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J-Type Aggregates of the Anionic Meso-Tetrakis(4-Sulfonatophenyl)Porphine Induced by "Hindered" Cationic Porphyrins*

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Porphyrin aggregation is a field of wide interest owing to the possible technological and biomedical applications. Under these premises, the possibility of tuning and driving the assembly processes turns out to have a central role in achieving specific structures and, therefore, functions. Recently, we have demonstrated that self-aggregation of water-soluble porphyrins on opposite charged polymeric templates is not simply related to the tendency of a given porphyrin towards aggregation, but is driven by specific molecular recognition processes.¹⁻³

Also the interactions between porphyrins bearing opposite charged groups have been widely investigated.⁴⁻⁷ However, to the best of our knowledge no systematic studies have been performed to understand if the steric and electronic features of the porphyrins may lead the

formation of specific hetero-aggregates. In the present paper we show that also the processes leading to aggregation between opposite charged porphyrins are driven, in specific cases, by molecular recognition processes, which in turn may be useful to drive the aggregation process toward the formation of specific porphyrin assemblies.

The anionic porphyrin we chose for our study is the mesotetrakis(4-sulfonatophenyl)porphine (H₂TPPS, λ_{\max} =414 nm, Figure 1), whose protonated form (H₄TPPS, pK_a=4.8, λ_{\max} =434 nm)⁸⁻¹² gives both J- (edge-to-edge) and H-type (face-to-face) self-aggregates (Figure 2).⁸ In particular, the J and H forms are characterized by absorption maxima close to 490 nm⁹ and 422 nm,¹⁰ respectively (Table I).¹³ The formation of these self-assemblies depends strongly on porphyrin concentration, pH and ionic strength.^{9,10} In particular, J aggregates are stabilized by the electrostatic interactions between the protonated

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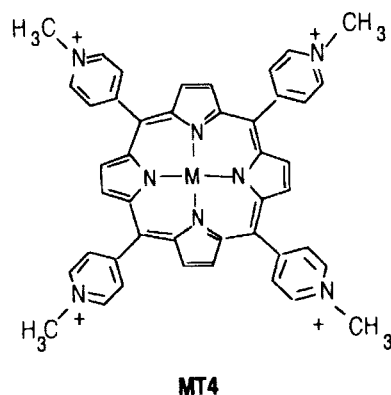
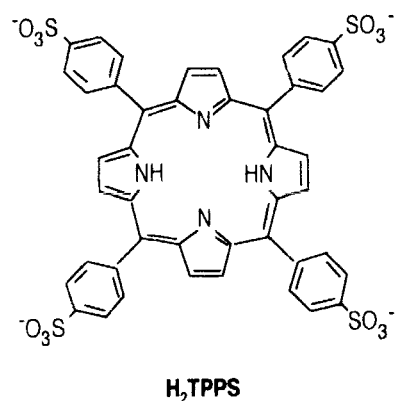


FIGURE 1 Schematic structure of H₂TPPS and MT4

core of one porphyrin (cationic) with the peripheral anionic groups.

As *cationic* porphyrins we used the meso-tetrakis(N-methylpyridinium-4-yl)porphine (H₂T4, $\lambda_{\max} = 423$ nm), and its copper(II) ($\lambda_{\max} = 423$ nm), gold(III) ($\lambda_{\max} = 403$ nm), manganese(III) ($\lambda_{\max} = 465$ nm) and zinc(II) ($\lambda_{\max} = 423$ nm) derivatives (MT4) (Figure 1). The first two metallo-derivatives are planar, whilst the latter two are hexa- and penta-coordinated, respectively.¹⁴ We chose to employ these various derivatives because,^{14,15} as anticipated, the different steric and electronic features lead to the formation of specific supramolecular species.

