Propagation of chirality from gemini surfactants to porphyrin/surfactant heteroaggregates: transcription of the stereochemical information into an organizational feature

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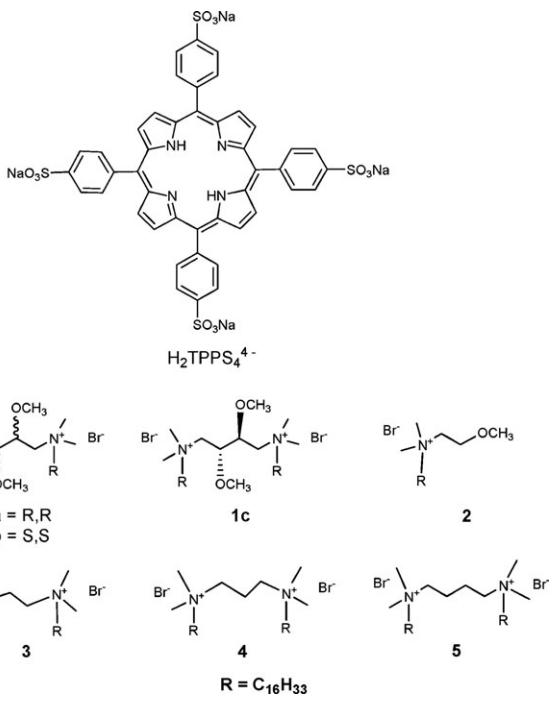
The interaction of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin with the chiral gemini surfactants (2*R*,3*R*)- and (2*S*,3*S*)-2,3-dimethoxy-1,4-bis(*N*-hexadecyl-*N*,*N*-dimethylammonium)butane bromide gives, below the critical micellar concentration, porphyrin/surfactant heteroaggregates of defined stoichiometry, where the dye molecules have a column-packed, H-type arrangement. The results of a CD investigation suggest that the gemini structure controls both the chirality of the porphyrin-surfactant unit and the chiral morphology of H-type aggregates.

Introduction

The mechanisms of propagation of asymmetry from biomolecules to the level of complex biological systems, such as plants and animals, have yet to be clarified, though elegant investigations have been carried out on this topic and some mechanism hypotheses proposed.[1]

The interactions of ionic surfactants with dyes of opposite charge give, under certain conditions, the formation of dye-surfactant heteroaggregates.[2–4] Recently, we reported the propagation of asymmetry from chiral cationic surfactants to porphyrin-surfactant heteroaggregates of defined stoichiometry.[2] We have found that in heteroaggregates formed by non-chiral, water soluble 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin, $H_2TPPS_4^{4-}$, and certain chiral cationic surfactants derived from benzylamine and ephedrine, the asymmetry of the surfactant is translated to the aggregates *via* electrostatic and hydrophobic interactions. Such heteroaggregates are good models to investigate the propagation of asymmetry from molecules to complex systems.

Here, we report about the heteroaggregates formed in water by the tetrasodium salt of $H_2TPPS_4^{4-}$ and the enantiomeric gemini surfactants (2*R*,3*R*)- and (2*S*,3*S*)-2,3-dimethoxy-1,4-bis(*N*-hexadecyl-*N*,*N*-dimethylammonium)butane bromide, **1a** and **1b** (Scheme 1). Comparing the heteroaggregates formed by $H_2TPPS_4^{4-}$ with the non-chiral single head surfactant *N*-(2-methoxyethyl)-*N*,*N*-dimethylhexadecan-1-ammonium bromide (**2**) and the non-chiral gemini surfactants (2*R*,3*S*)-2,3-dimethoxy-1,4-bis(*N*-hexadecyl-*N*,*N*-dimethylammonium)-butane bromide (**1c**), 1,2-bis(*N*-hexadecyl-*N*,*N*-dimethylammonium)ethane bromide (**3**), 1,3-bis(*N*-hexadecyl-*N*,*N*-dimethylammonium)propane bromide (**4**) and 1,4-bis(*N*-hexadecyl-*N*,*N*-dimethylammonium)butane bromide (**5**) gives important information on the role of the spacer, of its stereochemistry and length on the translation of the stereochemical information from the surfactant to the heteroaggregates.



