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Self-Aggregates of Cationic *meso*-Tetratolylporphyrins in Aqueous Solutions

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Aggregation properties of *meso*-tetratolylporphyrins bearing cationic substituents of a lipophilic nature such as ammonium, pyridinium, phosphonium, sulfonium, and isothiuronium were studied by UV/vis and resonance light scattering spectroscopy. The exciton point–dipole approximation was used to predict the structural alignment of the porphyrin units within the aggregate. The contribution of various types of aggregates depends on the porphyrin substitution, ionic strength, and temperature of aqueous solution of the porphyrin. In general, the preferred structure of an aggregate formed by temperature-induced aggregation is the J-aggregate exhibiting the characteristically narrow, red-shifted Soret band indicating a parallel “side-by-side” arrangement of the porphyrin units. The formation of aggregates of cationic tetratolylporphyrins is controlled by both electrostatic and hydrophobic interactions. Observed aggregation properties of porphyrin derivatives bearing trimethylammonium, trimethylphosphonium, pyridinium, dimethylphenylphosphonium, and triphenylphosphonium substituents are in very good agreement with a theoretical model based solely on electrostatic interactions.

Introduction

Molecular assemblies of chromophores play crucial roles in nature's most important systems, including light harvesting¹ in photosynthesis,² and are important in technological applications.^{3,4} The main problem faced/encountered during the application of molecular assemblies and aggregates in the current technology is a difficulty to control the arrangement and orientation of monomers in the aggregates.

Molecular aggregates can form highly organized structures, which are classified according to the orientation of the induced transition dipole of the constituent monomers.⁵ The transition dipole moments of monomers assembled into H-aggregates are *perpendicular* to the line connecting their centers (a “face-to-face” arrangement), producing a characteristic blue shift in the UV/vis absorption spectrum. In contrast to the above, the transition dipole moments of monomers in J-aggregates are *parallel* to the line connecting their centers (a “side-by-side” arrangement). Such an arrangement of monomers in J-aggregates results in the formation of an intense narrow absorption band, red shifted with respect to the absorption spectrum of the monomer. The origin of this band is explained by the formation of an excitonic state through the electronic coupling of tightly packed dye molecules.^{6,7}

Porphyrins are a typical example of chromophores that show a strong tendency to form several different types of aggregates^{8,9} that differ in their spectroscopic properties. The formation of porphyrin aggregates in aqueous solutions can be affected by the structure and substitution of the respective porphyrin, the ionic strength, the temperature, the pH, and the presence of surfactants. The rational functionalization of the porphyrin peripheral substituents allows preparation of porphyrin derivatives of a different charge, size and hydrophobicity. The interest in porphyrins bearing polar–lipophilic substituents or substituents with low polarizability stems from the fact that such substituents can facilitate a transport of the porphyrin through biological membranes.¹⁰ By the same token, lipophilic substituents cause the porphyrins to aggregate in aqueous solutions. Before any potential biological application of such porphyrins could be considered, one must address the aggregation behavior, which is the subject matter of this article.

The most widely studied porphyrins are derivatives of *meso*-tetraphenylporphyrin (Figure 1A), and its close relatives, *meso*-tetra(*N*-methylpyridyl)porphyrins (Figure 1B). In this study, we present a unique set of *meso*-tetratolylporphyrins with a wide variety of cationic substituents of lipophilic nature (Figure 1C). The reason we decided to synthesize and investigate the *meso*-tetratolylporphyrins is that the water-solubilizing, positively charged substituents are insulated from the porphyrin chromophore by a methylene bridge (–CH₂–). This

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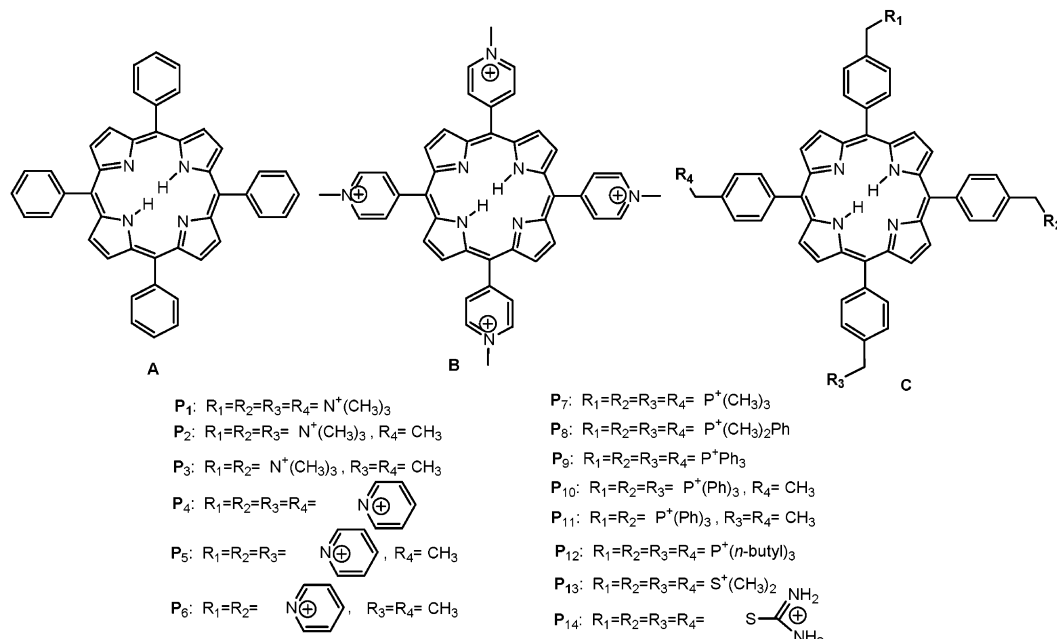


