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Chiral Aggregates

Reversible "Chiral Memory" in Ruthenium Tris(phenanthroline)–Anionic Porphyrin Complexes**

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In the last few years, transfer and memory of chirality have been attracting growing interest for potential technological applications.[1] In general, this phenomenon occurs through two steps: 1) transfer of chirality from a chiral template to an achiral covalent or noncovalent "polymeric" species and 2) "removal" of the chiral cast which leaves its chirality permanently imprinted on the "polymer". The chiral memory relies on the kinetic inertness of the "polymeric" species and most examples rely on systems that have a "static" memory: that is, once imprinted and memorized, chirality becomes an intrinsic but nontunable feature of the complex. Only recently has a system with a "dynamic memory" for which it is possible to cyclically store and release the "memorized chirality" been reported.[2] We report herein a new and more intriguing "dynamic" supramolecular memory system (SuMe).

We have recently reported that the Λ and Δ enantiomers of $[Ru(1,10\text{-phenanthroline})_3]^{2+}$ ($[Ru(phen)_3]^{2+}$, $\lambda_{max} =$ 262 nm, Figure 1) induce chiral aggregation of various achiral anionic porphyrins.[3] Our interest in this complex system stems from two considerations. Firstly, porphyrins are ideal building blocks for supramolecular architectures because of their unique spectroscopic properties (extinction coefficients of ca. 10^5 and intense emission signals, the position and intensity of which can be tuned by insertion of a central metal ion) and the possibility of modulation of their self-aggregation.[4] Secondly, ruthenium (II) complexes can transfer two kind of molecular information—energy and chirality—to porphyrins and their aggregates.[3,5]

The interaction between meso-tetrakis(4-sulfonatophenyl)porphine (H_2TPPS4, $\lambda_{max} = 412$ nm, Figure 1) and an equimolar amount of $[Ru(phen)_3]^{2+}$ (pH ≈ 6.0, NaCl (0.3 M)) is indicated by variations in the absorption spectra of both $[Ru(phen)_3]^{2+}$ and H_2TPPS4. The strongest evidence of interaction, however, comes from the appearance of an induced circular dichroism (ICD) band in the absorption region (Soret band) of the achiral porphyrin (Figure 2). The relationship between chirality of the cationic metal complex and that transferred to the anionic porphyrins is straightforward because interactions of H_2TPPS4 with the Λ- and Δ-$[Ru(phen)_3]^{2+}$ lead to mirror-image ICD signals (Figure 2).

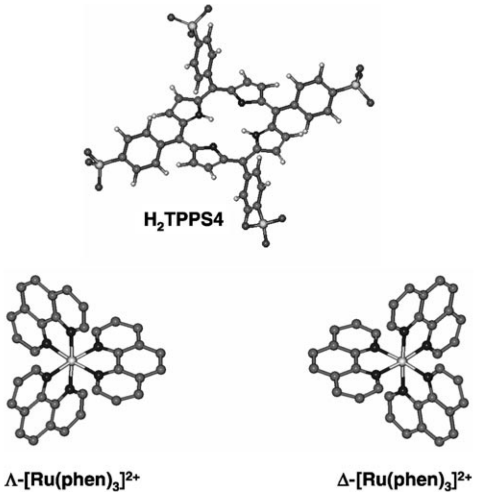

Figure 1. Structure of the anionic porphyrin H_2TPPS4 and of the Λ and Δ enantiomers of $[Ru(phen)_3]^{2+}$.

At a pH value lower than 3 and in the presence of millimolar concentration of salt, the protonated species of H_2TPPS4 (H_4TPPS4, $pK_a \approx 5$, $\lambda_{max} = 436$ nm) is zwitterionic and self-assembles to give both face-to-face (H, $\lambda_{max} =$ 422 nm) and edge-to-edge aggregates (J, $\lambda_{max} = 490$ nm, Figure 3).[6] Yashima and co-workers have shown very