Scheme 1

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Results and discussion

Interaction of $H_2TPPS_4^{4-}$ with chiral gemini surfactants 1a and 1b

UV-vis and fluorescence experiments. Investigations concerning the chiral gemini surfactants were carried out at $[H_2TPPS_4^{4-}] = 1$ μM and **[1a(b)]**/$[H_2TPPS_4^{4-}]$ ratios ranging between 1 : 1 and 100 : 1, *i.e.* at concentrations of surfactant ranging from below to above the critical micellar concentration (cmc) of **1a(b)**, 6.9×10^{-5} M.[5] From here onwards, **1** will refer either to **1a** or **1b**. UV-vis spectra at characteristic [**1**]/[porphyrin] ratios are shown in Fig. 1. The presence of the surfactant strongly affects the Soret and Q-band transitions with respect to the absorption spectrum of the porphyrin in water (dashed line in Fig. 1), both below and above the cmc. At [**1**]/$[H_2TPPS_4^{4-}]$ = 2 : 1, the Soret band of the monomeric porphyrin (413 nm) shows a hypo- and hypsochromic effect towards the broad non-symmetric band, with an absorption maximum at 404 nm (Fig. 1a, solid line). Furthermore, the Q-bands show a ~18 nm blue shift. Such spectral changes must be ascribed to the formation of porphyrin-surfactant heteroaggregates.[2–4] The hypsochromic shift of the Soret band is the signature of H-aggregates, *i.e.* a face-to-face or stacked geometrical arrangement of porphyrins.[6] Therefore, the UV-vis spectrum indicates that the porphyrin heteroaggregates formed below the cmc and at low [surfactant]/[porphyrin] ratios are in a column-like arrangement. In contrast at [**1**]/$[H_2TPPS_4^{4-}]$ = 100 : 1 (*i.e.* above the cmc of **1**), the Soret band centered at 417 nm (Fig. 1b, solid line) must be ascribed to the monomeric porphyrin included in the cationic micellar aggregates, as reported previously for monocationic surfactants.[2,3] The spectra of these samples remained unchanged for weeks, by analogy to what was observed in the case of the interaction of the same porphyrin with chiral single head surfactants,[2] thus demonstrating the stability of both species (heteroaggregates and micellized porphyrin).

The porphyrin H-aggregation also occurred at concentrations of surfactants lower than 2 μM, as shown by the shoulder in the Soret band (413 nm) of the monomeric porphyrin; see, for example, the UV-vis spectrum of the sample at [**1**]/$[H_2TPPS_4^{4-}]$ = 1 : 1 reported in Fig. 2a (solid line). On the other hand, the spectrum at [**1**]/$[H_2TPPS_4^{4-}]$ = 4 : 1 shows features of both heteroaggregates (404 nm) and the micellized monomeric porphyrin (Fig. 2b, solid line). However, in this case, the concentration of surfactant was 4 μM, *i.e.* one order of magnitude below the expected cmc; therefore, the obtained results could be ascribed either to the formation of micelles due to a decrease of cmc induced by the presence of the porphyrin (as already reported for other anionic organic solutes[7]) or to the formation of pre-micellar aggregates, a peculiarity of gemini surfactants,[8] where the porphyrin is included without a definite organization. The porphyrin included in these pre-micellar aggregates would show an absorption spectrum similar to that of the micellized porphyrin. Interestingly, in this case, the shape of the UV-vis spectrum changes as a function of time (Fig. 2b, dotted line), showing a decrease of the component at 417 nm and an increase of the component at 404 nm, *i.e.* the pre-micellar aggregates evolve into stable heteroaggregates, where the porphyrin is organized in H-aggregates.

Fluorescence spectroscopy experiments confirmed the presence of different species in solution, depending on the [**1**]/$[H_2TPPS_4^{4-}]$ ratio (Fig. 3).

At [**1**]/$[H_2TPPS_4^{4-}]$ = 2 : 1, the emission spectrum shows a decrease in quantum yield and a significant red shift of the emission maxima (662 nm and 725 nm) with respect to the porphyrin in water (644 and 704 nm, dashed line), in agreement with the formation of porphyrin aggregates. Moreover, the lack of dependence of the shape and position of the emission band upon the excitation wavelength indicates that the H-aggregate is the predominant species in solution at this [surfactant]/[porphyrin] ratio. At [**1**]/$[H_2TPPS_4^{4-}]$ = 100 : 1, *i.e.* for the micellized porphyrin, we observed an increase of the quantum yield, which indicates that the porphyrin is in a lipophilic medium, and a red shift of the emission bands with respect to those of the free porphyrin in water (though blue-shifted with respect to the spectrum of the 2 : 1 sample). At [**1**]/$[H_2TPPS_4^{4-}]$ = 1 : 1, the intensity of the emission bands and the wavelengths of the emission maxima depended upon the selected excitation wavelength, confirming the presence of the free porphyrin and the H-ordered porphyrin.