Figure 1. Structures of tetraphenylporphyrin (A), tetra(4-*N*-methylpyridyl)porphyrin (B), and cationic tetratolylporphyrin derivatives **P**₁–**P**₁₄ (C).

way we made sure that the spectroscopic properties of the porphyrin chromophore do not depend on the structure of the solubilizing group, but solely on the nature of the aggregate. This functionalization does not appear to affect the protonation equilibria of the porphyrin pyrrole nitrogens characterized by the same value of $pK_a = 4.8$ (Figure 1C).¹¹

Several studies describing aggregation of tetraarylporphyrins have been published. A typical example is 5,10,15,20-tetrasulfonatophenylporphyrin, which forms J-aggregates in an acidic solution.^{7,12–14} Here, the *N*-protonation creates positively charged sites in the porphyrin macrocycle, thus promoting the electrostatic attraction to the negatively charged sulfonate groups and facilitating aggregation.

Similarly, the formation of both types of aggregates with the blue- and red-shifted Soret band was also described for tetracationic porphyrins. While tetra(*N*-methyl-4-pyridyl)porphyrin dimerizes only at high ionic strength in an aqueous solution,^{15–17} the increased lipophilicity of porphyrins containing pyridinium groups and longer nonpolar alkyl chain results in a pronounced tendency toward aggregation.^{9,15}

Despite the extensive studies devoted to the pyridinium porphyrins, a few other types of positively charged meso-substituted porphyrins have been prepared. These include porphyrins with trialkylammonium,^{11,18–20} anilinium,¹⁵ guanidinium,^{21–23} trialkyl/triarylphosphonium,^{11,24,25} and

sulfonium¹¹ groups. However, all the studies describe behavior of tetrakis-substituted porphyrins, while little attention has been devoted to porphyrins with only two or three cationic substituents. Such cationic porphyrins with a lower number of polar substituents are expected to aggregate readily, and form very stable aggregates compared to their tetracationic congeners.^{16,26}

Here, we present the results of a study describing the aggregation of di-, tri-, and tetrasubstituted derivatives of tetratolylporphyrins **P**₁–**P**₁₄ with positively charged ammonium, pyridinium, phosphonium, sulfonium, and isothiuronium group, respectively (Figure 1C), in aqueous solutions. It appears that the formation of different types of aggregates can be tuned, to a large extent, by the character of the peripheral substituents. This is an important feature because it may allow for predetermination of the aggregate structure by chemical design and synthesis. Likewise, the physical factors such as ionic strength and temperature of the medium play an important role in the aggregation. All of these factors will be discussed for the tetratolylporphyrins **P**₁–**P**₁₄.

This study is based mainly on spectroscopic observations that allow estimation of the aggregation behavior. Determination of the position and shape of the Soret bands allowed us to distinguish between monomeric porphyrins and various types of aggregates. Extended aggregation was evaluated by resonance light scattering (RLS).²⁷ Experimental data are discussed within the theoretical model based on exciton point–dipole interactions. This

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enables us to understand the role of substituents in the formation of different types of porphyrin aggregates, as well as their contribution to aggregate stability.

Experimental Section

Syntheses of **P**₁, **P**₄, and **P**₇–**P**₁₄ were described in previously published papers.^{25,26} The starting 5,15-bis(α -bromo-4-tolyl)-10,20-bis(4-tolyl)porphyrin and 5,10,15-tris(α -bromo-4-tolyl)-20-(4-tolyl)porphyrin for syntheses of **P**₂, **P**₃, **P**₅, and **P**₆ were prepared in two steps according to the previously published procedure.^{11,26}

General Procedure for Preparation of Trimethylammonium-Substituted Porphyrins **P₂ and **P**₃.** The pressure reaction vessel was charged with starting α -bromo-4-tolylporphyrin (0.5 mmol) suspended–dissolved in methanol (100 mL) followed by 40 wt % trimethylamine solution in water (20 mL), and sealed. The reaction was heated to 95 °C overnight. The reaction mixture was evaporated in a vacuum, and the residue was thoroughly washed with hot tetrahydrofuran (THF) and cold methanol on the frit. Further purification was performed by dissolving the solid in hot water with an addition of THF to promote crystallization.

5,10,15-Tris(α -[trimethylammonium]-p-tolyl)-20-(4-tolyl)porphyrin **P₂.** The yield was 0.418 g (77%).

¹H NMR (DMSO-*d*₆) δ : –2.92 (brs, 2H, pyrrole NH), 2.69 (s, 3H, Ph–CH₃), 3.33 (s, 27H, N–CH₃), 4.94 (s, 6H, CH₂N), 7.67 (m, 2H, aromatic CH), 8.00 (m, 6H, aromatic CH), 8.12 (m, 2H, aromatic CH), 8.37 (m, 6H, aromatic CH), 8.85–8.99 (s, 8H, β -pyrrole CH).

