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## COMMUNICATION

# Surfactant-induced chirality on reluctant aggregates of a chiral amphiphilic cationic (L)-proline-Zn(II)porphyrin conjugate in water

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**Self-assembly of a chiral amphiphilic Zn(II)porphyrin derivative in water gave CD silent species. If the aggregation process occurs in aqueous solutions of chiral surfactants, CD active species are formed with highly specific molecular recognition effect.**

The study of the formation of porphyrin aggregates characterised by supramolecular chirality is an important issue amenable to wide applications.<sup>1</sup> These architectures may be formed by the presence of chiral substituents on the periphery of the macrocycles that act as specific chiral effectors during the molecular recognition event.<sup>2</sup> The interaction of achiral porphyrin derivatives with chiral surfactants also offers a valuable tool for controlling the chirality and hence the chiroptical properties of the final assemblies. Recent studies indicate the crucial importance of the hydrophobic interaction on the efficiency of the transfer of chirality, from the monomers to the assembly.<sup>3, 4</sup>

Chart 1. Molecular structures of porphyrin and surfactants studied in this work.

We herein report our recent results on the effect of chiral surfactants in the aggregation of the chiral amphiphilic porphyrin derivative in water. The porphyrin used in the work is a Zn-tetraphenyl derivative functionalised by a cationic (L)-proline residue, ZnPL(+),<sup>5</sup> whereas the surfactants are the two amidic anionic derivative of a (L)- or (D)-proline ((L)- and (D)SDP; Chart 1).<sup>6</sup> The results have been compared with those obtained in the case of achiral sodium dodecylsulphate (SDS), a surfactant featuring cmc and aggregation number similar to SDP.<sup>7</sup>

We initially studied the aggregation properties of the title porphyrin in ethanol/water solvent mixtures in the absence of surfactants. In

pure ethanol the porphyrin is in monomeric form. The presence of water as a co-solvent fosters a specific self-recognition path, promoting the formation of extended J-type aggregates, featuring supramolecular chirality. The optimal solvent composition for high reproducibility of the results, has been found to be 25 % (v:v) ethanol/water. The process occurs with an initial fast decrease of the Soret band, which is complete during the sample preparation, followed by a slow evolution into a new J-band shifted at 450 nm (Fig. 1A).

Figure 1. (A) UV-Vis spectral changes observed in the aggregation of ZnPL(+) 2.5  $\mu$ M in EtOH/H<sub>2</sub>O 25:75 (v:v) at 298 K, and (B) corresponding CD spectra.

Interestingly, the corresponding CD spectra (Fig. 1B) show the gradual formation of a peculiar spectral pattern resulting from the superimposition of two bands; a more intense one at lower energy ( $\lambda_{\text{max}} = 450$  nm) with a -/+ sign, and a weaker band at higher energy ( $\lambda_{\text{max}} = 430$  nm) featuring a -/+ spectral profile in direct correspondence with the electronic spectra. This pattern, according to studies recently reported in the literature,<sup>8</sup> indicates the formation of porphyrin architectures with rod-like morphology, in which the J-aggregate species show excitonic coupling along preferential space directions.<sup>9</sup> It is important to remark that the CD spectral pattern shows great differences, with respect to the ones observed in the case of the free-base derivatives,<sup>2b,c,d</sup> indicating that the presence of the central Zn(II) ion should play a striking role in the self-recognition, likely by coordinative interaction with the amidic group of the proline residue of a vicinal porphyrin platform. The structures show high stability, as indicated by the constancy of the UV-Vis and CD spectral patterns over months of storage.

Conversely, when the aggregation occurs in pure water the process yields only species featuring broadened and marginally

red shifted UV-Vis bands and silent CD spectra, indicating the formation of random structures; no signals appear even after prolonged storage of the solutions (months).

On the other hand, interesting results have been obtained in aqueous solutions of chiral surfactants below their cmc,<sup>#</sup> in the range between  $1.0 \times 10^{-5}$  and  $1.0 \times 10^{-3}$  M, for both (L)- and (D)SDP. In the case of (L)SDP at the lowest concentrations ( $10^{-4}$  and  $10^{-5}$  M) the Soret band of the porphyrin is broad and centred at 429 nm. At  $10^{-3}$  M a shift up to 432 nm and an increase of the B-band intensity is observed, indicating the occurrence of interactions favoured at higher concentration of surfactant (Fig. 2A).

Figure 2. UV-Vis spectral changes (A), and corresponding CD plots (B) for the aggregation of ZnPL(+) 10  $\mu$ M in (L)SDP aqueous solutions at 0.01 (a), 0.1 (b) and 1.0 mM (c).