At [**1**]/$[H_2TPPS_4^{4-}]$ = 4 : 1, the dependence of the intensity and wavelength of the emission maxima on the excitation wavelength confirmed that the two peaks in the absorption spectrum (404 and 416 nm) were due to two different species,

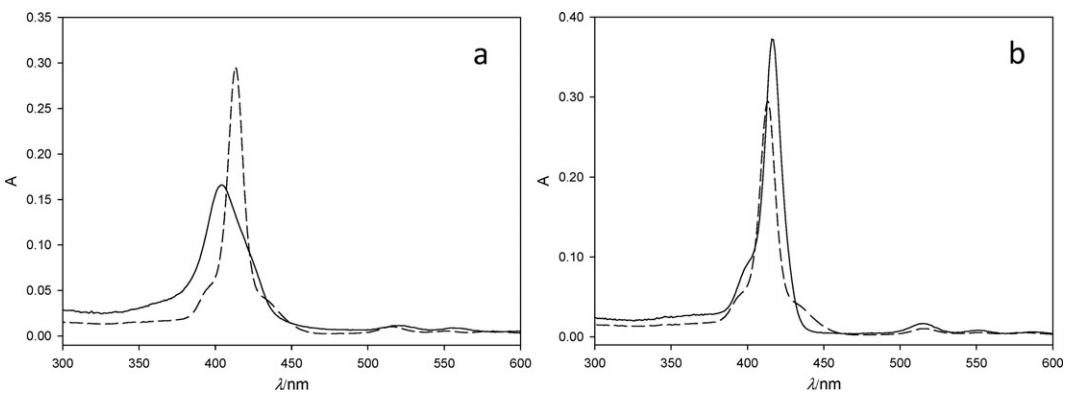

Fig. 1 The Soret region of the absorption spectrum of 1 μM $H_2TPPS_4^{4-}$ in the presence of surfactant **1a** (solid line) at [surfactant]/[porphyrin] ratios of (a) 2 : 1 and (b) 100 : 1, compared with the spectrum of the porphyrin in water (dashed line).

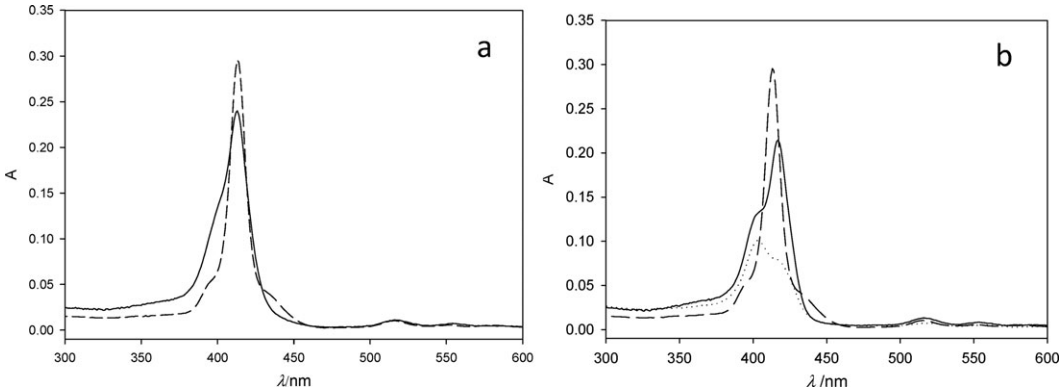

Fig. 2 The Soret region of the absorption spectrum of 1 μM $H_2TPPS_4^{4-}$ in the presence of surfactant **1a** at [surfactant]/[porphyrin] ratios of (a) 1 : 1 (—), and (b) 4 : 1 at t = 0 (—) and t = 48 h (···) compared with the spectrum of the porphyrin in water (---).

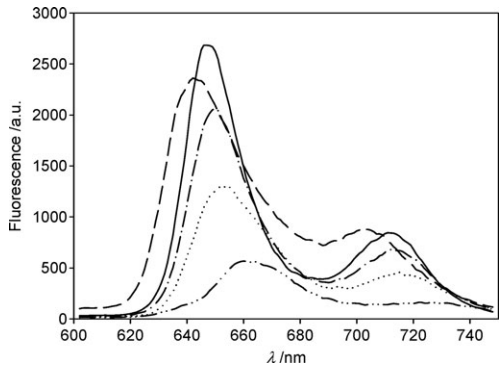

Fig. 3 Fluorescence emission spectra of 1 μM $H_2TPPS_4^{4-}$ in water (---), and in the presence of surfactant **1a** at various [surfactant]/[porphyrin] ratios and excitation wavelengths: at 2 : 1, λ_{ex} = 404 nm (dash-dot-dot line), at 4 : 1 and λ_{ex} = 404 nm (···), at 4 : 1 and λ_{ex} = 416 nm (---), and at 100 : 1 and λ_{ex} = 416 nm (—).