TABLE I Visible-absorption and RLS features of J- and H-aggregates of H₂TPPS

	Absorption Spectra ^a		RLS Spectra ^b
	Soret band	Q bands	
J-aggregates	489	668, 707	490
H-aggregates	422	575, 625	not observed

a. pH 3.5; 4×10^{-5} M < [H₂TPPS] < 5×10^{-4} M; Reference 9

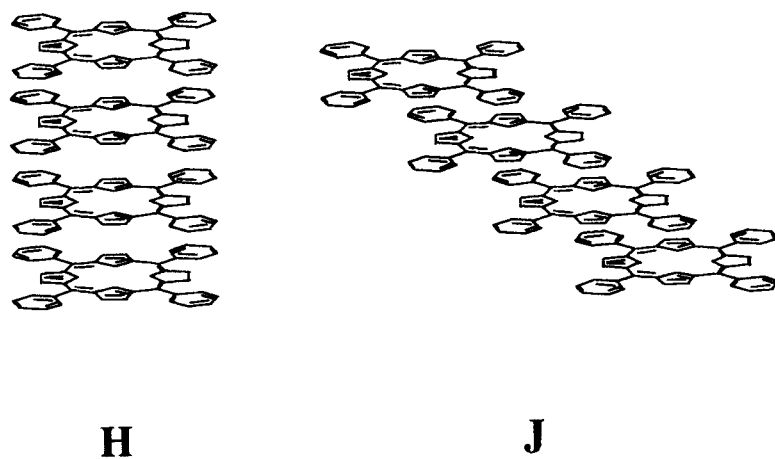
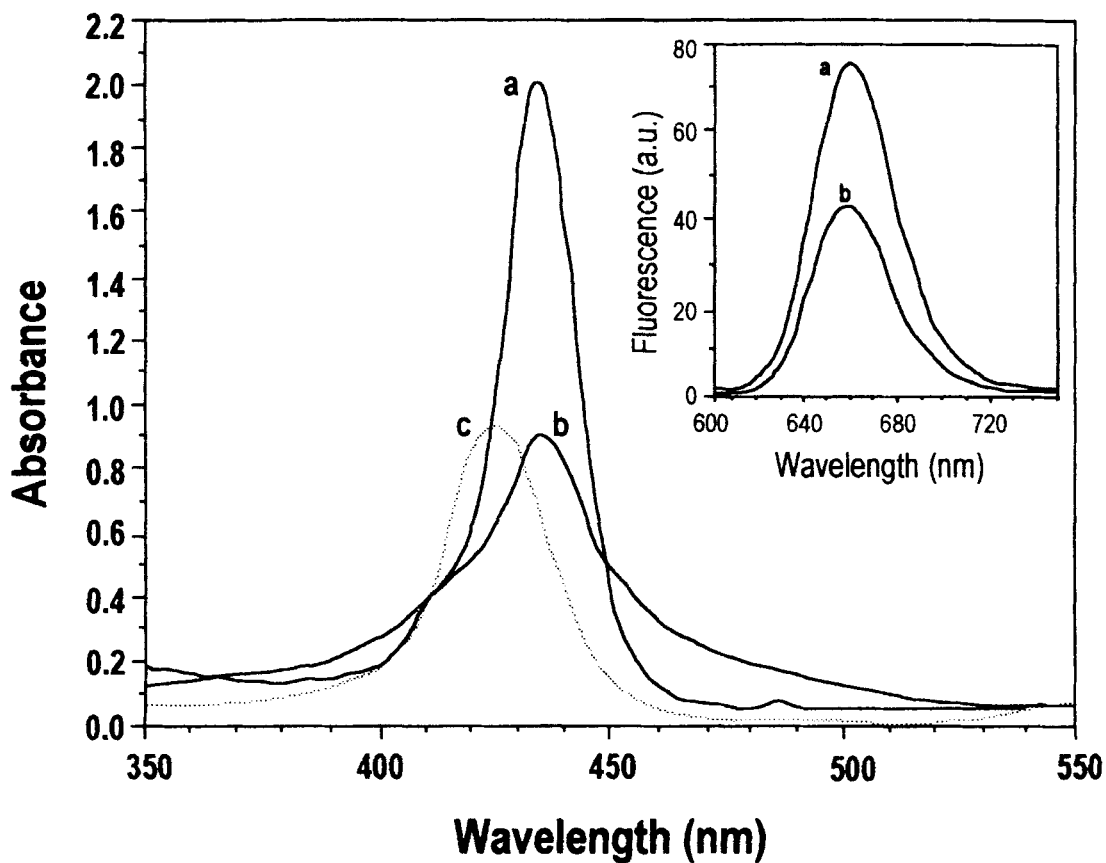
b. pH 1.2; I=0.1M, [H₂TPPS] = 2.5×10^{-6} M; Reference 10.