¹³C NMR (DMSO-*d*₆) δ : 21.1, 52.1, 67.7, 119.0, 119.2, 120.6, 127.7, 128.2, 131.4, 134.3, 134.6, 137.47, 138.1, 143.0.

MS/FAB⁺ (*m/z*) 1002 [M – Br].

For C₅₇H₆₂Br₃N₇, calcd: C 63.11, H 5.76, N 9.04; found: C 63.39, H 5.51, N 9.21.

5,15-Bis(α -[trimethylammonium]-p-tolyl)-10,20-bis(4-tolyl)porphyrin **P₃.** The yield was 0.383 g (81%).

¹H NMR (DMSO-*d*₆) δ : –2.90 (brs, 2H, pyrrole NH), 2.71 (s, 6H, Ph–CH₃), 3.34 (s, 18H, N–CH₃), 4.96 (s, 4H, CH₂N), 7.70 (m, 4H, aromatic CH), 8.05 (m, 4H, aromatic CH), 8.15 (m, 4H, aromatic CH), 8.37 (m, 4H, aromatic CH), 8.89–9.05 (s, 8H, β -pyrrole CH).

¹³C NMR (DMSO-*d*₆) δ : 20.9, 51.5, 67.5, 118.5, 119.0, 120.4, 126.2, 129.7, 133.5, 137.7, 143.3.

MS/FAB⁺ (*m/z*) 787 [M – 2Br], 866 [M – Br].

For C₅₄H₅₄Br₂N₆, calcd: C 68.50, H 5.75, N 8.88; found: C 68.69, H 5.71, N 8.91.

General Procedure for Preparation of Pyridinium-Substituted Porphyrins **P₅ and **P**₆.** The pressure reaction vessel was charged with starting α -bromo-4-tolylporphyrin (0.5 mmol) dissolved in pyridine (20 mL). The reaction was heated to 95 °C overnight. The reaction mixture was evaporated in a vacuum, and the residue was thoroughly washed with hot tetrahydrofuran (THF) and cold methanol on the frit. Further purification was performed by dissolving the solid in hot water with an addition of THF to promote crystallization.

5,10,15-Tris(α -[pyridinium]-p-tolyl)-20-(4-tolyl)porphyrin **P₅.** The yield was 0.441 g (77%).

¹H NMR (DMSO-*d*₆) δ : –2.95 (brs, 2H, pyrrole NH), 2.68 (s, 3H, Ph–CH₃), 6.27 (s, 4H, CH₂N), 7.64 (m, 2H, aromatic CH), 7.94–8.00 (m, 6H, aromatic CH), 8.08 (m, 2H, aromatic CH), 8.28–8.32 (m, 6H, aromatic CH), 8.37 (m, 6H, pyridine CH), 8.75–8.89 (m, 11H, β -pyrrole CH + pyridine CH), 9.52 (m, 6H, pyridine CH).

¹³C NMR (DMSO-*d*₆) δ : 21.00, 63.17, 118.9, 119.1, 120.5, 127.3, 127.6, 128.6, 134.9, 134.1, 134.8, 137.4, 138.1, 142.0, 145.2, 146.2.

MS/FAB⁺ (*m/z*) 1062 [M – Br].

For C₆₃H₅₀Br₃N₇, calcd: C 66.09, H 4.40, N 8.56; found: C 66.00, H 4.32, N 8.42.

5,15-Bis(α -[pyridinium]-p-tolyl)-10,20-bis(4-tolyl)porphyrin **P₆.** The yield was 0.439 g (89%).

¹H NMR (DMSO-*d*₆) δ : –2.95 (brs, 2H, pyrrole NH), 2.67 (s, 6H, Ph–CH₃), 6.29 (s, 4H, CH₂N), 7.63 (m, 4H, aromatic CH), 7.97 (m, 4H, aromatic CH), 8.08 (m, 4H, aromatic CH), 8.30 (m, 4H, aromatic CH), 8.37 (dd, 4H, *J* = 6.6, *J* = 6.4, pyridine CH), 8.75–8.89 (m, 10H, β -pyrrole CH + pyridine CH), 9.55 (d, 4H, *J* = 6.4, pyridine CH).

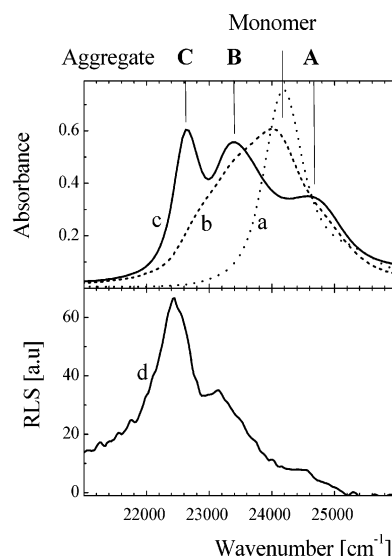


Figure 2. Soret band of monomeric **P**₇ in 0.1 M NaCl at 22 °C (a), partially monomeric **P**₉ in 0.0 M NaCl, at 85 °C (b), and aggregated **P**₉ in 0.7 M NaCl at 22 °C (c). The lower panel shows the corresponding RLS spectrum of aggregated **P**₉ in 0.7 M NaCl at 22 °C (d). All experiments were performed in 20 mM phosphate buffer, pH 7.0.