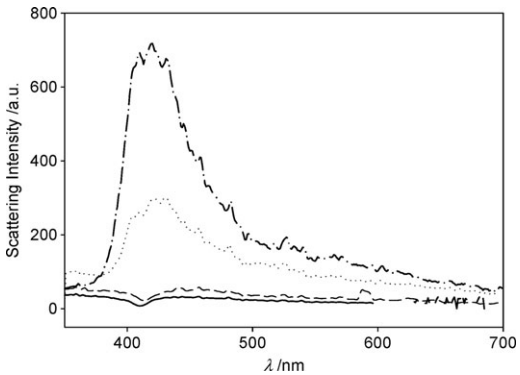

Fig. 4 RLS profiles of 1 μM $H_2TPPS_4^{4-}$ in the presence of surfactant **1a** at [surfactant]/[porphyrin] ratios of 2 : 1 (---), 4 : 1 (···) and 10 : 1 (---), compared with the RLS profile of the porphyrin in water (—).

i.e. heteroaggregates with H-organized porphyrins and pre-micellar species.

Resonance light scattering (RLS) spectra[9] confirmed the range of [**1**]/[$H_2TPPS_4^{4-}$] ratios where an extended stacking of porphyrin molecules occurs. The RLS spectra (Fig. 4) show that the blue-shifted Soret band at 404 nm corresponds to a strongly coupled excitonic absorption;[10] in fact, at [**1**]/[$H_2TPPS_4^{4-}$] ratios between 1 : 1 and 4 : 1, the RLS spectra show an intense scattering signal, which is the signature of a strongly coupled excitonic state.

At [**1**]/[$H_2TPPS_4^{4-}$] > 10 : 1 (*i.e.* at [**1**] > cmc), in correspondence with the micellized porphyrin, no enhanced scattering is observed in the Soret region (as well as for the free monomeric porphyrin), and a scarcely visible minimum appears as a result of the inner filter effect by self-absorption.[9]

In conclusion, the UV-vis, fluorescence and RLS spectra indicate that the predominant species at [**1**]/[$H_2TPPS_4^{4-}$] above the cmc is the monomeric porphyrin included in lipophilic sites of surfactant micelles. In the [**1**]/[$H_2TPPS_4^{4-}$] range between 1 : 1 and 4 : 1, a heteroaggregate system is formed that shows H-type aggregation of the porphyrin with strongly coupled excitonic states. At surfactant concentrations below the cmc and intermediate [**1**]/[$H_2TPPS_4^{4-}$] ratios (*e.g.* 4 : 1), pre-micellar species are formed where the porphyrin chromophore is embedded in a lipophilic medium similar to that found in micellar aggregates.

CD experiments. CD investigations were carried out at [$H_2TPPS_4^{4-}$] = 10 μM to ensure a reasonable absorbance value.

Experiments carried out at [**1**] > cmc showed that the monomeric porphyrin included in the micellar aggregates is CD silent. On the other hand, heteroaggregates formed with surfactant **1a** and **1b** at [**1**]/[$H_2TPPS_4^{4-}$] = 2 : 1 show CD bands in the Soret region (Fig. 5) that are enantiomeric, as expected, and feature a shape that suggests the superimposition of different contributions.‡ The physical origin of the CD signal can be ascribed to an enantiomeric excess of a chiral conformation of the porphyrin stabilized by its interaction with the chiral surfactant, as suggested previously in the case of single head surfactants,[2] and/or to a chiral organization of the porphyrin chromophore induced by the chiral surfactant. Note that both for gemini surfactants **1** and single head surfactants,[2] the CD signal occurs in correspondence with the detection of an RLS signal. Therefore, a contribution to the CD spectrum could be due to an intrinsically chiral exciton,

‡ None of the samples showed linear dichroism signals, meaning that the obtained spectra must be totally attributable to real chiral CD absorptions.