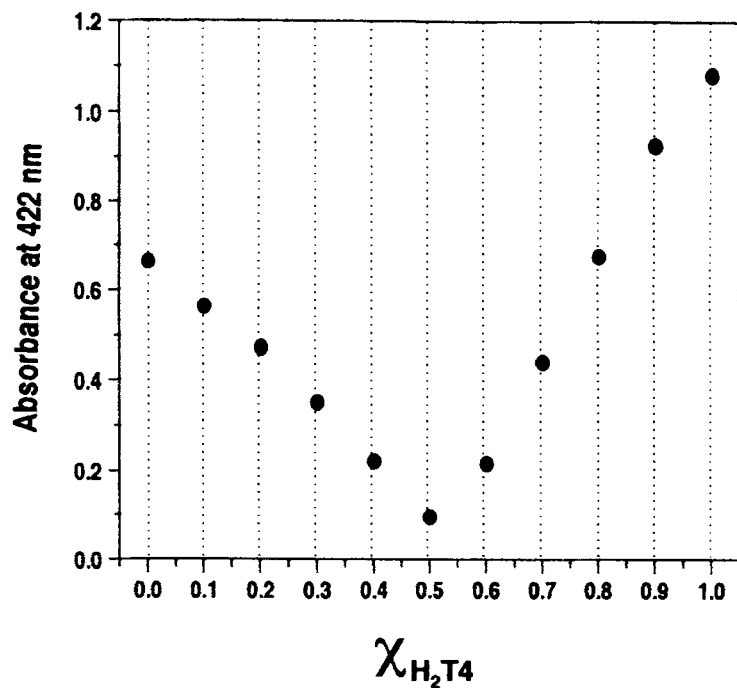
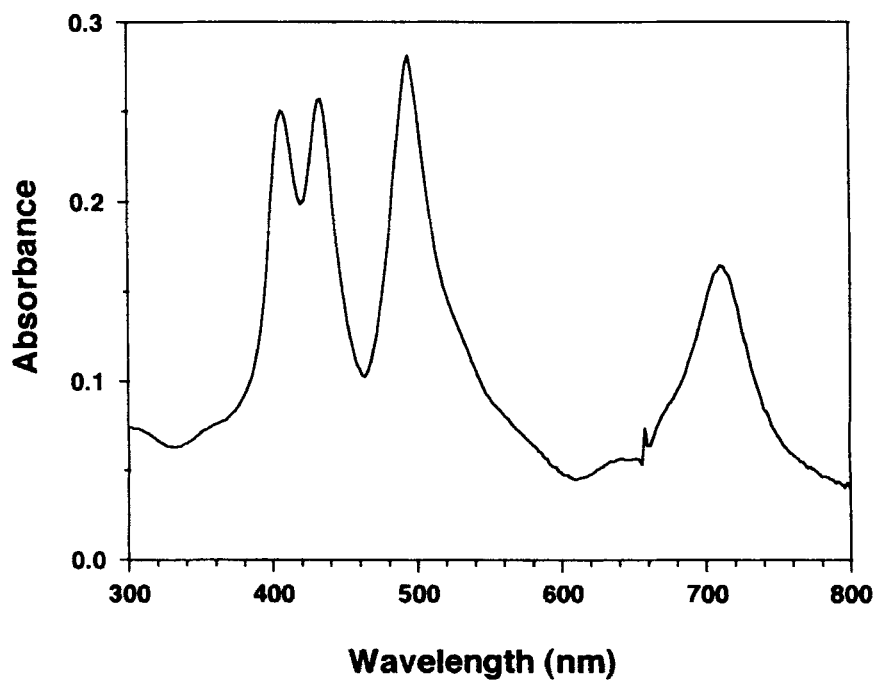
EXPERIMENTAL SECTION