¹³C NMR (DMSO-*d*₆) δ : 21.1, 63.2, 118.6, 119.1, 120.3, 120.4, 127.4, 127.7, 128.7, 134.0, 134.2, 134.82, 137.4, 138.2, 142.2, 145.3, 146.2.

MS/FAB⁺ (*m/z*) 905 [M – Br].

For C₅₈H₄₆Br₂N₆, calcd: C 70.59, H 4.70, N 8.58; found: C 70.38, H 4.64, N 8.49.

Stock solutions of **P**₁–**P**₁₄ (100–200 μ M) were prepared in methanol (Riedel-de Haën, HPLC grade), and stored in the dark. The absorption spectra were recorded in 1 \times 1 cm quartz cuvettes using a Perkin-Elmer Lambda 19 spectrophotometer. The Soret bands of **P**₁–**P**₁₄ were monitored as a function of temperature (22–90 °C) and ionic strength (0–2 M NaCl) in 20 mM phosphate buffer, pH 7.0. Resonance light scattering experiments (RLS) were performed using simultaneous scans of the excitation and emission monochromators through the range of 300–600 nm using a Perkin-Elmer LS 50B luminescence spectrophotometer.

The semiempirical quantum chemistry method, PM3 (ChemBats3D Ultra, CambridgeSoft Corp.), was used to optimize the geometry of substituents and for determination of dipole moments μ and mean polarizabilities α .²⁸ The COSMO approach was used to estimate the influence of water solvation.²⁹

Results

The absorption spectra of porphyrins **P**₁–**P**₁₄ in their monomeric state were recorded in methanol, and in the cases of **P**₁, **P**₂, **P**₄, **P**₅, and **P**₇ also in aqueous solutions.³⁰ In UV/vis spectra, monomeric porphyrins display sharp Soret maxima and extinction coefficients of $(2\text{--}4) \times 10^5$ M^{–1} cm^{–1} (Figure 2a), comparable to the values reported in the literature.³¹ As an opposite extreme, our studies indicate extensive formation of aggregates of porphyrins bearing triphenylphosphonium (**P**₉, **P**₁₀, **P**₁₁), tri(*n*-butyl)-phosphonium (**P**₁₂), sulfonium (**P**₁₃), and isothiuronium (**P**₁₄) groups in aqueous solutions even at concentrations lower than 10^{–6} M.

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Table 1. Positions of the Soret Bands of the Porphyrin Monomers P₁–P₁₄, of Aggregates (A, B, C),^a and the Estimated Degree of Aggregation *n*^b

		Soret band [cm ⁻¹]				
	n ^c	monomer	A	B	C	preferred struct.
P ₁	0.0	24 150				monomer
P ₂	0.1	24 150	(24 940)	(23 980)		monomer
P ₃	1.0	(24 150)	24 940	23 470	22 100	monomer A, B, C
P ₄	0.0	24 140				monomer
P ₅	0.1	24 130			(22 880)	monomer
P ₆	1.0		24 630	23 580	22 860	A, B, C
P ₇	0.1	24 140			(22 070)	monomer
P ₈	0.6	24 120	25 770 ^d	22 720 → 22 060 ^e		B, C
P ₉	0.9	23 980	24 750	23 360	22 570 ^f	B
P ₁₀	1.0		24 630	23 470		B
P ₁₁	1.0		24 640	23 470 → 22 930 ^e		B, C
P ₁₂	1.0		24 690	23 320	22 220	B
P ₁₃	1.0		24 690	23 360	22 730	A
P ₁₄	1.0		24 620	23 030		B

^a The maxima of the Soret bands of all aggregates except for P₈ and P₁₁ do not depend significantly on solution aging (± 20 cm⁻¹). ^b The measurements were performed in 20 mM phosphate buffer, pH 7.0, 0.1 M NaCl, at 22 °C. ^c The degree of aggregation *n* was estimated using UV/vis spectra as a ratio of the Soret band area of aggregates to the total sum of the Soret band area of aggregates and a monomer. The shapes of the individual Soret subbands were analyzed using a Voigt function⁴³ (convolution of a Lorentzian function with a Gaussian function). ^d The wavenumber of the band is changed to 24 720 cm⁻¹ after the heating/cooling cycle. ^e The red shift and broadening of the Soret band were observed upon solution aging. ^f This band is formed after a heating/cooling cycle or at high ionic strength above 0.3 M NaCl.

Aggregation of porphyrins is typically accompanied by splitting, hypochromicity, and broadening of the Soret band. This tendency is particularly strong at ionic strengths greater than 0.5 M NaCl where it can be clearly distinguished between at least three aggregate structures A, B, and C based on the position of the respective Soret bands. Typical spectra of porphyrins in aqueous solutions are shown in Figure 2. The Soret bands of the porphyrin monomer of P₇ (Figure 2a) and P₉ (Figure 2b) are observed at 23 980–24 150 cm⁻¹, while aggregate A has a blue-shifted Soret band (ν_{\max} = 24 630–25 770 cm⁻¹, Figure 2c). The corresponding weak feature in the RLS spectra (Figure 2d) suggests that aggregate A consists of significantly fewer porphyrin units than aggregates B and C. Aggregates B and C are characterized by red-shifted Soret bands. Aggregate B displays a broad Soret maximum at ν_{\max} = 23 030–23 980 cm⁻¹, while aggregate C is characterized by a narrow Soret band at ν_{\max} = 22 060–22 860 cm⁻¹. The RLS spectra shown in Figure 2d reveal a strong-intensity feature corresponding to aggregate C. The intense RLS signal confirms a colloidal size of aggregate C.²⁷ In comparison, the weaker signal of aggregate B indicates its smaller dimension. It should be noted that porphyrin monomers and small aggregates do not show any RLS profiles.