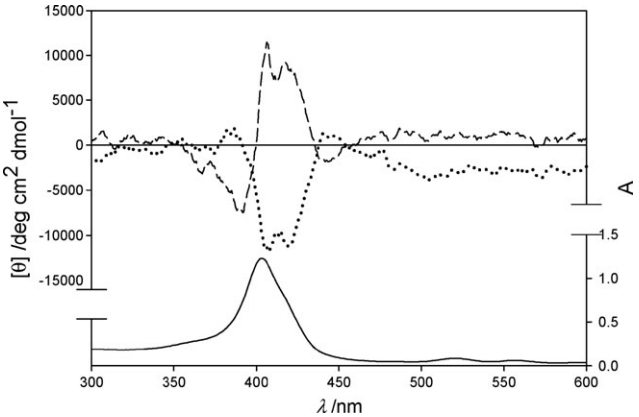

Fig. 5 The CD spectrum of 10 μM $H_2TPPS_4^{4-}$ at a [surfactant]/[porphyrin] ratio of 2 : 1 in the presence of surfactant **1a** (---) and **1b** (···) superimposed over the UV-vis spectrum (—).

i.e., to supramolecular chirality. In the results reported here, it is probably the consequence of a helical arrangement of the porphyrin H-aggregate columns, whose chiral bias would be induced by the chiral surfactant bound and organized around the porphyrin columns by electrostatic and hydrophobic interactions. Note that the induction of an intrinsically chiral exciton can occur only in the presence of mutual porphyrin interactions, *i.e.* at low [surfactant]/[porphyrin] ratios, whereas high [surfactant]/[porphyrin] ratios suppress porphyrin homoassociation. It follows that a crucial parameter to clarify and identify the organization of surfactant/porphyrin heteroaggregates is their stoichiometry, which is discussed later.

The role of the spacer of the gemini surfactant on the porphyrin arrangement within the heteroaggregate

An analogous investigation was carried out on aqueous solutions of the non-chiral gemini surfactants **1c**, **3–5**, and on the non-chiral single head surfactant **2**, to clarify the role of the stereochemistry of the spacer, its length and the covalent link between the head groups on the interactions involved in surfactant-porphyrin systems and, in particular, on the organization of the heteroaggregates.

Spectroscopic investigations (UV-vis and fluorescence experiments) of the interaction between $H_2TPPS_4^{4-}$ and gemini surfactant **1c**, the *meso* diastereomer of surfactants **1**, was carried out in the same conditions as those used for **1a** and **1b**, with $[H_2TPPS_4^{4-}]$ = 1 μM and $[\mathbf{1c}]/[H_2TPPS_4^{4-}]$ ratios ranging between 1 : 1 and 100 : 1. The results were analogous to those obtained in the presence of surfactants **1a(b)**, with the formation of H-heteroaggregates as the major species in solution at $[\mathbf{1c}]/[H_2TPPS_4^{4-}]$ = 2 : 1, the inclusion of the monomeric porphyrin in micellar aggregates at high [surfactant]/[porphyrin] ratios, and the simultaneous detection of heteroaggregates and pre-micellar aggregates at intermediate ratios. These results imply that the stereochemistry of the spacer does not influence the behavior of the surfactant-porphyrin system.

Note that the heteroaggregates of **1c** are CD silent, ruling out any contribution to the CD spectrum due to spontaneous symmetry breaking, as in the case of the J-aggregates of diprotonated amphiphilic porphyrins.[11]

The interaction of $H_2TPPS_4^{4-}$ with gemini surfactants **3–5** was explored under the same experimental conditions as those for surfactants **1**. In general, the results obtained with **3**, **4** and **5** did not differ significantly from those obtained with surfactants **1**. In fact, depending on the concentration, we observed the formation of porphyrin-surfactant heteroaggregates with H-aggregate porphyrins, and porphyrins included in surfactant micellar and pre-micellar aggregates. The differences between the effects of the three surfactants concerned the abundances of the different species at the various [surfactant]/$[H_2TPPS_4^{4-}]$ ratios (Fig. 6).

In the case of surfactant **3**, for example, the presence of the heteroaggregates is still relevant at $[\mathbf{3}]/[H_2TPPS_4^{4-}]$ = 10 : 1 (Fig. 6a), whereas in the case of surfactants **4** (Fig. 6b) and **5** (Fig. 6c), the major species at the same concentration is the porphyrin included in surfactant aggregates, as seen for surfactants **1**.

