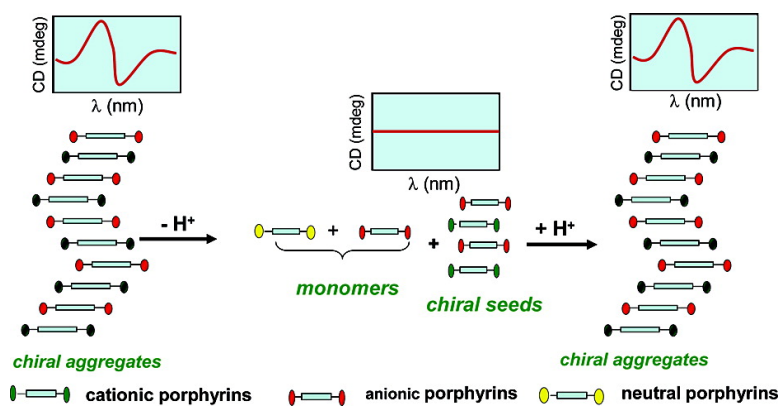


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Switching Off and On the Supramolecular Chiral Memory in Porphyrin Assemblies

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Chirality in noncovalent assemblies springs from either asymmetric arrangements of achiral molecules and/or the presence of chiral components. Concerning the latter examples, it has been shown that, in spite of the removal or substitution of chiral components with achiral ones, certain supramolecular species still retain the imprinted chirality.^{1–14} For these systems, now, chirality is an intrinsic property of the supramolecular memory systems (SuMeS). The ability of these SuMeS to store chiral information mainly originates from their kinetic inertness: they do not reach the lowest thermodynamic level but remain trapped in local, intermediate thermodynamic minima. The stored chiral information can be removed by overcoming the activation energy (E_a) of the intermediate state—with increasing temperature (if E_a is high) or just with time (if E_a is low)—but once removed, chirality cannot be restored anymore. Here we show that, by taking advantage of the remarkable properties of SuMeS built with opposite charged porphyrins and using tailored components, it is possible to accurately design supramolecular systems for which it is possible to perform a complete cycle of imprinting, storing, releasing, and restoring of the memorized chirality.

We have recently published some examples of SuMeS^{2,6,8,9} formed by achiral tetra-cationic (H_2T4 and its planar metallo derivatives, Figure 1a)¹⁵ and tetra-anionic porphyrins (H_2TPPS , Figure 1b). Their aggregation in pure water does not lead to chiral species. However, addition (for example) of CuT4 and H_2TPPS to an aqueous solution containing a chiral template (such as covalent² or noncovalent⁸ amino acid polymers) leads to porphyrin chiral SuMeS.⁹ In particular, it has been recently shown that they retain a chiral structure (an helix) even after removal of the noncovalent chiral template.¹⁶ The main features of these complexes include the following: (i) their formation is driven by the electrostatic interactions between the tetra-cationic and tetra-anionic porphyrins; (ii) they are kinetically inert (their memory lasts for many years) and thermodynamically stable (they resist up to 80 °C); and most importantly, (iii) they are very efficient templates for their own self-propagation: addition of the achiral porphyrin monomer to a 10^{-13} M solution of the SuMeS leads to an enantiospecific growth yield close to 100%.⁸

The relationship between these properties is relevant because it led us to design a new, but very similar, system for which it is possible to imprint, store, release, and restore chirality.

An easy way to “erase” the memory is by “switching off” the electrostatic interactions that hold the porphyrin aggregated. This can be achieved by replacing the four cationic groups in the *meso* position with four *ionizable*, cationic (acid) groups (Scheme 1a). Deprotonation of the four pyridines causes the loss of the positive charges (Scheme 1a) and consequently the disassembly of the supramolecular complex (Scheme 1b). The next (and from a