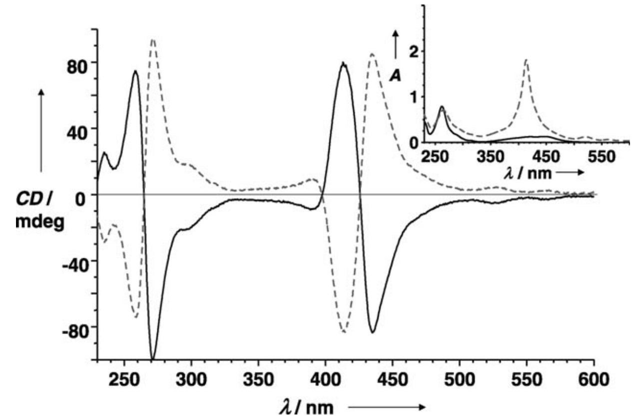

Figure 2. CD spectra of H_2TPPS4 (10 μM) at pH ≈ 6.0, NaCl (0.3 M) in the presence of Λ- (solid curve) and Δ- $[Ru(phen)_3]^{2+}$ (dashed curve, 10 μM). The inset shows the absorption spectrum of $[Ru(phen)_3]^{2+}$ (solid curve) and of the complex species (dashed curve). Spectra were recorded about one hour after mixing the reagents.

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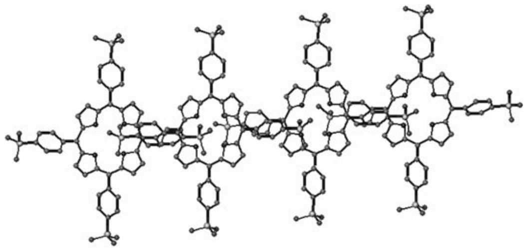

Figure 3. Schematic structure of H$_4$TPPS4 J aggregates. Two anionic sulfate groups are present above and below the porphyrin cationic core. Hydrogen and double bonds have been omitted for clarity.

recently that the J aggregates formed from H$_4$TPPS4 gain chirality when templated from helical poly(phenylacetylene) and memorize the imprinted chirality.[1g]

We thought therefore to expand our previous investigation (performed at pH 7) to more acidic conditions in which H$_4$TPPS4 aggregates. We show that the J aggregates described herein have memory of the chirality imprinted at a pH value of around 6.0 by Λ- or Δ-[Ru(phen)$_3$]$^{2+}$.[7] The memory is not only retained but can also be switched on and off by simply modulating the pH.

Figure 4 shows the spectroscopic variations of the Λ- or Δ-[Ru(phen)$_3$]$^{2+}$/H$_2$TPPS4 complexes following the decrease of the pH value from around 6.0 to 2.5.[7] Protonation of the central nitrogen atoms immediately causes the disappearance of the absorption band at 412 nmm and the appearance of a band at 436 nm (Figure 4, inset). After around ten minutes, a new absorption band, which arises from the formation of the J aggregates, appears at 490 nm (Figure 4, inset). The CD spectrum changes accordingly: the exciton-coupled CD band centered at 422 nm disappears soon after the addition of HCl (Figure 4, red curve) and after around ten minutes two new sets of exciton couplet bands centered at 422 nm (H aggregates) and 490 nm (J aggregates) appear (Figure 4).

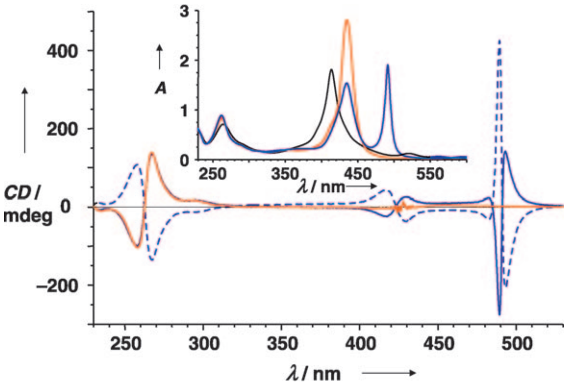

Figure 4. CD spectra of H$_4$TPPS4 (10 μM, pH 2.5, NaCl (0.3 M)) in the presence of Λ- (dashed blue) and Δ-[Ru(phen)$_3$]$^{2+}$ (blue, both 10 μM). The red line shows the CD spectrum of Δ-[Ru(phen)$_3$]$^{2+}$/H$_4$TPPS4 system at pH 2.5 soon after the addition of HCl (the spectrum of Λ-[Ru(phen)$_3$]$^{2+}$/H$_4$TPPS4 is identical and not shown for simplicity). The inset shows the absorption spectra of the solution at pH 7 (black) and at pH 2: soon after the addition of HCl (red) and after ten minutes (blue).