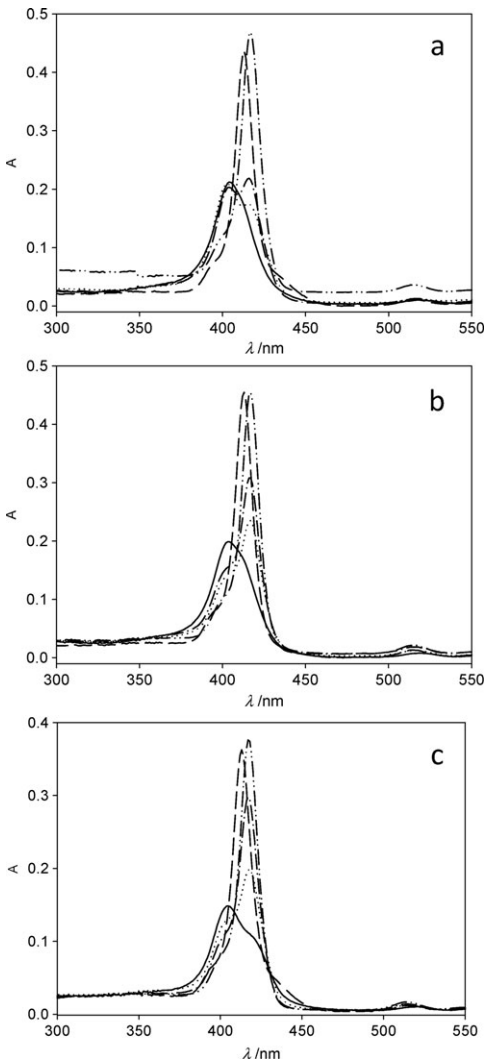

Fig. 6 The Soret region of the absorption spectrum of 1 μM $H_2TPPS_4^{4-}$ in the presence of surfactant (a) **3**, (b) **4** and (c) **5** at [surfactant]/[porphyrin] ratios of 2 : 1 (—), 4 : 1 (···), 10 : 1 (---) and 100 : 1 (dash-dot-dot line) compared with the spectrum of porphyrin in water (---).

Because the cmcs of gemini surfactants **3–5** are very similar,[12] their different tendencies to form either heteroaggregates or micelles are probably driven by different charge repulsions between the head groups and/or by differing entropy gains.

Finally, we explored by UV-vis and fluorescence experiments the interaction of $H_2TPPS_4^{4-}$ with single head surfactant **2**, the monomer of gemini surfactants **1**. In this case, we also observed the formation of surfactant-porphyrin heteroaggregates, with H-type porphyrin organization, and micellized porphyrin, depending on the concentration. However, for **2**, the formation of H-aggregates was observed at higher [surfactant]/[porphyrin] ratios with respect to the gemini surfactants, with the highest abundance at a 10 : 1 ratio.

Note that the formation of H-type heteroaggregates was also reported for the interaction of cetyltrimethylammonium bromide (CTAB) with $H_2TPPS_4^{4-}$ at [CTAB]/[$H_2TPPS_4^{4-}$] = 4 : 1 (*i.e.* at charge neutrality).[3] The large concentration difference between **2** and CTAB at which the formation of heteroaggregates was observed can probably be ascribed to the screening of the head charge by the methoxyethyl group, which disfavours the electrostatic interaction with the porphyrin.§

Recently, we have reported CD active heteroaggregates formed by single head cationic surfactants derived from benzylamine or ephedrine and $H_2TPPS_4^{4-}$ at a stoichiometry corresponding to an excess of negative charge (3 : 1).[2] The results reported here, as well as those reported previously,[2,3] raise a question about the charge features of porphyrin-surfactant heteroaggregates, which are discussed below.

Job plots of $H_2TPPS_4^{4-}$ with monocationic CTAB and dicationic 1

Two procedures were used to evaluate whether porphyrin-surfactant heteroaggregates are formed at a stoichiometry corresponding to charge neutralization or to an excess of electrical charge. The formation of heteroaggregates at charge neutrality was suggested, in the case of CTAB, by titration experiments,[3] whereas the formation of negatively-charged examples, in the case of single head chiral surfactants, was demonstrated by the continuous variation method (Job plot).[2]

Titration experiments generally only give an estimation of the exact stoichiometry of a complex. In contrast, the continuous variation method[13] gives its exact stoichiometry when the species in solution are only the monomer and the complex. Therefore, we performed a Job plot analysis on the $H_2TPPS_4^{4-}$/CTAB system.

The Job plot relative to CTAB measured at the Soret band of the $H_2TPPS_4^{4-}$ monomer (413 nm), reported in Fig. 7a, shows a minimum absorption at 4 : 1, in agreement with the titration experiments reported previously.[3] However, the Job plot measured at the maximum absorption of the H-aggregate Soret band (404 nm) shows two minima at the 5 : 1 and 3 : 1 ratios (Fig. 7b), thus suggesting that the decrease in monomer absorption (413 nm) is due to the formation of two different types of heteroaggregates with H-organized porphyrins (404 nm), one mono-anionic (3 : 1) and the other mono-cationic (5 : 1). Note that a decrease in absorbance of the H-aggregate Soret band (404 nm) could also be due to the formation of larger H-aggregates, characterized by a lower extinction coefficient.

