigid skeleton of the phthalocyanine macrocycle excludes such an expansion.

This argumentation is not entirely convincing in our opinion, for several reasons. First, the metal–nitrogen distance in the uncoordinated nickel phthalocyanine is actually rather small compared to those for other phthalocyanines in which the metal ion is indeed inserted inside the macrocyclic cavity: for example, in copper phthalocyanine, the Cu–N distance is 1.935 Å; the bis(pyridinate) adducts of the iron or manganese phthalocyanines have a metal–nitrogen distance of 1.99 Å. Moreover, metal–nitrogen distances greater than 2.0 Å are easily enough acco-

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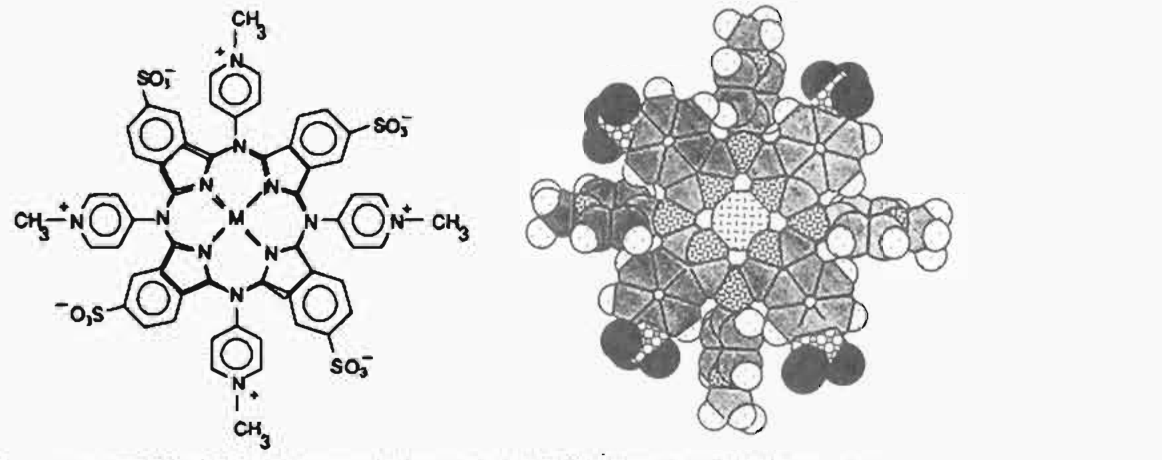

Figure 16. Molecular models of MTMPyP/M′PcTS dimer obtained with 4,4′,4″,4‴-tetrasulfonated phthalocyanines.

modated with a slight displacement of the metal ion out of the plane of the four nitrogens: thus, in the PcOs(CO)(pyridine) phthalocyanine, the osmium ion is displaced out-of-plane by 0.15 Å toward the axial pyridine. The Os–N distances are 1.978, 2.034, 1.983, and 2.027 Å.[32] Finally, the Pb(II) ion is readily complexed by the phthalocyanine macrocycle, although its radius is 1.20 Å. Several crystalline varieties have been described. The mean Pb–N distance is 2.36 Å in the triclinic form[33] and 2.21 Å in one of the monoclinic forms.[34] In the bis(imidazole)(*meso*-tetrakis(*N*-methylpyridinio-4)porphyrinato)nickel(II) structure determined by Kirner et al.,[35] the high-spin Ni(II) ion is indeed inserted in the plane of the four porphyrin nitrogen atoms, with an average Ni–N distance of 2.038 Å. From the preceding data, one sees that such a distance would by no means be exceptional for a phthalocyanine. All these examples clearly show that the steric hindrance argument invoked by Schäffer et al. in the case of a high-spin Ni(II) is not supported by experimental evidence. Our finding that copper or nickel phthalocyanines may be axially coordinated in some cases, though unprecedented, is therefore not in contradiction with theory.