While aggregates A and B are typically formed solely by adding a stock solution of a porphyrin in methanol into aqueous solutions, the formation of aggregate C is achieved by increase in ionic strength (NaCl concentration >0.5 M). Similarly, aggregate C is also formed upon heating the mixture of porphyrin aggregates to 85 °C followed by slow cooling, even at lower NaCl concentration (ca. 0.1 M).

Without the presence of NaCl, porphyrins P₁–P₁₄ tend to decompose during heating. Most importantly, the aggregation behavior of the porphyrins is predetermined by the structure and a number of polar substituents. In general, a decrease in polar character and increase in the size of the functional groups result in a stronger tendency toward aggregation. These aspects are discussed in detail in the following paragraphs. The results presented in Table 1 show that the aggregation ability of tetracationic porphyrins at laboratory temperature and constant ionic strength increases in the following order: P₁ = P₄ < P₇ < P₈ < P₉ < P₁₂ = P₁₃ = P₁₄.

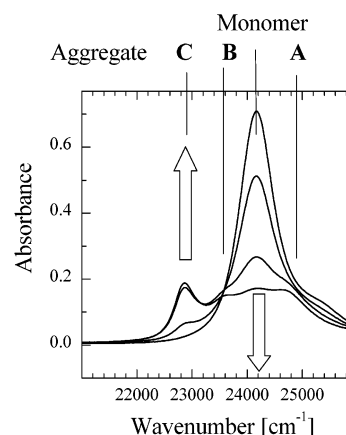


Figure 3. Soret band of tricationic P₅ (2.4 μM): concentration of NaCl was 0.0, 0.1, 0.2, and 0.4 M, respectively. The arrows show changes induced by increasing concentration of NaCl. All experiments were performed in 20 mM phosphate buffer, pH 7.0.

Tricationic and dicationic porphyrins show an increased tendency toward aggregation when compared to their tetracationic congeners. The order of aggregation is P₁ (tetracationic) < P₂ (tricationic) < P₃ (dicationic), P₄ (tetracationic) < P₅ (tricationic) < P₆ and P₉ (tetracationic) < P₁₀ (tricationic) = P₁₁ (dicationic) for trimethylammonium, pyridinium, and triphenylphosphonium substituents, respectively.

The tendency toward aggregation as well as the relative abundance of various types of aggregates depends on temperature and the ionic strength controlled mainly by concentration of NaCl.

We show typical NaCl-induced spectral changes of P₅ (Figure 3). Without the presence of NaCl, P₅ is predominantly monomeric as indicated by the sharp and narrow Soret band and validity of Lambert–Beer's law. Increase in the NaCl concentration (up to 0.4 M NaCl) induced a dramatic decrease of the absorption of the monomeric band and a formation of aggregate C. The formation of aggregates was observed for all studied porphyrins except for tetracationic P₁ and P₄, respectively, with trimethylammonium and pyridinium peripheral groups predominantly monomeric even at high ionic strength (1 M NaCl).

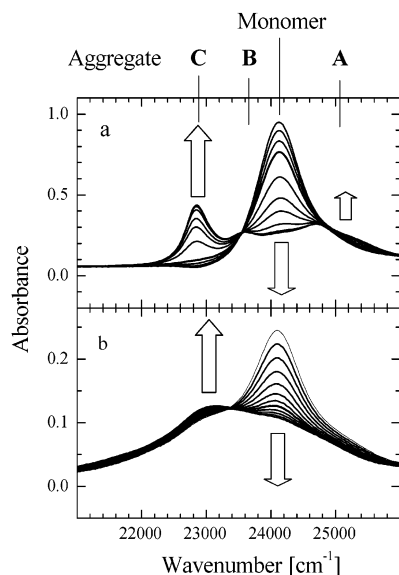


Figure 4. Soret band of tricationic **P**₅ (2.4 μM): 0.5 M NaCl, temperature 80, 75, 70, 65, 60, 55, 50, 40, 30, and 25 °C, respectively (a). Soret band of dicationic **P**₆ (2.0 μM): 0 M NaCl, temperature 80, 75, 70, 65, 60, 55, 50, 40, 30, and 25 °C, respectively (b). All experiments were performed in 20 mM phosphate buffer, pH 7.0. The arrows show changes induced by decreasing temperature.

With the exception of **P**₁₂, **P**₁₃, and **P**₁₄, increasing the temperature from 22 °C to 85 °C results in a partial or complete monomerization of the porphyrin aggregates **A**, **B**, and **C**. The decrease in the temperature from 85 °C to 22 °C results in the monomer reaggregation. The result of this process, however, is the formation of thermodynamically stable aggregates **A** and **C**. Here, the structure of the substituent determines the relative abundance of the respective aggregate.

