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Vortexes and Nanoscale Chirality**

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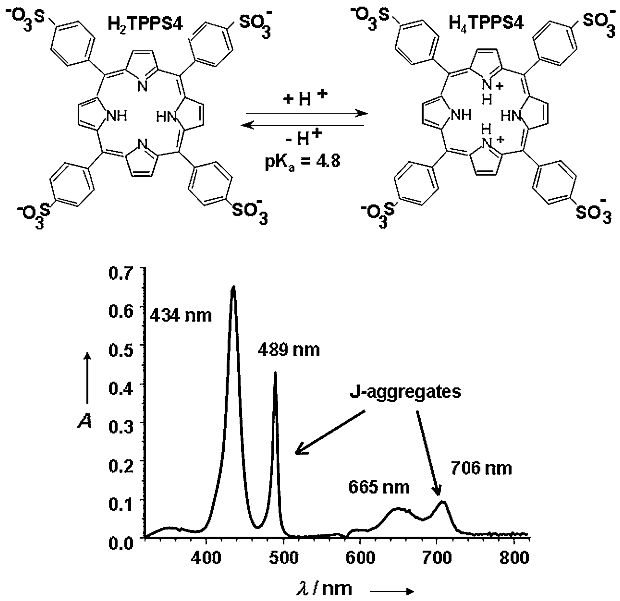
The relationship between vortexes and chirality of large assemblies is a very intriguing problem which might lead to understanding fundamentals of nature and, from this, to possible technological applications.[1] Since 1990 several different reports have dealt with this topic: some of them describe the formation of one enantiomeric form decided by stirring sense ("static" situation).[2–4] Others describe a more "dynamic" situation in which clockwise (CW) and counter clockwise (CCW) stirring of noncovalent assembly solutions causes an increase of circular dichroism (CD) intensity and a dependence of the CD signs on the stirring sense:[5–8] stopping of stirring restores the initial situation. Interpretation of the dynamic-situation results is still quite controversial: is the CD observed under stirring arising from instrumental artifacts, such as fiber alignment into the vortex, or is there also a contribution from real chirality?

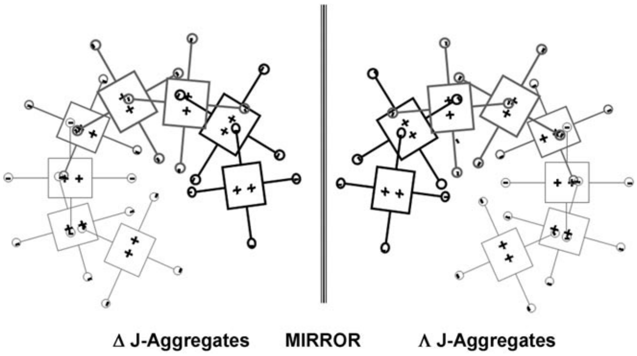
Herein we describe the behavior under stirring of non-covalent J-aggregates of the protonated form of *meso*-tetrakis(4-sulfonatophenyl)porphyrin (H_2TPPS4 (**1**), Scheme 1 and Scheme 2). They respond to mechanical stirring in a dynamic fashion in that their CD signal inverts with stirring sense and the signal intensity increases (Figure 1). Herein we show that different from previous reports, for this particular system, static and dynamic aspects coexist. Artifacts arising from fiber alignment during stirring are taken for granted,[7,8] even if recent data have indicated that the signal contains contributions from chirality.[9] On the other hand, theoretical models predict an enantiomeric enrichment in the vortex.[10] However, our goal in this case is to understand if eddies have an impact on supramolecular chirality. Is a vortex able to affect nanoscale chirality? If yes, how?

Before presenting our data we describe some peculiarities of this chemical system.

