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Scaling the Chirality in Porphyrin J-Nanoaggregates

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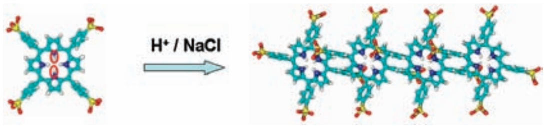
S *Supporting Information*

Chirality expression in supramolecular assemblies is a highly investigated topic both because of the strict relationship with biological systems and for its fundamental importance in understanding the origin of life itself.[1,2] Porphyrins have been widely used as molecular components because of their rich spectroscopic properties that strictly depend on the microenvironment and the mutual geometrical arrangement. In particular, the zwitterionic diprotonated form of the water-soluble tetrakis-(4-sulfonatophenyl)porphyrin ($TPPS_4$) is able to self-assemble into J-aggregates, depending on the concentration, pH, and ionic strength of its solutions. Within these aggregates, the porphyrins are stacked side-by-side and are stabilized by electrostatic, hydrogen-bonding, and dispersive interactions (Scheme 1),[3−10] and a variety of interesting structural features have been described going from nano- up to microsized rod,[11−13] nanotubes,[3,14,15] and fractal clusters.[16−20] So far, chiral J-aggregates of $TPPS_4$ have been reported at the air/water interface[21,22] or using polypeptides[23−25] (or even simple aminoacids)[26] as scaffolds. Stirring the solution during the aggregation kinetics can also lead to symmetry breaking, and a statistical correlation with the stirring sense has been reported.[4] Recently, we have shown that, when optically active tartrate is used, different chiral assemblies have been obtained as a result of a structural transition,[12] posing the intriguing problem of the transmission of chirality from a local or molecular level up to the mesoscopic regime. Here we exploit chiral J-aggregates templated by tartrate and encapsulated in the inner water-pool of water/sodium bis(2-ethylhexyl)sulfo succinate (AOT)/decane microemulsions. This confined environment allows the size and coherence length of such J-aggregates to be easily controlled simply by changing the ratio $w_0 = [H_2O]/[AOT]$.[27] We anticipate that the chirality scales with the size of the aggregates from a few up to hundreds of nm.

Chiral J-aggregates of the $TPPS_4$ porphyrin can be prepared inside the water pool of AOT microemulsion by mixing equal volumes of two microemulsions containing concentrated porphyrin in water (80 μM) and tartrate buffer (100 mM; pH = 2.7), respectively. The ratio w_0 was varied in the range 32 − 65, being $w_0 \geq 32$ the threshold value in order to observe the formation of confined J-aggregates.[27] Quasi-Elastic Light Scattering (QELS) experiments have been performed using a Malvern 4700 correlator and a 20 mW polarized Nd/YAG laser. For dilute solutions of monodispersed particles, the standard second-order cumulant analysis of the autocorrelation functions allows to determine the effective hydrodynamic radii (see Supporting Information), that, in our case, have been measured both before mixing and after reaching equilibrium. The formation of the J-aggregates can be easily followed by the appearance of the typical J-band at 490 nm, and the H-band at 422 nm in the UV/vis absorption spectra (data not shown). Figure 1 reports typical CD spectra obtained by using D or L-tartrate buffer as chiral agent. Even if not completely symmetric, the two spectra are quasi-mirror images, as expected for aggregates of opposite handedness. An exciton split CD signal is located at 422 nm, while a more intense CD feature is centered at 490 nm.

Scheme 1. Schematic Model for the Diprotonated $TPPS_4$ Porphyrin Assembling into J-Nanoaggregate



It is interesting to note the correlation between the sign of the Cotton effects observed in the presence of L-tartrate buffer within the microemulsions as compared to the bulk solution (Table 1). As already reported,[12] in the bulk two different structures, i.e. fractal objects and nanorods, are obtained under different experimental conditions, and they exhibit opposite CD features. The sign of the Cotton effect observed for the J-aggregates in the microemulsions is analogous to that of the fractal clusters in bulk solution. This observation can be explained in terms of a similar local arrangement of the chromophores for the two cases due to a close similarity in the ionic strength .[13]

To estimate the correlation between the size and the chirality of these J-aggregates, we have used the dissymmetry g-factor ($g = \Delta\varepsilon/\varepsilon$) calculated at 420 nm. This wavelength has been chosen since resonant light scattering is largely present in these samples,[28] mainly contributing at the red-edge of the 490 nm band. Consequently we cannot exclude the occurrence of