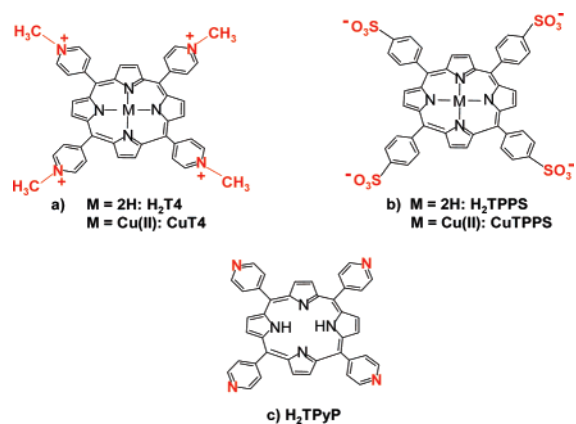
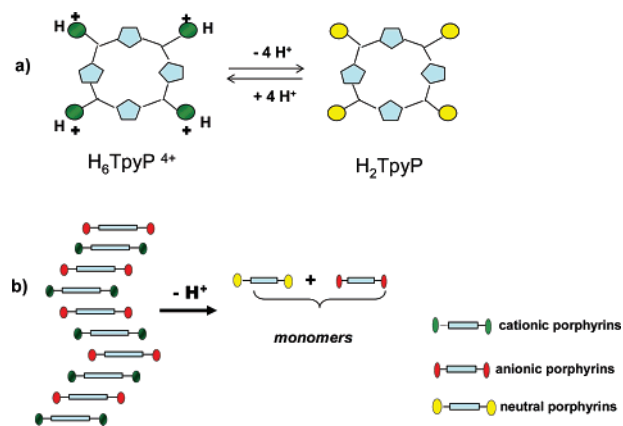


Figure 1. Schematic representation of the porphyrins.

Scheme 1



conceptual viewpoint more multifaceted) step is the reassembly of the *chiral* supramolecular porphyrin complex. Apparently, “switching on” the electrostatic interactions by reprotonating the four *meso* basic groups (Scheme 1a) should lead to the *achiral* complex between the two porphyrins because the chiral information should be lost after the erase reaction (Scheme 2, route a). Yet, recalling that the SuMeS are (a) kinetically inert and (b) excellent chiral templates for their self-propagation, it is conceivable that (a) deprotonation of the four acid groups should be slow and then retard the complete destruction of the chiral assemblies, leaving small amounts of chiral seeds (Scheme 2, route b), and (b) this lasting amount of chiral seeds is enough to promote the formation of the chiral supramolecular complex (Scheme 2, route b). Therefore, route b should be prevalent over route a (Scheme 2).

To make the formation–destruction of the complex reversible, we have substituted CuT4 (Figure 1a) with the free base of the non-methylated analogous H_2TPyP (Figure 1c). Protonation of the peripheral nitrogen atoms ($pK_a \approx 4$) induces four positive (H_6 -

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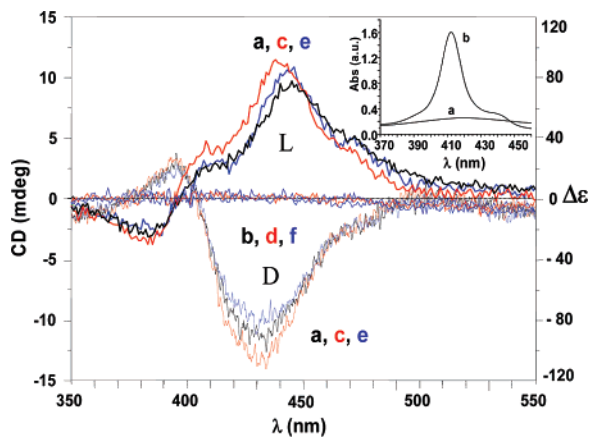
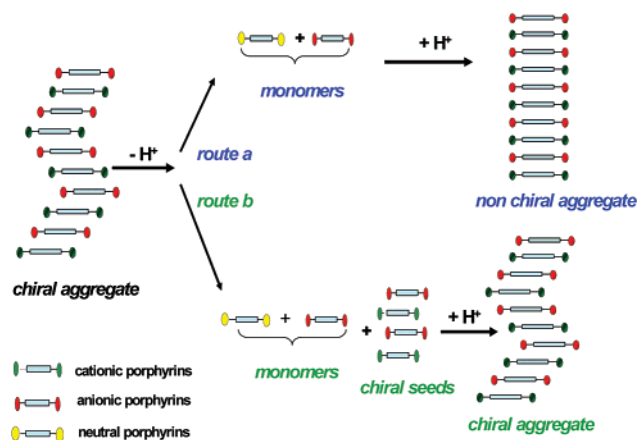


Figure 2. CD spectra of SuMeS at pH 2.3 (a, c, e) and 9 (b, d, f) for the L- and D-imprinted aggregates. The inset reports the absorption spectra at pH 2.3 (a) and 9 (b), respectively. For the sake of simplicity, we report only two absorption spectra.