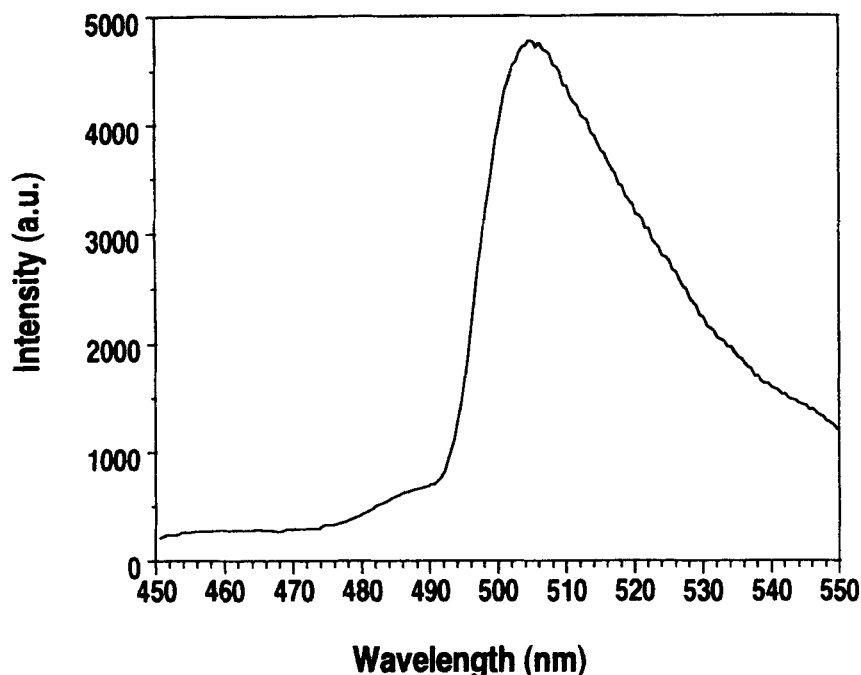
Meso-tetrakis(4-sulfonatophenyl)porphine and meso-tetrakis(N-methylpyridinium-4-yl)porphine were obtained from Mid-Century as sodium and chloride salts, respectively. Porphyrin metallation was performed by following literature methods.¹⁶ Fluorescence and resonance light scattering (RLS)¹⁷ measurements were recorded on a Jasco FP-777 and were carried out using disposable metacrylate cuvettes. Absorption measurements were carried out on a HP8452 A. Job plots have been built by plotting the absorbance at a given wavelength *vs.* the molar fraction of cationic porphyrins (X_{MT4} , where M = 2H⁺ for the free porphyrin). The total concentration of the porphyrins was kept constant and equal to 1×10^{-5} M.¹⁸ All measurements were carried out in 5 mM citrate buffer pH 2.8, and doubly distilled water was used throughout.

RESULTS

Before presenting and discussing the experimental data, it is worth recalling, that, under the experimental conditions used in this work (pH 2.8 and I=0.003 M), all porphyrins are monomeric and H₂TPPS is protonated by about 98%. To characterize the interactions and determine the stoichiometric ratio of the complexes formed between the cationic and anionic porphyrins of H₂TPPS with MT4 we have performed Job plots.

FIGURE 2 Schematic structure of H_4TPPS H and J aggregatesFIGURE 3 Absorption spectrum at pH 2.8 of H_2TPPS ($4 \mu M$, curve a), $CuT4$ ($4 \mu M$, curve c) and a mixture of the two porphyrins ($4 \mu M$ each, curve b). The inset show the fluorescence emission spectra of the corresponding solutions

FIGURE 4 Job's plot for the system H₂T4 – H₄TPPSFIGURE 5 Absorption spectrum at pH 2.8 of AuT₄ (3 μM) and H₄TPPS (7 μM)

FIGURE 6 RLS spectrum of the system AuT4 – H₄TPPS

For the sake of clarity we will present the data following a classification based on the steric features of the cationic porphyrins.