Compound **1** is not chiral, however self-aggregation of its protonated (zwitterionic) form (Scheme 1)[11–15] induces a split CD in the absorption region (Figure 2).[16] Both positive (Λ) and negative (Δ) couplets are observed randomly (Figure 2 blue and red curves, respectively). There are different explanations for the "spontaneous" emergence of aggregates chirality: 1) they are not chiral and gain chirality for the presence of picomolar traces of chiral contaminants,[17,18] 2) they are inherently chiral (Scheme 2) and the 1:1 distribution of enantiomers undergoes to statistical breaking of parity rule, 3) they are inherently chiral and traces of chiral contaminants shift the 1:1 racemate equilibrium.



Scheme 1. Top: schematic structure of H_2TPPS4 (**1**) and its protonated form (H_4TPPS4). Bottom: absorption spectrum of an aqueous solution of **1** (at pH 3, [NaCl] = 0.3 M). Absorption bands of J-aggregates are at 489 and 706 nm.



Scheme 2. A possible structure of chiral J-aggregates of **1**.

In our opinion, the hypotheses (2) and (3) are the most likely. In fact, when working with the J-aggregate in very clean water, just a small monosignated CD signal is observed in the Soret region (Inset A of Figure 2).

Our hypothesis is that J-aggregates are inherently chiral and exist in aqueous solution as racemate: we will show that their distribution is affected by vortexes.

These aggregates have tendency to stick onto the cuvette walls,[19] their deposition is revealed from absorption and CD

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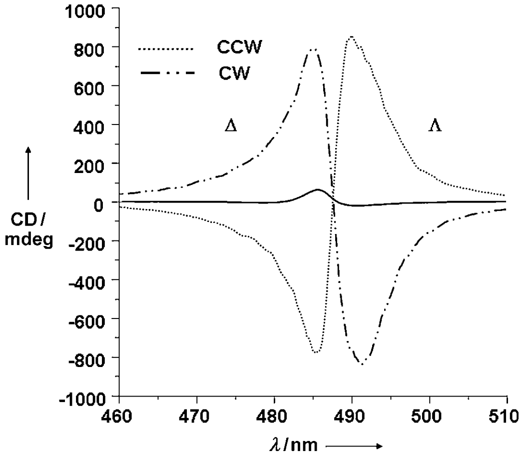


Figure 1. CD spectra of **1** (10 μm, pH 3, [NaCl] = 0.3 m) aqueous solutions during CW (dashed-dotted line) and CCW (dotted line) stirring. The black continuous line shows the spectrum of the standing solution. pH value, porphyrin and NaCl concentrations are the same in all experiments unless stated.

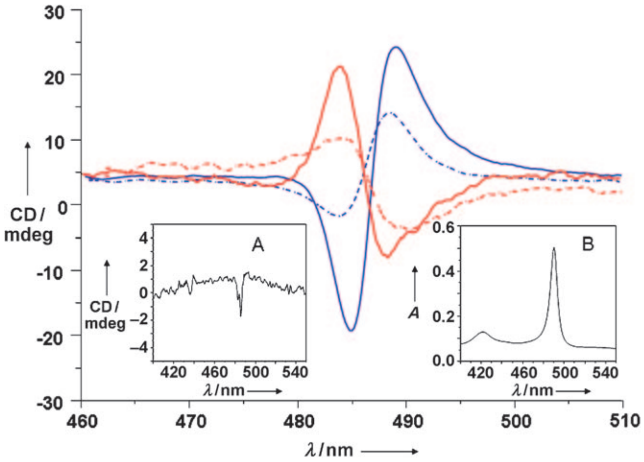


Figure 2. CD spectra of standing solution soon after J-aggregation (continuous lines) and empty cuvettes after standing with J-aggregates for 24 h (dashed lines) of Λ J-aggregates (blue lines) and Δ J-aggregates (red lines). Inset A shows the CD of J "racemate" in pure water. Inset B shows the absorption spectrum of the species deposited onto the cuvette wall.

spectra of the empty cuvette after the removal of the J-aggregates solution which had been standing in the cuvette for 24 h. The dashed lines in Figure 2 show the CD spectra of the empty cuvette indicating that: 1) the species which deposit onto the wall is the enantiomer present in solution with the higher concentration; 2) deposition phenomena do not induce any change in the CD shape (that is, there are no artifacts). Interestingly, the absorption spectrum (Inset B of Figure 2) does not show any absorption of the monomeric protonated species: only the bands of the J-aggregates at 489 nm and 422 nm are observed.[5] This result shows that only J-aggregates stick to the wall under these experimental conditions. This information is very important for the interpretation of the next data. We will show that vortexes enable separation of enantiomers: the enantiomer favored by stirring is deposited on the cuvette wall, the other remains in solution.