The CD spectra clearly show that porphyrin aggregates gain chirality by interactions with the inorganic cationic complexes: the exciton bands of the H and J aggregates formed with the two enantiomers are, in fact, the mirror image of each other. Addition of (for example) an excess of Λ-[Ru(phen)$_3$]$^{2+}$ (15 μM) to J aggregates preformed in the presence of Δ-[Ru(phen)$_3$]$^{2+}$ (10 μM) should therefore lead to an inversion of the CD bands both in the UV region (the spectroscopic region where absorption of the inorganic complex occurs) and in the visible region (where the absorption features of porphyrins dominate).

The experiment reported in Figure 5 shows that this hypothesis is only partially valid; inversion of the CD spectrum is observed only in the region where the ruthenium complex absorbs and not in the absorption region of the J aggregates. From these data it is clear that the J aggregates "remember" the chirality imprinted at the very onset of their formation.

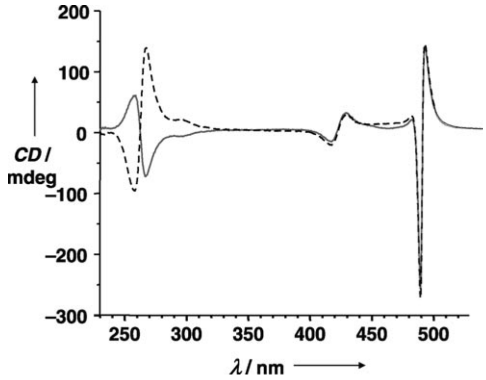

Figure 5. CD spectra of the H$_4$TPPS4 J aggregates formed in the presence of 10 μM Δ-[Ru(phen)$_3$]$^{2+}$ before (dashed curve) and after (solid curve) the addition of an excess (15 μM) of Λ-[Ru(phen)$_3$]$^{2+}$.

We have recently reported[2] the first example of a system in which it is possible to erase and restore the ICD of porphyrin aggregates that borrow and memorize the template chirality. The reversibility of the system arises from spectroscopically undetectable chiral "seeds" that are present in low concentrations and catalyze the correct "refolding" of the species (Figure 6).[2]

It is possible to switch the CD signal of the title aggregates on and off because of: 1) the presence of chiral seeds and 2) the remarkable "catalytic" ability of the seeds in driving the "refolding" of the memorized supramolecular architecture. In particular we have performed a pH cycle (2.5→≈6.0→2.5) on a solution containing chiral J aggregates of H$_4$TPPS4 templated from Δ-[Ru(phen)$_3$]$^{2+}$ but in the presence of an excess of Λ-[Ru(phen)$_3$]$^{2+}$ (the system discussed in Figure 5). The absorption changes are predictable: 1) the jump from pH 2.5 to around 6.0 will cause porphyrin deprotonation and disassembly of the J aggregates and 2) the following decrease of the pH value to 2.5 will lead to (re)protonation of porphyrins and, with time, to the reassembly of the chiral J aggregates. In contrast, the results of the CD experiments are not easily predicted. In fact, under these

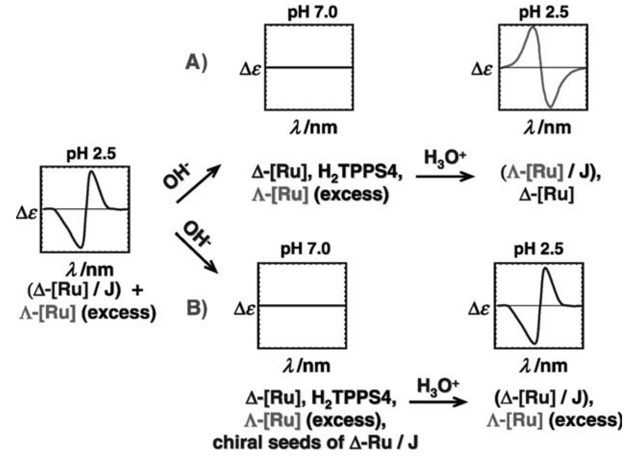

Figure 6. Scheme of the two possible reassembly pathways following disassembly of the J aggregates formed for interaction with Δ-[Ru(phen)$_3$]$^{2+}$ but in the presence of an excess of Λ-[Ru(phen)$_3$]$^{2+}$.

experimental conditions, two routes are possible (Figure 6): the first (A) leads to the enantiomeric form (Λ-[Ru(phen)$_3$]$^{2+}$/J aggregates) of the starting aggregates (Δ-[Ru(phen)$_3$]$^{2+}$/J aggregates), whilst the second route (B) proceeds with retention of the starting chirality. Route A should be followed if the Δ-[Ru(phen)$_3$]$^{2+}$/J aggregates are completely destroyed upon porphyrin deprotonation: in this case the excess of the Λ enantiomer will cast the opposite chirality to that initially present. The second route (B) should prevail if the remarkable inertness of the J aggregates (demonstrated by their ability of memorizing the chirality) permits only a partial disassembly to leave a spectroscopically undetectable concentration of Δ-[Ru(phen)$_3$]$^{2+}$/J aggregates.