A typical example of the temperature-induced aggregation of tri- and dicationic porphyrins **P**₅ and **P**₆ bearing pyridyl groups is shown in Figure 4. In this figure, we can clearly see the predominant formation of aggregate **C** together with a small amount of aggregate **A**. The Soret bands of a monomer and aggregates of dicationic porphyrins are broader than those of their tetra- and tricationic analogues. Such drastic temperature-induced changes in porphyrin spectra are very rare.⁹ In case of some porphyrins such as **P**₉, the temperature-induced deaggregation–reaggregation process is arrested at high ionic strength.

Discussion

Considering the positive charge located on the peripheral substituents and facilitation of aggregation by NaCl, which permitted neutralization of the high positive charge density of the aggregate, we anticipated that electrostatic factors would be a significant factor in stabilizing porphyrin aggregates. Therefore, we compare the types of aggregates of cationic *meso*-tetratolylporphyrins in the frame of a point–dipole approximation, originally developed by Kasha,⁵ which is based on the assumption that all driving forces are purely electrostatic. In addition, in an aqueous solution, the so-called hydrophobic forces, which are controlled by changes within the microstructure of water around the solute and exhibit a large entropic contribution, could also play an important role.³²

Electronic interactions between porphyrin chromophores cause splitting of the Soret band. The theory based on the

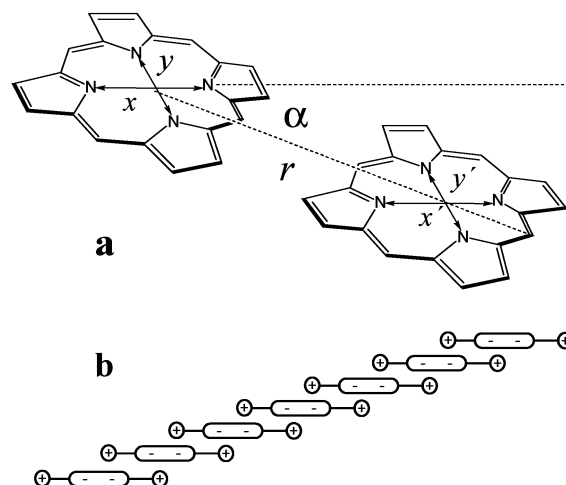


Figure 5. Exciton point–dipole coupling model for two interacting parallel porphyrin rings: α is the angle between the transition moment and the line connecting the centers of the porphyrins, and r is the distance between porphyrin planes. Orientation of both dipole transition moments is according to Gourterman's four-orbital model.³⁶

calculation of an exciton point–dipole interaction was used to predict the shift of the absorption frequencies ($\Delta\nu$) corresponding to the difference between the energy levels of the monomer and the dimer:

$$\Delta\nu \approx \frac{\langle M^2 \rangle}{r^3} (\cos \theta - 3 \cos \phi_1 \cos \phi_2) \quad (1)$$

where $\langle M^2 \rangle$ is the mean square of the transition dipole moment of the monomer, r is the center-to-center distance between the monomers, and θ , ϕ_1 , and ϕ_2 are the angles between the transition moments of both monomers and the vector of a distance r . The point–dipole approximation was applied to several complex systems³³ including cyanine dyes³⁴ and porphyrins.³⁵ According to Gourterman's four-orbital model,³⁶ porphyrins have two perpendicular degenerate transition moments, M_x and M_y , resulting in the formation of two degenerate Soret bands.³⁷ A contact of three or more porphyrin units induces additional changes in the energy level, mainly as a result of the interaction between neighboring porphyrin units. The contribution of more distant units to the shift $\Delta\nu$, however, decays very fast, as it is proportional to r^{-3} .

Aggregates **A**, **B**, and **C** of **P**₂, **P**₃, and **P**₅–**P**₁₁ are characterized by distinct Soret bands, indicating the different structural alignments of the porphyrin planes. For prediction of their structure we can assume the parallel arrangement of porphyrin planes, where α is the angle between the transition moment and the line connecting the centers of the porphyrins (Figure 5). This assumption is based on the recent observation of Kano et al.,⁹ who studied aggregation of cationic porphyrins (22 π -conjugated systems) by NMR and X-ray crystallography. Despite the bulky substituents, the π -conjugated system of the porphyrin planes was nearly coplanar in crystals. The coplanar arrangement is also typical for aggregates of cyanine dyes and porphyrin diacids.¹³ The factor $(\cos \theta - 3 \cos \phi_1 \cos \phi_2)$ determines the sign of $\Delta\nu$. The

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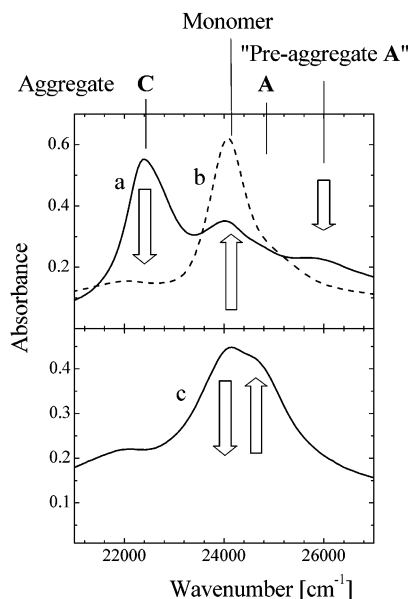


Figure 6. Soret band of **P**₈ (4.7 μ M) in 20 mM phosphate buffer, pH 7.0, 0.7 M NaCl: 22 $^{\circ}$ C (a), after heating to 85 $^{\circ}$ C (b), and after cooling to 22 $^{\circ}$ C (c). Arrows show changes during the heating/cooling cycle.

magnitude of $\Delta\nu$ of the studied porphyrins in similar geometric arrangements is determined mainly by the interporphyrin distance r and transition dipole moments of porphyrin units M_x and M_y (eq 1).