Interestingly, the corresponding CD spectra show coupled bisignated +/- bands, whose intensities increase by increasing the concentration of the surfactant (Fig. 2B). Remarkably, in the case of the solutions at  $1.0 \times 10^{-4}$  and  $1.0 \times 10^{-3}$  M, a slow evolution of the spectral UV-Vis patterns has been observed with time (e.g. broadening, decreased intensities, and further shift to 435 nm, during a week of storage). Corresponding CD spectra show a concomitant evolution with the appearance of complex +/-/+ and +/- features, at ca. 450 and 425 nm respectively (Fig. 3), with opposite signs with respect to those observed for the aggregates in EtOH/water, indicating the formation of fractal-type structures.<sup>9b</sup> The final intensities are highest in the case of the surfactant solution at  $10^{-3}$  M.

On the basis of the obtained results we may surmise a mechanistic frame in which in a fast initial step driven by electrostatic interactions, weakly chiral aggregate (type-I) are formed. This step is then followed by a slow molecular rearrangement likely governed by Van der Waals and dispersion forces with the hydrophobic hydrocarbon chains, to give fractal species (type-II aggregates).<sup>¶</sup> It is worth noting that alike type-I species have been observed in the case of both the (D)SDP enantiomer and achiral SDS, but without further evolution toward the formation of type-II structures (Fig. ESI\_1). This indicates that the type-I chirality should be triggered by the cationic (L)-prolinium residue of the macrocycle. The role of surfactants in the formation of these

Figure 3. CD spectra evolution of ZnPL(+) 10  $\mu$ M in (L)SDP aqueous solutions at  $1 \times 10^{-3}$  M.

species is likely that to keep separate the aromatic platforms primarily by electrostatic interaction, overwhelming the aspecific  $\pi$ - $\pi$  stacking, irrespectively of the chirality of the polar heads. A schematic picture of this phenomenon is reported in Scheme 1.

Scheme 1. Schematic drawing of heteroaggregates evolution in the conditions studied in the work. Surfactants and porphyrin counterions have been omitted for clarity.

The fact that the CD features are, although weaker, similar to those of the free-base macrocycles,<sup>2b-d</sup> may indicate a similar supramolecular arrangement, hence without the involvement of the Zn(II) ion. The further specific rearrangement toward type-II structures can be induced only in the case of the surfactant with (L)-proline functionality, likely mediated by the interaction with the hydrocarbon chains, which have been found to play a key role in the transmission and propagation of

the molecular information stored in the polar heads.<sup>3a, 3b, 6</sup> The fact that the effect is higher at higher (L)SDP concentration indicates and effect of stabilisation of the heteroaggregates.

Fluorescence and Resonance Light Scattering (RLS) spectroscopies gave further insights on the obtained results. Although the emission of ZnPL(+) in water is highly quenched with respect to that in ethanol (i.e. non aggregative conditions) by several order of magnitudes, the corresponding surfactant solutions still show appreciable emission intensities, with maxima at ca. 600 and 640 nm ( $\lambda_{exc} = 550$  nm; Fig. ESI 2A). Notably, the emission intensities increase with the concentration of the surfactants, indicating a reduced extent of self-quenching (i.e.  $\pi$ - $\pi$  stacking) upon interaction with the surfactant species. Moreover, as far as (L)SDP solutions are concerned, the emission intensities slowly decrease with time, confirming the molecular evolution of the species toward the formation of the chiral, organised heteroaggregates, in line with CD results. The corresponding excitation spectra ( $\lambda = 602$  nm; Fig. ESI 2B), gave further support, showing the gradual appearance with time of the "spiked" Soret band attributable to the rod-type heteroaggregates species. Conversely, the (D)-enantiomer showed only a mere broadening of the band with a much less defined shoulder on the "red side" of the Soret entanglement (see ESI\_Rev1). RLS experiments further corroborate the above described results (Fig. ESI\_3).<sup>10</sup> i) No RLS signals can be detected in non-aggregative conditions of the porphyrin, such as in ethanol or at surfactant concentration above cmc, i.e. in micellised form. ii) RLS spectra of aggregates in water are weaker (about one order of magnitude) with respect to spectra in (L)- or (D)-surfactants. iii) The signal intensities increase by increasing the concentration of the aqueous surfactant solutions, confirming the CD evidences that the formation of the heteroaggregates yields better organised systems, with more extended electronic coupling among the macrocycles. Striking evidence of the effect of the surfactants are finally given by Microscopy Fluorescence studies on drop casted solutions, showing heteroaggregates of different morphology, depending on the aggregation conditions. In the case of aggregates of type-II fractal structures are formed (Fig. 4A), whereas in the case of type-I structures, undefined layered material is formed (Fig. 4B and 4A-inset).