In the case of gemini surfactants **1** the results obtained from Job plots can only be considered an approximation because, even below the cmc, different equilibria occur in solution that control the formation of H-type heteroaggregates and the inclusion of the porphyrin in pre-micellar aggregates. However, they give significant information that could not be obtained from titration experiments.

The Job plots relative to surfactants **1** indicate that the heteroaggregates formed with $H_2TPPS_4^{4-}$ are not characterized by the charge neutralization stoichiometry 2 : 1, but feature an excess of positive charge. Actually, the measurement of the monomer absorption (413 nm) gives a minimum at a 7 : 2 ratio, and also a local minimum at charge neutrality (2 : 1 stoichiometry), as shown in Fig. 8a. However, the Job plot at the maximum absorption of the heteroaggregates (404 nm), reported in Fig. 8b, gives a clear minimum at 7 : 2 and a maximum at 3 : 1 (no minimum or maximum at 2 : 1). The detection of a maximum or a minimum in the Job plot at 404 nm can be explained by assuming that the Soret band corresponds to heteroaggregates characterized by non-identical optical properties, *i.e.* differences in the absorption (apparent absorption coefficient) and differences in the RLS (exciton coherence length). Therefore, in the heteroaggregate, the porphyrin column packing is determined by an excess of positive charge.

Conclusion

The results we have obtained in this investigation demonstrate the crucial role of the structure of the cationic head group on the interaction with the charged porphyrin and on the organization of the heteroaggregates. In fact, we have shown that the molecular structure of the cationic surfactant can control the [surfactant]/[porphyrin] ratio necessary to form the heteroaggregates or include the monomeric porphyrin inside pre-micellar or micellar aggregates.

In agreement with our previous results,[2] we have found that an excess of charge is necessary to form stable heteroaggregates. Actually, because both components (porphyrin and surfactant) are amphiphiles, charge neutralization would not allow interaction of the polar groups with water, thus yielding precipitation of a neutral complex.

The results we obtained investigating the propagation of asymmetry show that the chirality of the surfactant is propagated to porphyrin/surfactant heteroaggregates, whereas it is not sensed by monomeric porphyrins included in micelles. In general, the results, relative to the transfer of chirality, are similar to those obtained with the single head surfactants derived from methyl benzylamine and ephedrine. However, the complexity of the CD spectrum suggests that the gemini surfactant controls the aggregate structure at different size levels of the heteroaggregate. In fact, it controls both the chirality of the porphyrin-surfactant structural unit by stabilizing one of the enantiomeric forms of the porphyrin, where phenyl groups are tilted with respect to orthogonality (as hypothesized previously in the case of single head

§ Similar control would not work in the case of surfactants **1** because of conformational restraints due to the covalent link of the spacer. See also ref. 5.

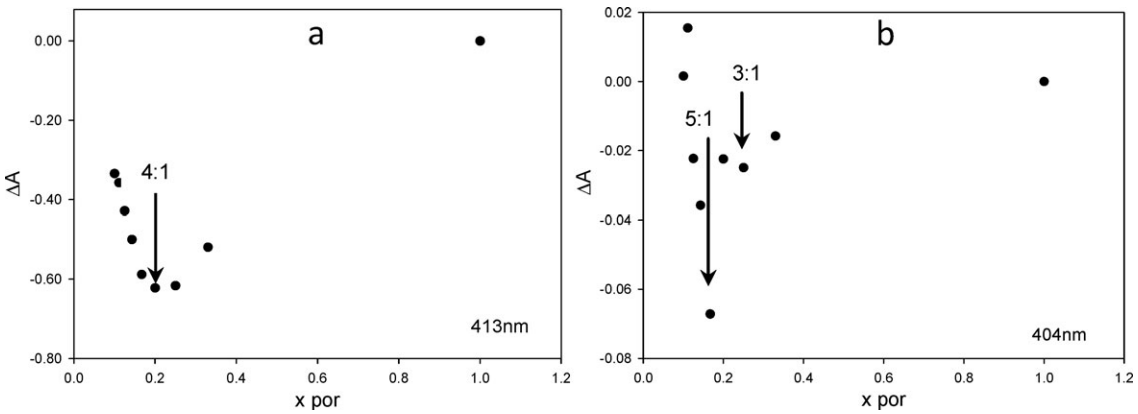

Fig. 7 Job plots for the interaction of $H_2TPPS_4^{4-}$ with CTAB obtained by plotting the corrected absorbance at (a) 413 nm and (b) 404 nm *vs.* porphyrin molar fraction (at a total concentration 10 μM).