Scheme 2



TpyP⁴⁺),¹⁷ peripheral charges, leading—from an electrostatic viewpoint—to a situation identical to that of CuT4–H₂TPPS. Accordingly, addition of H₆TPyP⁴⁺ (4 μM) and CuTPPS (4 μM) (Figure 1b) (at pH 2.3 by HCl) to an 8 mM solution of L- or D-phenylalanine (Phe)¹⁸ leads to an induced CD signal in the Soret region.¹⁹ No CD signal is observed when the two porphyrins are mixed in ultrapure water (at pH 2.3) in the absence of L- or D-Phe. Both in the absence and in the presence of Phe, however, porphyrin aggregation leads to about 90% of hypochromicity of the Soret band (see inset of Figure 2).

Elimination of Phe by ultrafiltration²⁰ does not affect the chirality of the aggregates, as shown by the persistence of the CD signal in the Soret region (Figure 2). The experiment shown in Figure 2 demonstrates that, indeed, the ICD of the Phe-free SuMe can be cyclically switched “on” and “off”. The CD of both the L- and D-imprinted aggregates disappears by increasing the pH from 2.3 to 9 (Figure 2, curves b, d, and f) and is restored by lowering the pH back to 2.3 (Figure 2, curves a, c, and e).²¹ CD changes are parallel to the remarkable absorption variations. Protonation at pH 2.3 of the H₂TPyP peripheral nitrogens leads to aggregation and to about 90% of hypochromicity (inset of Figure 2, spectrum a), whereas deprotonation (at pH 9) restores the Soret intensity (inset of Figure 2, spectrum b). We have performed up to 10 consecutive cycles, but there are no apparent limitations to the number of cycles that can be performed.²²

Apparently, the remarkable kinetic inertia of the imprinted aggregates allows for the persistence at pH 9 of (spectroscopically undetectable) chiral seeds which drive the reassembly of the chiral

structure when pH is lowered to 2.3 (Scheme 2, route b). The existence of these seeds can be inferred from the observation that the reassembly cycles of L- or D-Phe-imprinted aggregates lead to retention of the CD mirror image relationship. An even more direct evidence of the chiral seeds comes from experiments having this rationale: the supposed chiral seeds are inert; however, at pH 9, there must be a time after which they dissociate, eventually. From this moment on, chirality will not be reversible anymore, and the system will reassemble in a nonchiral fashion (see route a in Scheme 2). Therefore, we kept various solutions of the imprinted aggregates at pH 9 (that is in the “disassembled” state) for 2, 4, 6, 8, etc. hours before reassembling them (lowering the pH to 2.3). The chiral assemblies have been successfully rebuilt lowering the pH to 2.3 for up to 20 h, but after 24 h at pH 9, lowering the pH to 2.3, the CD is not restored anymore because the chiral seeds are now disassembled.

In conclusion, we have reported here an example of a totally noncovalent memory system able to cycle between “written” and “erased” states. We think that this example opens the route for a general approach and new pathways to design systems able to memorize imprinted chiral information and successively cycle between erased and rewritten states.

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- The pK_a of the inner nitrogen atoms in tetra-cationic porphyrins is around 0. Therefore, at pH 2.3, the percentage of species protonated in the core is about 1%.
- The threshold to observe an ICD is about 1 × 10⁻⁴ M; lower concentrations are not effective in inducing the formation of the chiral aggregates.
- The Soret band is the main feature in the visible region of the porphyrin absorption spectrum and is very sensitive to the aggregation state: porphyrin assembly causes broadening and hypochromicity.
- Phe was removed from the solution at pH 2.3, using Centricon filters (cut-off = 10 kDa), replacing the eluted solution with aqueous solution at pH 2.3. The residual concentration was checked by fluorescence. The lower detection limit for protonated Phe is about 1 × 10⁻⁶ M. After the disappearance of Phe emission, we performed four additional filtration steps.
- No ICD is observed for the achiral aggregates when cycling between pH 2 and 12.
- The reassembly process is time dependent. The CD signal reappears 5 min after the pH-driven (from 9 to 2.3) aggregation and increases with time. The spectra reported in Figure 2 have been recorded for 10 min after the 9 → 2.3 pH variation.

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