Figure 4. Fluorescence Microscopy images of ZnPL(+) 10  $\mu$ M/surfactant heteroaggregates. (A): (L)SDP 1.0 mM at equilibrium (type-II); Inset: freshly prepared sample (type-I). (B) (D)SDP 1.0 mM (type-I)

## Conclusions

In conclusion, the studies show a diastereoselective interaction of amphiphilic chiral porphyrin derivatives with chiral surfactants below the cmc. The interaction yields chiral heteroaggregated species, despite the reluctance of the macrocycles to form chiral assemblies in pure water. This should give important results on the effects that drive the transfer and propagation of the chirality from molecular to supramolecular level.

## Notes and references

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† Electronic Supplementary Information (ESI) available: experimental details, UV-Vis, Fluorescence, RLS spectra, and Microscopy Fluorescence studies. See DOI: 10.1039/b000000x/

‡ The cmc and aggregation number for both (L)- and (D)SDP are 9.6 mM and 46; for SDS the values are 8.3 mM and 65, respectively.

# In our case we have no evidence of the presence in solution of “premicellar aggregates”. We may surmise at this stage the occurrence of interaction, mainly electrostatic in nature, between porphyrins and surfactant monomers. Moreover, experiments carried out with surfactants above cmc (i.e. 0.10 M) showed no chiral induction. UV-Visible and Fluorescence Spectroscopy showed that the macrocycles are included in monomeric form. The species showed no induced CD effect. However, this is in striking contrast with that found in our precedent studies for the case of surfactants and porphyrin possessing the same stereogenic anionic proline moiety.<sup>21</sup> In that case the inclusion occurred with an efficient chirality transfer. This, once more, indicates the importance of a fine balance between the interaction involved in the molecular recognition.

¶ The fact that a clear band at 450 nm does not emerge from the broad Soret band, indicates the onset of an equilibrium between different aggregates, i.e. homo-, type-I, and type-II hetero-associates. CD evidences indicate a prevalence of the type-II species over the type-I ones. We do not know at this stage the exact extent of equilibria involved. Experiments based on time-resolved fluorescence spectroscopy are unfortunately hampered by the low emission intensities of the aggregates. However, fluorescence excitation spectra clearly show the presence of type-II species as emissive structures (see text).

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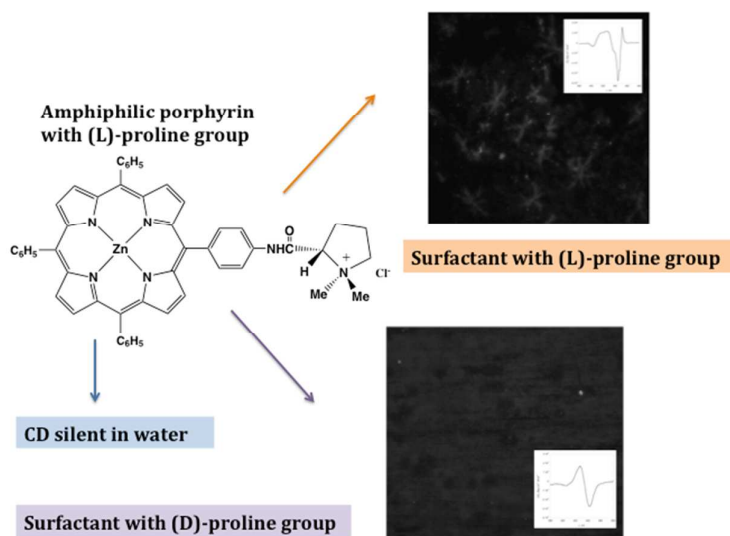
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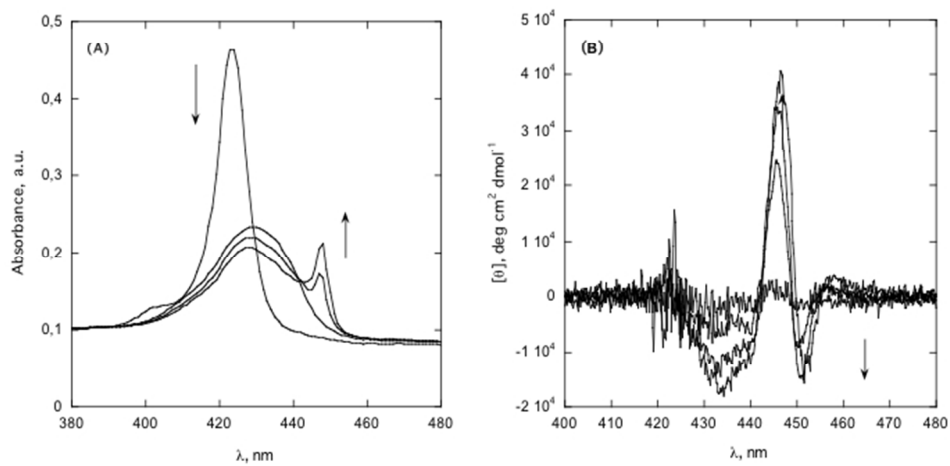
# Surfactant-induced chirality on reluctant aggregates of a chiral amphiphilic Zn(II)porphyrin derivative in water