To stress the surprising results arising from the effect of stirring we will first discuss data in which the starting solution has already an excess of one enantiomeric form of J-aggregates:[20] the following data show that CW and CCW eddies allow for deposition (onto the cuvette wall) of the Δ and Λ enantiomer, respectively, independently from the chirality of the enantiomer(s) initially present in solution.

Figure 3 shows the CD spectrum of a solution that presents an excess of Λ J-aggregates (continuous line). It is worth recalling that standing solutions would show Λ deposition. However, leaving the solution for 24 h in the cuvette under CW stirring (which favors the Δ species, Figure 1) we observe, after removal of the solution, a CD signal of the Δ aggregate (Figure 3, broken line). on the cuvette walls. The inset of Figure 3 shows that stirring CCW for 24 h a solution of Δ J-aggregates leads to deposition of Λ aggregates. In both cases (and hereafter in all cases but that shown in Figure 4) the CD spectrum of the solution after stirring is identical to the initial one (but for the intensity which is lower). For both systems only the absorption bands at 489 nm and 422 nm are detected (data not shown). The absence of the protonated monomer band at 434 nm indicates that the absorption results from adhesion of the J-aggregates and not from aggregation of the monomers onto the wall.

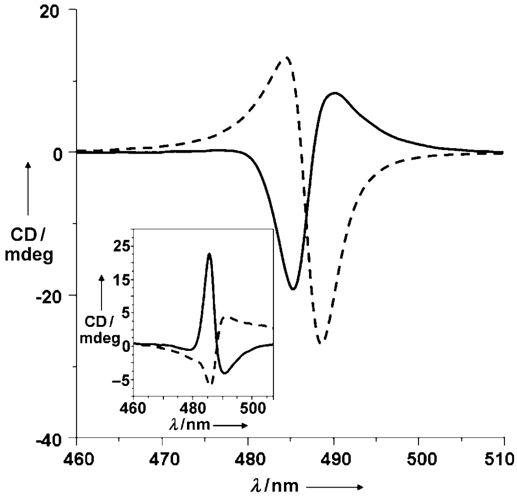
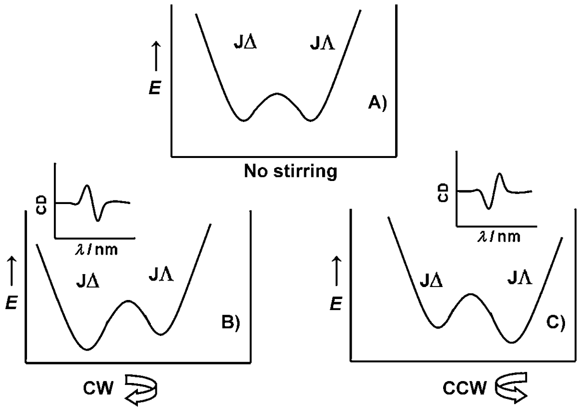


Figure 3. CD spectra of J-aggregates of **1**: (——) initial solution of the Λ enantiomer; (– – –) empty cuvette after 24 h of CW stirring in the dark showing deposition of the Δ enantiomer. Inset shows that CCW stirring leads to deposition of Λ aggregates on the cuvette wall (– – –) although starting from a Δ initial solution (——).

According to the absorption spectra and recalling the standing-system indications (the major species sticks onto the wall, Figure 2) it is possible to conclude that, under stirring, the major species in solution are the J-aggregates favored by vortex rotation sense. This means that stirring is inducing a thermodynamic unbalancing in the racemate (Scheme 3).