Similar findings were reported by Shelnutt and co-workers on uroporphyrins. Uroporphyrins are octaanionic species. In water, several of these porphyrins form van der Waals complexes with either 5-chloro-1,10-phenanthroline or methylviologen.[27a] The stoichiometry of the van der Waals complexes also depends on the formation of axial bonds: metallouroporphyrins with two strongly bound axial ligands, such as the bis(hydroxy)(uroporphyrinato)tin(IV), do not form any complex at all, even at high ionic strength or very low pH. Uroporphyrins in which the metal ion binds only one axial ligand form only 1:1 complexes, whereas for those in which the metal ion does not bind any axial ligand, 1:2 complexes and self-aggregation are observed at high ionic strength or low pH. When the axial ligands are only weakly bound, they may be displaced by π–π complex formation.[27b] The nickel uroporphyrin exists in solution under two forms in dynamical equilibrium: a planar form and a ruffled form, the latter having an S_4 symmetry. As the low-spin Ni(II) ionic radius is rather small, a large stabilization may appear if the central cavity of the porphyrin contracts strongly, the optimal Ni–N distance being about 1.85 Å, as in the phthalocyanine. In the planar form of the nickel uroporphyrin, the cavity radius corresponds to a Ni–N distance of 2.0 Å. Ruffling closes the Ni–N distance and increases the covalency of the metal–nitrogen bond. This, however, is in competition with the aromaticity of the porphyrin skeleton, which favors planarity. As a result of this competition, the two forms (planar and distorted) have about the same energy, hence the equilibrium. As both forms have very distinct Raman spectra in the 1500–1700-cm^{-1} range, Shelnutt and colleagues have been able to show that complexation with methylviologen induces an expansion of the uroporphyrin central cavity as well as a further ruffling of the macrocycle. It seems sensible to assume that the same occurs when NiPcTS is complexed with a porphyrin. Thus, the formation of a 1:1 complex in our case might induce a distortion of the phthalocyanine ring or an out-of-plane displacement of the nickel ion, sufficient to allow an axial coordination by a solvent or pyridine molecule. If this scheme is correct, then one might expect the complex to be paramagnetic (high-spin nickel ion). We have performed preliminary ESR experiments, unconclusive so far, in part due to the difficulties involved in working with highly polar solvents and also because of the formation of ill-defined aggregates at high concentrations. This issue may be of great interest, as geometrical distortions of naturally occuring porphyrin analogues are known to exert a marked influence on their reactivity. The case of heme and its derivatives is well-known. Another exemple concerns cofactor F430, in which the distortions of the macrocycle have been shown to govern directly the Ni(II) affinity for an axial ligand.[36] Finally, it has recently been suggested that distortions of the tetrapyrrolic macrocycles in photosynthetic reaction centers might be at the origin of their photophysical properties.[37]

4.3 Steric Effect and Stability of Heterodimers and Trimers. As discussed above, axial ligation effects have a dramatic influence on the nature of the complexes formed. The results obtained with the ZnTMPyP/AlPcTS system show that there is an additional effect which is related to the position of the substituents on the phthalocyanine moiety: while heterodimerization was almost quantitative with pure 4,4′,4″,4‴-tetrasulfonated phthalocyanine, only a small amount of complexation was observed with a sample containing about 50% of the sulfonate groups on the 3,3′,3″,3‴-positions. This result may be explained in terms of steric hindrance between sulfonate groups on the phthalocyanine and the pyridyl groups on the porphyrin. Space filling molecular models (Figure 16) show that there is practically no hindrance in the face-to-face conformation, when all the phthalocyanine substituents are on the 4,4′,4″,4‴-positions. On the contrary, a large steric repulsion is to be expected when one or several substituents are in any of the 3,3′,3″,3‴-positions.

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The association constant obtained for the 1/1 heterodimer is of the same order of magnitude than for the ZnTMPyP/CuPcTS couple (Table I). It can also be noted that the dimers are more stable when one of the chromophores is either a free-base porphyrin or a free-base phthalocyanine. The association constants are 2 orders of magnitude higher than for highly metalated heterodimers. At the present type, we dont have any simple explanation for such a difference. However, the following tentative argument may account for this phenomenon: when both moieties are metalated and able to bind a solvent molecule, each metal ion could be displaced out of the plane constituted by the four nitrogens. Therefore, a distortion of the two macrocycles in opposite direction could be expected, thus diminishing slightly the π–π interaction between them.

Conclusion

The systematic study of heterocomplexation of oppositely charged porphyrins and phthalocyanines allow one to demonstrate the existence of well-defined heterodimers and trimers. Their formation can be controlled by changing either the nature of the central metals of each moiety or the solvent. The ability of copper and nickel phthalocyanines to axially bind a donor ligand is clearly demonstrated for the first time in the present work. Up to the present time, such ligation was solely found for porphyrin-like compounds. The geometrical modifications (distortion of the macrocycles, displacement of the central metal) which often results from such ligation could have important implications in the biocatalytic or photoactivity of these compounds as it was previously suggested for uroporphyrins.[29,34,35]

The heterodimers are very stable and the two moieties are strongly coupled. Such dimers display very similar optical properties independently of the nature of the central metals and solvents. However, their photophysical properties may differ markedly. In a preliminary work on two heterodimer systems, ZnTMPyP/CuPcTS and ZnTMPyP/ClAlPcTS, we have shown that the excitation is preferentially localized on the phthalocyanine moiety in the former dimer, whereas a photoinduced charge transfer efficiently occurs in the latter, with the formation of very stable radical ions. We have undergone a systematic study to deepen the understanding of the photophysical behavior of such strongly coupled systems, with the aim of being able to predict and control the charge transfer process. Their comparison with strongly coupled lanthanide mixed porphyrin–phthalocyanine dimers and trimers, which present a strong charge–transfer character in the ground state, is also in progress.

Acknowledgment. The authors acknowledge the financial support of the CRSNG (Conseil de Recherche en Sciences Naturelles et en Génie), and J.F.L. thanks the Canadian Government for a Research Grant. Dr. S. Gaspard is gratefully acknowledged for the gift of some CuPcTS. Thanks are also expressed to Dr. R. Langlois for the supply of a sample of AlClPcTS and also for the HPLC analysis.

Supplementary Material Available: A detailed description of the analytical and graphical methods for the determination of the dimerization and trimerization constants of the heterocomplexes in two cases: (1) when absorption spectrometry is used for the titrations; (2) when fluorimetry is used for the titrations (12 pages). Ordering information is given on any current masthead page.