Edoardo Simoncini,<sup>a</sup> Fabrizio Caroleo,<sup>a</sup> Francesca Ceccacci,<sup>b</sup> Giovanna Mancini,<sup>b</sup> Manuela Stefanelli,<sup>a</sup> Roberto Paolesse,<sup>a</sup> Raffaella Lettieri,<sup>a</sup> Mariano Venanzi\*<sup>a</sup> and Donato Monti\*<sup>a</sup>

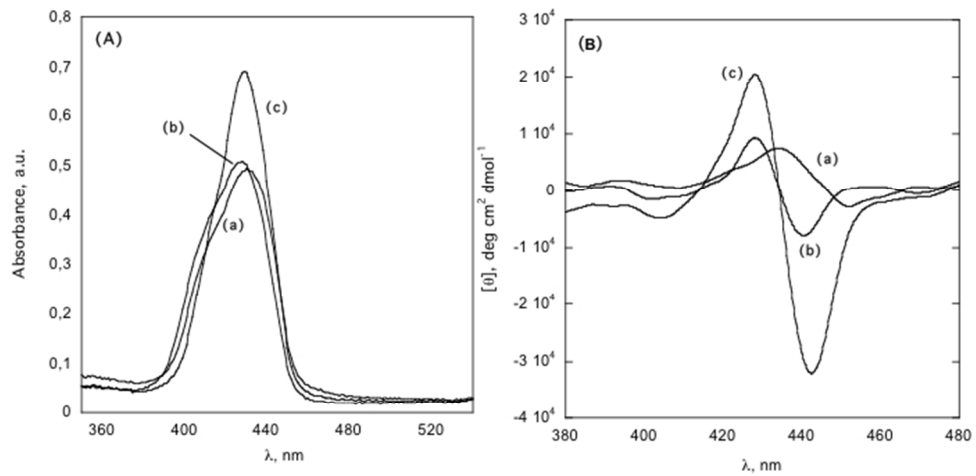
Abstract

The aggregation of an amphiphilic chiral Zn(II)porphyrin derivative occurs in aqueous solutions of chiral surfactants with highly specific molecular recognition.

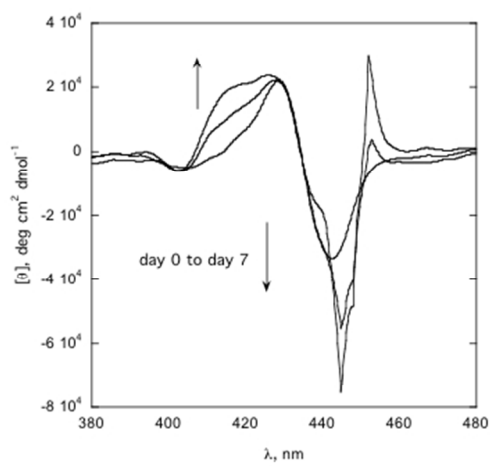




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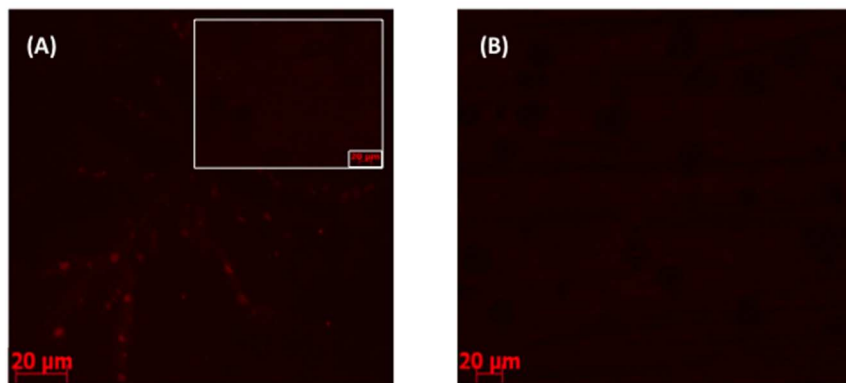


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