Starting from the "racemate" in "pure" water (see Inset A of Figure 2) we have obtained the same results: the species favored from stirring is on the wall and the "racemate"



Scheme 3. Schematic representation of the possible effect of the stirring on a racemate (A). CW (B) and CCW (C) stirring favor Δ and Λ J-aggregates, respectively.

remains in solution (data not shown). Only four times in almost thirty experiments with "pure" water, did we observe the enantiomer separation: the enantiomer "preferred" by stirring onto the wall the other one in solution (Figure 4). We understand that statistically the latter results might be considered scarcely significant; however, the significance increases taking into account the rare possibility of working with a system 100% free from chiral pollutants (pure water, pure acid and sodium chloride solutions, etc). In our opinion, these results reinforce the hypothesis that J-aggregates of **1** exist as racemic mixtures.

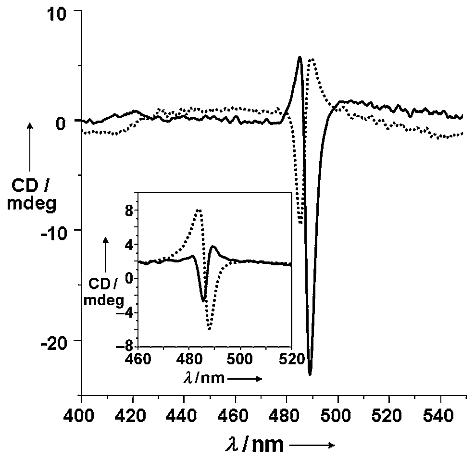


Figure 4. CD spectra of a racemate solution (see Inset A of Figure 2) after 24 h CCW stirring in the dark, the inner solution (——) and cuvette wall (– – –) show mirror image CD spectra. Inset shows the results obtained for CW stirring.

To corroborate this point further we performed J-aggregation in the presence of a racemate of the Λ and Δ enantiomers of $[Ru(Phen)_3]^{2+}$ (Phen = Phenanthroline). These chiral complexes induce chirality in the aggregates of **1**: a positive couplet for the Λ-isomer and a negative couplet for the Δ-isomers.[21] Also in this case the J-aggregates respond to stirring by increasing CD intensity and switching couplet sign with stirring sense (Figure 1). Thus the chiral J-aggregates induced by Λ- or Δ-$[Ru(Phen)_3]^{2+}$ should respond to mechanical stirring stimuli exactly as the previous racemate system did.

Figure 5 shows that indeed CW stirring induces deposition of Δ aggregates despite the starting solution showing a small Λ CD signal. Analogously, the inset of Figure 5 shows that CCW stirring induces deposition of Λ aggregates even from a starting solution showing a Δ signal. The absorption spectra show that also in this case only J-aggregates deposit onto the wall: porphyrin monomers and ruthenium complexes do not stick to the walls and remain in solution (data not shown). This result means that the ruthenium complexes are not a constitutive part of the J-aggregates.[18] The similarity between the data with and without the chiral matrix indicates that the presence of the ruthenium complexes does not induce any significant difference in the response of the J-aggregates towards the macroscopic chirality of vortexes.

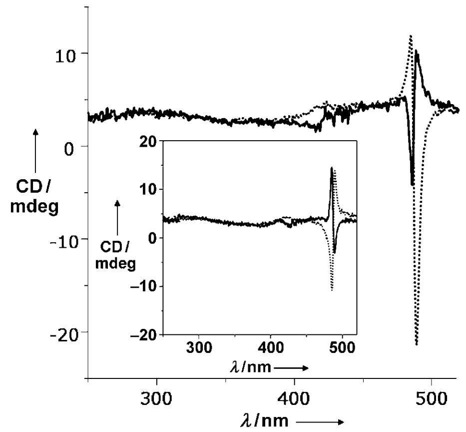


Figure 5. CD spectra of J-aggregates of **1** formed in the presence of the racemate of Λ and Δ enantiomers (10 μM each) of $[Ru(Phen)_3]^{2+}$ ions in which a small excess of Λ-J-aggregates is present. The spectra were recorded before (——) and after (– – –) 24 h of CW stirring in the dark. Inset shows data of a solution which initially contains a small excess of Δ-J-aggregates. (——) initial solution, (– – –) after 24 h CCW stirring in the dark.