Planar cationic porphyrins

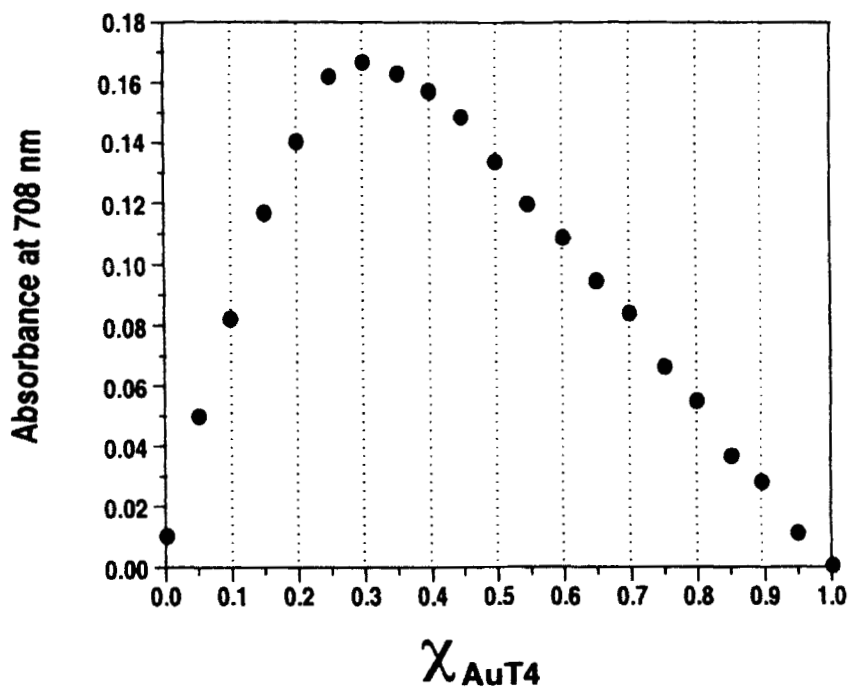
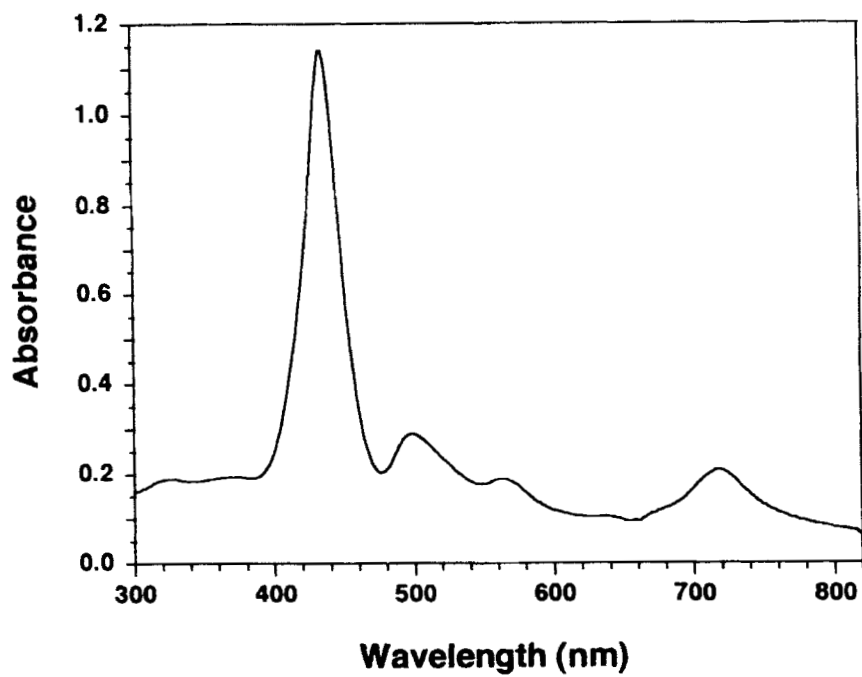
The interaction of H₂TPPS with H₂T4 and CuT4 is accompanied by a strong hypochromic effect (60%, Figure 3) and fluorescence quenching (insert Figure 3) testifying the occurrence of $\pi \rightarrow \pi$ interactions. The Job plots for these two systems show a clear break point at $X_{MT4}=0.5$ (Figure 4), indicating the formation of species in a 1:1 stoichiometric ratio.¹⁹