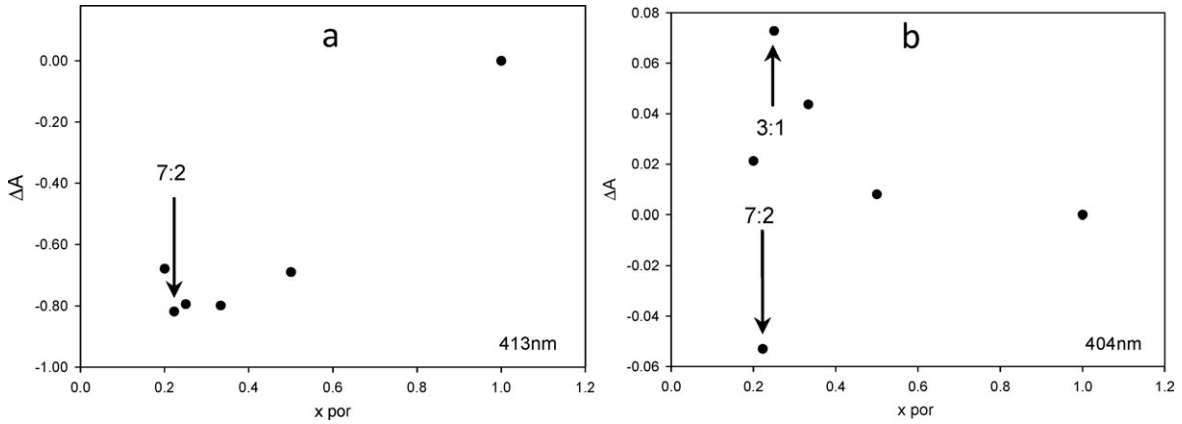

Fig. 8 Job plots for the interaction of $H_2TPPS_4^{4-}$ with gemini surfactant **1a** obtained by plotting the corrected absorbance at (a) 413 nm and (b) 404 nm *vs.* porphyrin molar fraction (at a total concentration 10 μM).

surfactants[2]) and the supramolecular chirality of the porphyrin column packing (H-aggregate). In other words, the gemini structure probably controls the propagation of stereochemical information towards a higher level of complexity in the hierarchical self-organization.

Experimental section

Preparation of the tetrasodium salt of $H_2TPPS_4^{4-}$

The synthesis of the tetrasodium salt of $H_2TPPS_4^{4-}$ was performed as previously described by the sulfonation of pure *meso*-tetrakis(phenyl)porphyrin. In order to avoid contamination by counterions other than sodium, the neutralization was performed using analytical grade NaOH and Na_2CO_3. The purification of $H_2TPPS_4^{4-}$ implies reverse HPLC chromatography and the final elimination of any inorganic salt impurities by filtration through MCI Gel CHP20P (Supelco) (see details in the supplementary information of ref. 14).

Preparation of gemini surfactants.

Gemini surfactants **1** were prepared as previously described.[5] Gemini surfactants **2–5** were prepared by quaternization of the corresponding commercial amines according to a previously reported procedure.[5]

Samples preparation

Samples for UV-vis, fluorescence and CD experiments were prepared as follows. Aliquots of a 0.1 mM porphyrin stock solution were added to a known amount of water (to obtain the necessary porphyrin concentration), followed by the addition of a known amount of a surfactant stock solution (0.1–0.5 mM) in order to obtain the required porphyrin/surfactant ratio.

The concentration of the porphyrin stock solutions was checked by UV-vis spectroscopy (ε) 480.000 mol^{-1} L cm^{-1} at 413 nm).

Water of Millipore Q quality (18.2 MΩ cm) was used for the preparation of all aqueous solutions.

Spectroscopic studies

Spectra were recorded within 5–10 min of sample preparation (when not specified) in quartz cuvettes with a path length of 1 cm. Experiments were performed at 25 °C at spontaneous pH (pH 6.5–7.0).

UV-vis spectra were recorded on a Carey-300 UV-vis spectrophotometer.

Fluorescence experiments were performed on a Carey Eclipse fluorimeter.

Resonance light scattering measurements were performed on a Carey Eclipse fluorimeter by operating it in synchronous scanning mode, in which the excitation and emission monochromators are coupled to scan simultaneously.

Circular dichroism (CD) spectra were recorded on Jasco J-715 spectropolarimeters.

Job plot analysis

The stoichiometry of the porphyrin-surfactant heteroaggregate was determined by the method of continuous variation (Job's method plot analysis).[13] The total concentration of the two components (porphyrin and surfactant) was kept constant at 10 μM. The absorption spectra were recorded immediately after sample preparation.

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