The next experiment is very useful to compare the stirring effect (which is a weak thermodynamic effect) with a stronger thermodynamic effect, such as that exerted by the presence of high concentrations of chiral templates. We anticipated that the next system would behave differently to the previous ones and helps in delineating a model.

Figure 6 shows CD data of a solution in which J-aggregation occurs in the presence of equimolar concentrations of porphyrin and Δ-$[Ru(Phen)_3]^{2+}$ ions. In this case not only is the system not racemic but concentration of the chiral matrix is equal to that of porphyrins. Also for this unbalanced system, stirring induces the spectral variations observed for the discussed systems above (inset of Figure 6).[22] The prolonged stirring experiment on a Δ-$[Ru(Phen)_3]^{2+}$ templated J-aggregates (24 h of CCW to favor Λ deposition) shows that, for this thermodynamically unbalanced system, stirring does not cause racemate "resolution": the starting Δ J-aggregates is in solution and also deposited onto the wall.

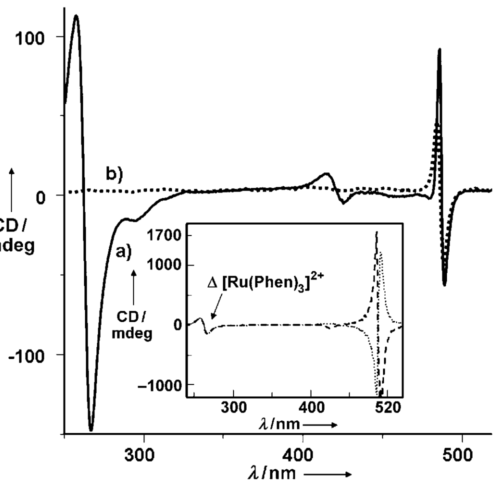
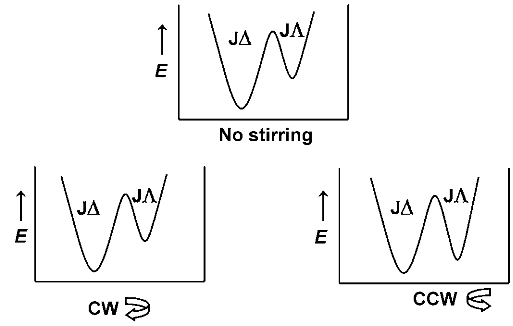


Figure 6. CD spectra of J-aggregates of **1** formed in the presence of Δ-[Ru(Phen)$_3$]$^{2+}$ ions (10 μM): a) standing solution (——), b) cuvette wall after 24 h CCW stirring in the dark (– – –). The inset shows the effect of stirring on the solution; (•••••) CCW, (– – –) CW stirring.

This indicates that Δ J-aggregates remain the major species in solution (despite the 24 h CCW stirring favoring, in principle, the Λ enantiomer, Scheme 4).[23]



Scheme 4. Schematic representation of the possible stirring effect on a J-aggregate solution in which a thermodynamic "unbalancing" factor is present throughout its formation (Δ-[Ru(Phen)$_3$]$^{2+}$ in this case). Stirring is not able to overcome the initial unbalancing.

This experiment is also very useful to rule out the possibility that the stirring causes deposition of aligned aggregates and to exclude the occurrence of instrumental artifacts such as linear dichroism (LD).[24]

All these data converge toward a simple thermodynamic model: in a (quasi-)racemic system of noncovalent aggregates, stirring drives a redistribution of (protonated) monomers between the two enantiomeric forms of assemblies and/or drives monomer complexation towards one enantiomer (Δ for CW, Λ for CCW stirring). If a competitive chiral "force" (such as a chiral template) is present in solution the fate of the system is related to the balance between different forces acting in solution, that is, a low or racemic concentration of chiral template will be overcome by stirring (see examples in Figure 3, Figure 4, and Figure 5), however, a high concentration of chiral matrix (see Figure 6) will drive the system towards the templating chirality (Scheme 4).[23]