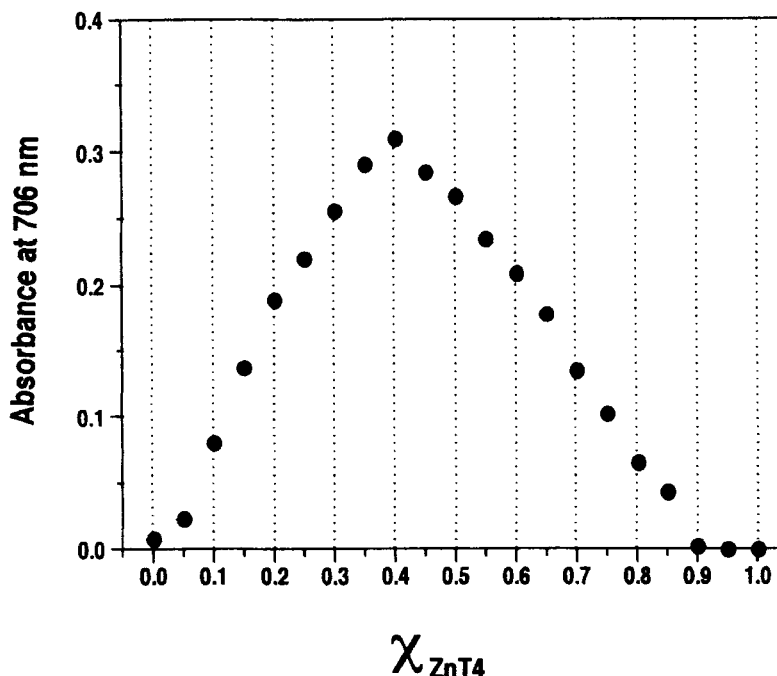
Also for the system Au(III)T4 – H₂TPPS the Soret bands experience a remarkable hypochromic effect. However, the absorption experiments also show that, already at a $X_{AuT4} = 0.1$, two new bands at 490 nm and 707 nm (Figure 5) grow in the spectra and maximizes at $X_{AuT4}=0.3$. The

wavelength of these absorption bands strongly suggests a J-type contact between the H₂TPPS molecules. This coupling is definitively confirmed by RLS spectra which show a quite intense scattering profile centered at about 500 nm (Figure 6), characteristic of H₂TPPS J-aggregates (Table I). The Job plot (Figure 7) does not show a sharp break point, but a smooth contour for $0.25 < X_{AuT4} < 0.4$, *i.e.* in a molar fraction region (about 0.33) which suggests the formation of a species having cationic to anionic porphyrins stoichiometric ratio ranging from 1:3 to 2:3.

Penta- and hexa-coordinated porphyrins

Also ZnT4 induces the formation of the J-aggregates in such unusual experimental conditions. In fact, as shown in Figure 8, together with the expected band at 436 nm (due to the absorption of both ZnT4 and H₄TPPS), there are

FIGURE 7 Job's plot for the system AuT4 - H₄TPPSFIGURE 8 Absorption spectrum at pH 2.8 of ZnT4 (4 μM) and H₄TPPS (6 μM)

FIGURE 9 Job's plot for the system ZnT4 – H₄TPPS

two additional bands at about 490 and 700 nm. In addition, the RLS spectrum shows a very intense band at about 500 nm. In this case the Job plot end point is quite well defined suggesting the formation of species having a cationic to anionic porphyrins stoichiometric ratio of 2:3 (Figure 9).

Very similar results have been obtained using the hexa-coordinated MnT4 (Figure 10).

DISCUSSION

It has been already reported in literature that the formation of the H₂TPPS J-aggregate solutions, in the low *micromolar* concentration range, occurs at pH close to 3 and salt concentrations higher than 0.1 M⁹ or, alternatively, at pH close to 1 and no salt added.¹⁰ It is worth recalling that at pH \approx 2.5 the two central nitrogen atoms of H₂TPPS are already fully protonated. Then, it is

conceivable that the formation of these aggregates at pH \approx 1 is due to the high ionic strength reached under these “extreme” experimental conditions rather than to a protonation effect.^[3d] Therefore, it turns out that *molar* concentrations of cationic species leads to H₄TPPS self-aggregation by shielding the electrostatic repulsion between the anionic sulfonic groups.

Interestingly, our spectroscopic data show that, on one hand, *micromolar* concentrations of the planar Au(III)T4, the penta-coordinated ZnT4 and the hexa-coordinated MnT4, induce drastic changes in the visible region of the spectra attributable to the formation of H₄TPPS J-type aggregates, while, on the other hand, identical concentrations of the planar CuT4 and H₂T4 do not.