The structure of aggregate **A** is attributed to the H-aggregate with the angle α close to 90° , and a face-to-face arrangement of interacting porphyrin planes. This arrangement results in the blue-shifted Soret band. In the majority of the studied porphyrin derivatives, the position of band **A** was found to be independent of substitution. Both the UV/vis and RLS spectra indicate that porphyrins **P**₂, **P**₃, **P**₆, and **P**₉–**P**₁₄ form small aggregates **A** of a similar size.

The only exception to this general behavior was dimethylphenylphosphonium porphyrin **P**₈. Upon the addition of a methanolic solution of **P**₈ to a phosphate buffer, the Soret band of the "preaggregate **A**" appears at 25 770 cm^{-1} (Figure 6a). This band is blue-shifted by 1100–1200 cm^{-1} from the band of aggregate **A** of the other porphyrins. We believe that this shift is caused by a higher number of porphyrin units in the "preaggregate **A**" of **P**₈ rather than by a lower distance r between the porphyrin planes in the respective aggregate (see eq 1). Monomerization of a **P**₈ solution by heating it to 85 $^{\circ}$ C (Figure 6b) followed by cooling it to 25 $^{\circ}$ C (Figure 6c) led to the formation of aggregate **A** with a position of the Soret band similar to found for porphyrins **P**₂, **P**₃, **P**₆, and **P**₉–**P**₁₄. In other words, the larger "preaggregate **A**" becomes, after being heated and cooled, the typical aggregate **A** exhibits the usual position of the Soret band and size of the aggregate.

The narrow, red-shifted Soret band of **C** corresponds to J-aggregates characterized by the angle α close to 0° , and a side-to-side arrangement of the porphyrin units. The Soret band of aggregate **B** exhibits a smaller red shift when compared to aggregate **C**. Most likely, aggregate **B** has a loose structure composed of J-dimers and short oligomers interacting with each other before the higher degree of organization is reached. A similar model was suggested to explain the spectroscopic behavior of cyanine dyes.³⁴

In pure J-aggregates, particularly in aggregate **C**, the resulting shift $\Delta\nu$ is not defined only by interaction between

neighboring porphyrin units, as described by eq 1, but also by a coupling of the tightly packed molecular transition dipoles. The coupling of the transition dipoles leads to the formation of a delocalized excitonic state through the coherent excitation of a number of monomers. The delocalized excitonic state is believed to migrate over large distances (hundreds of nanometers) within the J-aggregate through the transfer mechanism described as "hopping" of the exciton along the aggregate.³⁸ The theory³⁸ predicts that the width of the absorption band of the pure J-aggregate is narrower than that of the monomer by a factor of $N_{\text{eff}}^{1/2}$, where N_{eff} is the average number of porphyrin units in direct communication. The value of N_{eff} is different from the overall number of porphyrin units N in an aggregate that can be very high according to RLS experiments (Figure 2d). From our experimental data we calculated values of $N_{\text{eff}} \sim 2$ –4 for tetra- and tricationic porphyrins. The values of N_{eff} vary with the porphyrin substitution and a concentration of NaCl.

Broadening of the Soret bands of aggregates **A**, **B**, and **C** depends on the increased degree of the nonpolar character of the porphyrins, with tetracationic porphyrins being the least and dicationic being the most nonpolar. The occurrence of the larger nonpolar domains allows for increase in disordered arrangement of the porphyrins in the aggregates reflected by larger bandwidths of the Soret bands of aggregates (compare Figure 4a for tricationic **P**₅ and Figure 4b for dicationic **P**₆).

For further discussion on porphyrin aggregation, one can assume that the aggregate structure is not affected by peripheral substituents. Then the porphyrins may be treated as two independent parts, i.e., the tetraphenylporphyrin chromophore and the cationic substituent **S**. This is a plausible assumption because the substituent **S** is separated from the tetraphenylporphyrin by the methylene bridge ($-\text{CH}_2-$) (Figure 1C). Because of this insulation, the substituents have a minimal effect on the π -electron system of the porphyrin chromophore. One can also assume that self-aggregation is controlled mainly by electrostatic forces due to a high molecular polarizability of the porphyrin ring (38.7 \AA^3)³⁹ and the presence of positively charged groups **S**. The ability of porphyrins to form aggregates depends on charge–dipole and dipole–dipole interactions. The induced dipole corresponds to the mean value of polarizability α of both the substituents and the porphyrin chromophore. The magnitude of the permanent dipole is given by the dipole moments μ of the porphyrin. Electrostatic interactions are also proportional to the interporphyrin distance r^{-n} ($n \geq 2$) and a geometrical arrangement.^{40,41}