CD data of the pH cycles are shown in Figure 7 and demonstrate that route B prevails over route A. The absorption spectra (Figure 7, inset) show that, upon changing the pH value from 2.5 to around 6.0, the spectrum of the non-protonated H$_2$TPPS4 is restored: the subsequent decrease of pH to 2.5 leads again (within 5 min) to the J aggregates. The CD spectra are consequently modified in two ways: 1) when the pH is raised to around 6.0 the ICD (spectrum a) of the J aggregates disappears to give spectrum b[8] and 2) the CD signal of the J aggregates is immediately restored after the pH jump to 2.5 (spectrum c). Remarkably, the sign of the exciton couplet is the same as that of the starting J complex, which confirms the retention of chirality and the remarkable inertness of these chiral aggregates. The same results have been obtained starting from the Λ-[Ru(phen)$_3$]$^{2+}$/J aggregates. Up to ten consecutive pH cycles were performed without observing any inversion of the CD Soret couplet.[9,10] After these cycles the same solution was kept at a pH value of about 6.0 for 1, 2, 16, 24, 48 h and 1 week. After each time interval the pH value was lowered to 2.5 and an identical CD signal shape was obtained, which shows the remarkable stability of these species.[11]

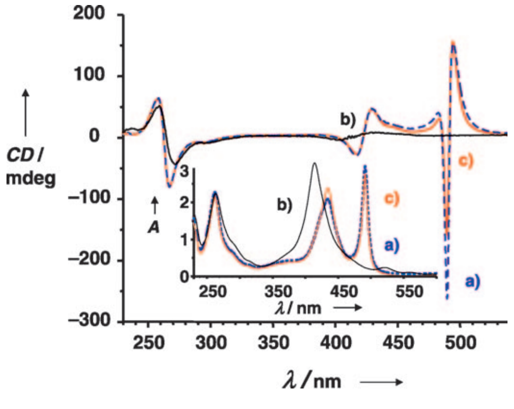

Figure 7. CD spectra of the solution used for the measurements shown in Figure 5 recorded: a) initially at pH 2.5 (dashed blue curve), b) then at pH ≈ 6.0 (black curve), and c) again at pH 2.5 (red curve). The inset shows the absorption spectra of the three experiments.

These results can be explained only by the inertness and catalytic properties[12] of the initially formed aggregates (seeds), which allow the J species to retain the memory of the templated chirality. The increase of the pH value to around 6.0[9] does not disassemble all the aggregates: a residual concentration of these species remains in solution (the chiral seeds) and is able to very efficiently drive the correct folding of the memorized chirality in spite of the presence of an excess of the template that has an "opposite" handedness.

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[5] The emission signal of $[Ru(phen)_3]^{2+}$ is centered at 590 nm. Porphyrins have absorption bands (Q bands) in this region. Energy transfer processes have been observed in their complex at pH 7.[3]

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[7] The formation of the J aggregates is hierarchically controlled. The only way to obtain these species is by allowing porphyrin aggregation with Λ- or Δ-$[Ru(phen)_3]^{2+}$ at a pH value of around 6 and then decreasing the pH to 2.5.

[8] The CD signal of the (Δ-$[Ru(phen)_3]^{2+}$/H_2TPPS4) complex is absent because the formation of the complex is slow. The signal appears after 10–15 min.

[9] Memory of chirality is lost if the pH value is raised to 8.

[10] After about five pH cycles the solution becomes milky and scatters because of the formation of extended aggregates: this causes a decrease of the CD intensity.

[11] Melting experiments were also performed: the ICD of Λ- or Δ-$[Ru(phen)_3]^{2+}$/J aggregates disappears at around 90 °C. By lowering temperature at 25 °C we have obtained the starting signal shape.

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