The lack of any evidence of J-type contacts between H₄TPPS molecules, together with the information obtained from the Job's plots, suggests that CuT4 and H₂T4 form with H₄TPPS,

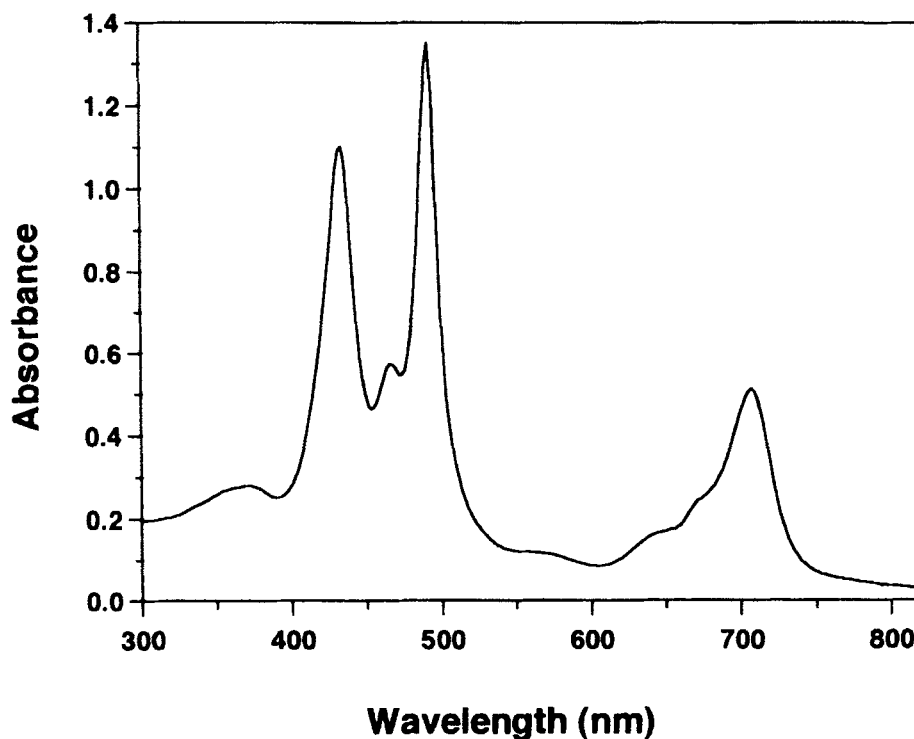


FIGURE 10 Absorption spectrum at pH 2.8 of MnT4 (4 μ M) and H₄TPPS (6 μ M)

complex species in a 1:1 stoichiometric ratio, in which the porphyrins are stacked in an alternated, face-to-face fashion (Figure 11).

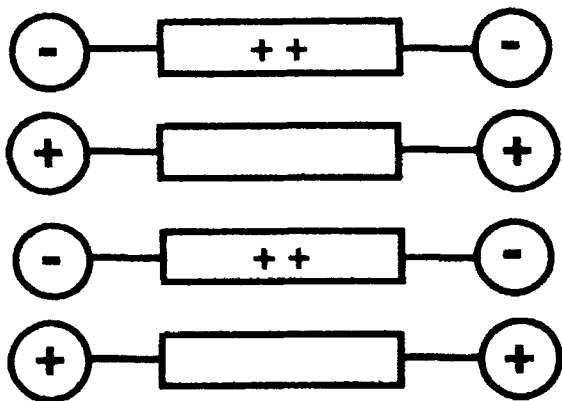


FIGURE 11 Schematic structure proposed for the aggregates formed by CuT4 or H₂T4 with H₄TPPS

The behavior observed for ZnT4 and MnT4 is, most likely, related to the presence axial ligand(s) on the central metal ion which hinder(s) a face-to-face arrangement, allowing only edge-to-edge contacts (Figure 12). This type of complex becomes a nucleation point for the growth of H₄TPPS J-type aggregates.