For the calculation of α , we have used the methyl–**S** fragment, and for the calculation of μ we have used the benzyl–**S** fragment ($\text{Ph}-\text{CH}_2-\text{S}$) (Table 2). This model can predict the aggregation behavior based on the calculated values α and μ for porphyrins bearing trimethylammonium, trimethylphosphonium, pyridinium, dimethylphenylphosphonium, and triphenylphosphonium substituents. The polarizability α increases in the following order: **S**₁ (trimethylammonium, **P**₁) < **S**₃ (trimethylphosphonium, **P**₇) < **S**₂ (pyridinium, **P**₄) < **S**₄ (dimethylphenylphosphonium, **P**₈) < **S**₅ (triphenylphosphonium,



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Table 2. Mean Polarizabilities α of the Model S-CH₃ Compounds and Dipole Moments μ of the Substituents S-CH₂-Phenyl Calculated by the PM3 Method with Respect to the COSMO Solvation Model

S	α [Å ³]	μ [Debye]	S	α [Å ³]	μ [Debye]
S ₁ N ⁺ (CH ₃) ₃	5.2	8.8	S ₅ P ⁺ (Ph) ₃	25.0	3.6
S ₂ 	7.9	7.5	S ₆ P ⁺ (<i>n</i> -butyl) ₃	16.3	4.8
S ₃ P ⁺ (CH ₃) ₃	6.5	10.0	S ₇ S ⁺ (CH ₃) ₂	5.8	9.9
S ₄ P ⁺ (CH ₃) ₂ Ph	12.4	3.5	S ₈ 	6.5	17.3

P₉) (Table 2). The tendency toward self-aggregation as shown in the case of tetracationic porphyrins does not entirely follow the order of the polarizability α . In fact, porphyrin **P₇** bearing trimethylphosphonium moieties S₃ aggregates somewhat more than porphyrin **P₄** with the pyridinium substituents S₂. This fact is explained by a significantly higher dipole moment μ of trimethylphosphonium S₃. The calculated values of α and μ for tetracationic porphyrins provide a good tool for estimating the aggregation properties.

The investigation of tetracationic porphyrins **P₁₂–P₁₄** revealed certain exceptions to the proposed model. Consideration of other parameters including charge distribution, flexibility, steric factors, or a capability to form hydrogen bonds may be essential for correct understanding of self-aggregation and physical–chemical properties of **P₁₂–P₁₄** in an aqueous solution. The London dispersion forces contribute to aggregation of porphyrins with a longer hydrophobic chain. Specifically, the porphyrin **P₁₂** bearing nonpolar *n*-butyl groups of tri(*n*-butyl)phosphonium displays a broad and unresolved Soret band compared to well-resolved bands of aggregates of triphenylphosphonium porphyrin **P₉**. Here, aggregation may be augmented by repulsion between the hydrophobic *n*-butyl and the solvent, or by a hydrophobic interaction of *n*-butyl chains similar to the behavior of hydrophobic chains of micelle constituents.⁴²

The calculated polarizability of the dimethylsulfonium substituent S₇ in **P₁₃** is comparable with those of **P₁**, **P₄**, and **P₇** containing trimethylammonium, pyridinium, and trimethylphosphonium groups that are largely monomeric in aqueous solutions, in contrast to **P₁₃**, which forms strong aggregates. We explain this behavior by dimethylsulfonium substituent S₇ being relatively small, which could enable closer contacts of cationic substituents and the porphyrin planes. By the same token, the small substituent

S₇ allows decrease of the distance *r* between the porphyrin units, thus inducing considerable negative charge on the porphyrin ring. Redistribution of the charge could also induce a deviation from our simple electrostatic interaction based model. A similar perspective may provide an insight into the strong tendency of isothiuronium porphyrin **P₁₄** to form extended aggregates. Here, we note that the nature of the isothiuronium substituent may give rise to additional effects that support aggregation of this compound. Such effects may include multiple hydrogen bonding and a formation of salt bridges.

Conclusion

A comprehensive study describing the aggregation properties of the unique set of *meso*-tetratolylporphyrins with various cationic substituents of lipophilic nature such as phosphonium, ammonium, pyridinium, sulfonium, and isothiuronium is presented. Particularly, the porphyrins bearing phosphonium-type substituents encompass a wide variety of aggregation behavior, ranging from predominantly monomeric to extended aggregates. The exciton point–dipole theory was successfully used to predict the position of the aggregate bands in the absorption spectra.

The tendency toward aggregation as well as the relative abundance of various types of aggregates depends on the ionic strength controlled mainly by the concentration of NaCl, and temperature changes. Particularly, the latter factor has a dramatic and unexpected effect on the relative distribution of the aggregate mixture. In general, the preferred structure formed from temperature-induced aggregation is the J-aggregate (**C**) with a parallel arrangement of porphyrin units, which is associated with the narrow, red-shifted Soret band. The formation of the J-aggregate **C** is enhanced by increased high ionic strength. As expected, the di- and tricationic porphyrins with extended hydrophobic domains aggregate more extensively compared to their tetracationic congeners while displaying broader Soret bands.

The formation of aggregates of cationic tetratolylporphyrins is controlled by electrostatic and hydrophobic interactions. The model based on electrostatic interactions was applied to the prediction of aggregation behavior of porphyrin derivatives bearing various positively charged substituents. Particularly the trimethylammonium, trimethylphosphonium, pyridinium, dimethylphenylphosphonium, and triphenylphosphonium substituents showed very good agreement with the theoretical model.

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