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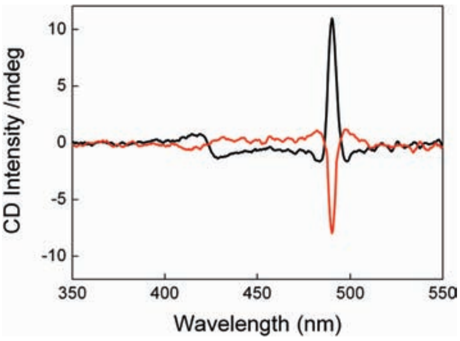

Figure 1. Typical CD spectra of chiral J-aggregates of $TPPS_4$ inside AOT microemulsions in the presence of D- (red line) or L-tartrate (black line): $[TPPS_4] = 40\ \mu M$, 50 mM tartrate buffer at pH 2.7, $w_0 = 65$, $T = 293$ K. Reproducibility is fairly good within an experimental set of samples from the same stock solutions.

Table 1. Comparison on the Signs for the Various CD Bands in the Spectra of $TPPS_4$ J-Aggregates Prepared in Microemulsions and in Bulk (Fractal and Rodlike Structures) Using L-Tartrate As Chiral Agent

	CD (422 nm)	CD (490 nm)	I(NaCl)/M
rod[a]	+/−	−/+/−	0
fractal[a]	−/+	+/−/+	1.5
microemulsion[b]	−/+	+/−/+	0.92−1.73[c]

[a] Different structures have been prepared using the protocol described in ref 12. [b] This work. [c] Ionic strength at the inner surface has been evaluated by geometrical considerations on the volume of the inner water pool, using the measured hydrodynamic radii of the microemulsions. For a microemulsion with $w_0 = 40$: $I \approx 1.35$ M.

artifacts in CD spectra due to the contribution of enhanced differential scattering.

Figure 2 reports in a double logarithmic plot the absolute values of *g*-factors for the J-aggregated $TPPS_4$ in the microemulsions as a function of the corresponding hydrodynamic radii corrected by the length of the external microemulsion coronae (hollow circles). Interestingly, when the data obtained for a rod of 500 nm is included in the analysis (filled circle), all the data, which span 2 orders of magnitude from 6 up to 500 nm ($|g| \propto R_H^{\beta}$, $\beta = (0.87 \pm 0.02)$), obey a well-evident scaling law. This observation suggests that: (i) the CD strength is increasing with the size of the aggregates and that almost linear or helicoidal assemblies of porphyrins are probably responsible for this behavior, (ii) the nature of the repeating monomeric units in the fractal clusters obtained in the bulk is very similar to that constituting the rodlike aggregate in the microemulsion confined environment, and (iii) a very efficient mechanism for the propagation of the CD strength is operative within these aggregates. A possible explanation could be related to their very high coherence length, namely the capability to delocalize the exciton along a certain number of electronically coupled monomers.[27,29] Previous results showed that the coherence length is actually coincident with the length of the nanorods confined in the microemulsions that, in the case of $w_0 = 65$, have been estimated to be formed by ∼40 monomeric units.[27] Electro-optical response in these aggregates embedded in a polymeric matrix have indicated the occurrence of even higher coherence lengths, probably related to the water content of the matrix.[30] To what extent a dipolar theory[31] similar to that proposed to explain the large CD in ψ-DNA is operative is still a matter of investigation.

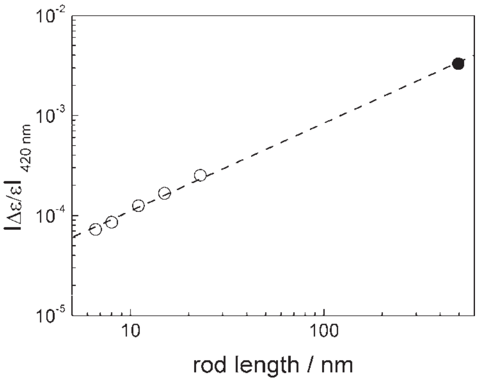

Figure 2. Double logarithmic plot of the absolute value for the dissymmetry *g*-factor ($\lambda = 420$ nm) vs the size of the J-aggregates formed in microemulsions (hollow circles), or in bulk (filled circle). The linear fit of the data gives a slope of (0.87 ± 0.02). $[TPPS_4] = 40\ \mu M$, 50 mM D-tartrate buffer at pH 2.7, $T = 293$ K; in microemulsions: $w_0 = 32-60$.

Our findings clearly demonstrate that it is possible to control size and optical properties of J-aggregates using microemeulsions and that their chirality can propagate from nano- up to mesoscopic domain. Therefore, the present investigation sheds further light on the fundamental issue of chirality transmission and propagation in supramolecular assemblies, opening the way to a better control of the chirality at the nanoscale.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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