The behavior of the planar Au(III)T4 could apparently be considered anomalous. In fact, owing to its planar nature one might imagine a behavior similar to that observed for CuT4 and H₂T4. However, the Au(III)T4 peculiar behavior can be explained recalling that this metallo-derivative has a (partial) positive charge on the gold which plays a similar role of axial ligands, *i.e.* it presents some kind of "electronic" hindrance. In fact, because of the electrostatic repulsion between the above charge and the positive charges in the center of the protonated

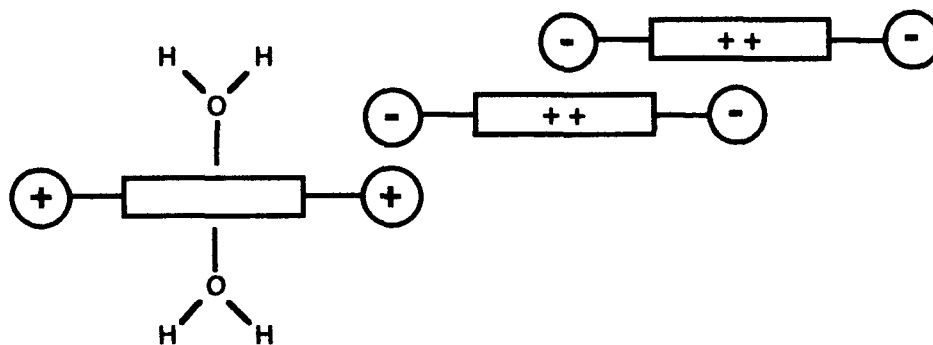


FIGURE 12 Schematic structure proposed for the aggregates formed by MnT4 or ZnT4 with H₄TPPS

H₂TPPS, the edge-to-edge interactions become favored over the face-to-face ones (Figure 13). Therefore, again the formation of H₄TPPS J-aggregates is promoted by the particular "nature" of the cationic porphyrin.

CONCLUSIONS

Our data show that specific cationic porphyrins, induce the formation of H₄TPPS J aggregates

under very "mild" experimental conditions. The remarkable difference of the cationic species concentration required to promote the formation of the J-aggregates (*millimolar* for 'salts' *vs. micromolar* for porphyrins) suggests that the assembly processes are driven by specific molecular recognition processes. In particular, the formation of these species is observed when the porphine core is 'hindered' for steric or electronic reasons. In these cases an edge-to-edge interaction becomes preferred over a face-to-face.

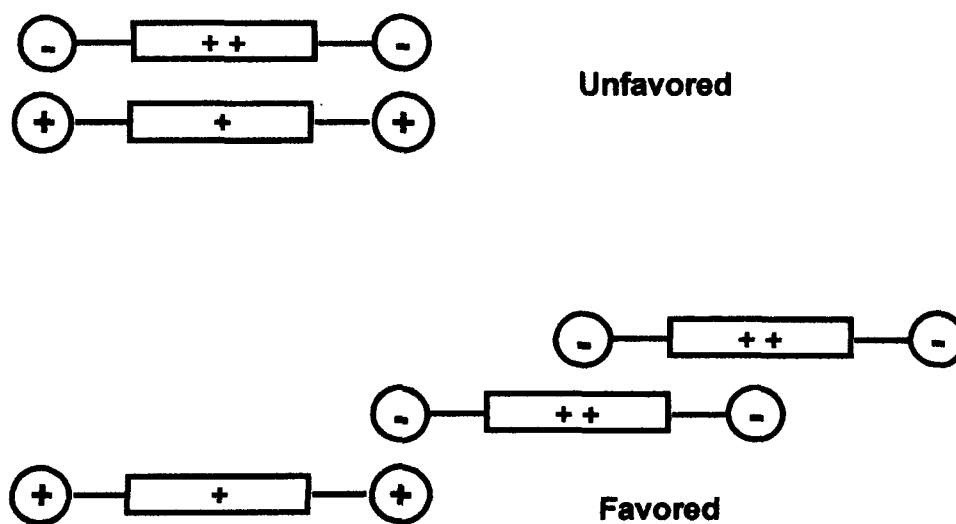


FIGURE 13 Schematic structure proposed for the aggregates formed by AuT4 with H₄TPPS

Furthermore, to the best of our knowledge there are only few data showing that the interactions of opposite charged porphyrins can lead to the formation species with stoichiometric ratios different from 1:1.^{20,21}

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