If this model is correct, then there should be a concentration of chiral ruthenium complexes at which they behave as chiral "pollutants": that is, they will initially template the chirality of the J-aggregates (in standing solutions) but stirring will prevail and drive the system toward the formation of species favored from the vortex chirality (Scheme 3). Indeed, at a concentration of chiral metal complex of 10 nM (that is 1000-times more diluted than **1**) the chirality of the initially formed aggregates is templated by the tiny concentration of chiral complexes (Figure 7). However, different to the experiment shown in Figure 6, this time the J-aggregates favored from a given stirring sense are deposited onto the cuvette wall after 24 h of stirring (broken lines of Figure 7): thus in this case Λ- or Δ-[Ru(Phen)$_3$]$^{2+}$ behave like chiral contaminants (Scheme 3).

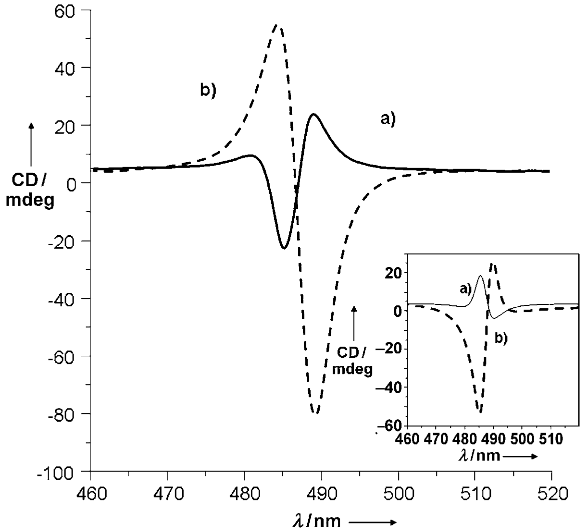


Figure 7. CD spectra of the J-aggregates of **1** (10 μM) formed in the presence of 10 nM of Λ-[Ru(Phen)$_3$]$^{2+}$: a) standing solution (solid line) and b) cuvette wall after 24 h CW stirring (broken line). Inset shows the CD spectra of J-aggregates templated from 10 nM of Δ-[Ru(Phen)$_3$]$^{2+}$ ions: a) standing solution and b) cuvette wall after 24 h CCW stirring.

So we can conclude that for this specific system the action of vortexes is at least twofold causing: 1) fiber alignment in solution (mainly a "mechanical" action leading to increase of the CD signal and inversion of the sign) and 2) enantiomer separation/enrichment (thermodynamic in nature, driven by a chiral field and leading to redistribution and/or enrichment of monomers onto the chiral aggregate favored by the swirling sense). The cuvette walls represent a kind of "trap" which freezes the deposited J-aggregates in the conformation chosen in solution from the vortex chirality: deposition is fundamental in going from a dynamic to a "static" regime.

In our opinion this work reports quite strong experimental evidence that, for the investigated systems, stirring is shifting the equilibrium of a racemic mixture towards the side chosen by the vortex chirality. It is not clear at the moment if, under the effect of a vortex, there is chiral enrichment (monomers caught from the eddy sense and pushed to self-aggregate) and/or a racemate resolution. To understand if this simple scheme is more general we are testing other similar chemical systems.

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[22] The UV part of the CD spectrum, reporting $[Ru(Phen)_3]^{2+}$ chirality, is not affected by stirring confirming that ruthenium complexes are free in solution and not part of the J-aggregates. Also for the analogous system with the Λ enantiomer no deposition of the Δ enantiomer is observed in spite of the CW stirring.

[23] Δ- or Λ-$[Ru(Phen)_3]^{2+}$ are free in solution (10 μM): therefore they can drive a preferential chiral aggregation despite the vortex chirality.

[24] Following suggestions from a referee we have halved the cuvettes. Both faces show CD signals which have the same shape as that of the empty cuvette: this enables LD contributions to be excluded (Supporting Information).