

Electronic Supplementary Information to:

Chiral Shape and Enantioselective Growth of Colloidal Particles of Self-assembled *meso*-Tetra(phenyl and 4-sulfonatophenyl)porphyrins

Joaquim Crusats,^b Josep Claret,^b Ismael Díez-Pérez,^b Zoubir El-Hachemi,^a Héctor García-Ortega,^a Raimon Rubires,^a Francesc Sagués^b and Josep M. Ribó*^a

^a Department of Organic Chemistry, University of Barcelona, Martí i Franquès 1, 08028-Barcelona, Catalonia, Spain. E-mail: jmr@qo.ub.es Fax: 34 93 3397878; Tel: 34 93 4021251

^b Department of Physical Chemistry, University of Barcelona, Martí i Franquès 1, 08028-Barcelona, Catalonia, Spain.

Compounds: Sodium salts of the phenyl-and-sulfonatophenyl *meso*-substituted porphyrins were prepared and purified as described elsewhere.^{1,2} H₂TPPS₄²⁻ was tested both as its tetrasodium salt and as its free metal-cation form, obtained as a suspension in water as described elsewhere.³ Solutions of the diprotonated porphyrins were obtained by acidification of the sodium salts of the corresponding porphyrin free bases.

UV/Vis spectra, used to measure the extension of the aggregation, were recorded in a Cary-Varian 5E instrument.

Polarized fluorescence spectroscopy was performed using an SLM Aminco-Browman instrument equipped with calcite polarizers in L-format. All spectra were corrected for blank solution, excitation lamp and detector sensitivity.

Circular Dichroism (CD) measurements were performed in a Jasco J720 instrument. In order to avoid alignment of the aggregates along the walls of the recipient, only long-path cuvettes were used. All reported results correspond to solutions giving the same CD spectra when they were recorded before and after a 90° rotation of the cuvette around the incident light. The experimental procedure to avoid linear dichroic (LD) contributions^{2,4} was followed for all samples. The signature of chirality at the molecular level was the detection of both signs of stable bisignate signals at the absorption wavelengths of the aggregates, as expected from the chiral exciton coupling model.^{5,6}

Experiments on the chirality sign selection by stirring: Several sets of different experimental conditions performed on H₂TPPS₃⁻ showed that not only a symmetry-breaking occurred in this case, but also that the resulting chiral sign could be effectively selected by the polarization associated to the direction of the vortical stirring during aggregation. Similar sets of experiments performed on the other members of the series did not show similar trends of sign selection. However, in the case of H₂TPPS₃⁻, and as expected for any such subtle bifurcation, small experimental differences, i.e. the synthetic batch of the porphyrin, or the purity grade of the inorganic salts regulating ionic strength, may lead to different selectivity degrees by vortical stirring. Further results be published elsewhere.

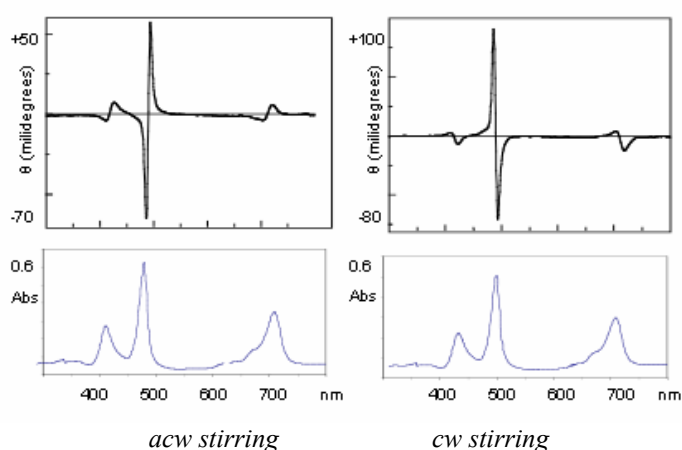


Fig. S1 CD and UV/vis characteristic spectra of a pair of experiments (cw and acw rotary evaporation) of those discussed on the report ($\sim 3 \mu\text{M}$ H₂TPPS₃⁻). Cell optical path: 1 cm. The CD samples consisted of large volumes (2-3 mL) corresponding to representative volumes of the tested solutions. The bisignate CD signals are a consequence of the degenerate character of the transitions.^{5,6}

After optimization, the following general procedure was followed: In a typical experiment, aggregation under vortical stirring was carried out by gentle rotary (cw or acw) evaporation of 500 mL of $\sim 0.12 \mu\text{M}$ aqueous (Milli-Q

purified water: resistivity: 18.2 M Ω) solution of porphyrin after the addition of 0.4 g of NaCl and 14 μ L of 98% H₂SO₄ (Suprapur[®], Merck). The evaporation takes place under vacuum at 40°C (300 rpm, inclination of 45°, ~30 Torr) to a final volume of ~20 mL (about 90±10 min). Aggregation by sudden acidification in unstirred solutions was performed in solutions having the same concentrations of porphyrin and inorganic salts than those of the final solutions obtained by slow evaporation. Reported CD measurements were performed on solutions obtained during the previous days which gave stable bisignate dichroic bands. The stability of these dichroic absorptions bands was corroborated when measured after three months. The Fig. S1 shows the result of a pair of characteristic experiments.

Atomic Force Microscopy (AFM) measurements:

AFM images: The images were obtained by using a Nanoscope IIIa Multimode AFM (Digital Instruments, Santa Barbara, CA) operating in tapping mode in air at room temperature (around 20°C) and typical relative humidity of 40%. Working setpoint amplitude and scan rate were typically between 2-3 nm (typical measured cantilever sensitivity of around 270 mV/nm for the used cantilevers) and 1.5-2 Hz respectively. The AFM probes employed in this work were Silicon cantilevers with integrated conical-shape Silicon tips (Nanosensors, Norderfried Richskoog, Germany) and with an average resonance frequency of 300 kHz and spring constant of 35 N/m. Nominal tip radius and cone angle were 10 nm and 35° respectively. The reported results correspond to the observation of at least three samples aggregated in the same, or very similar, experimental conditions and were imaged in several points of the surfaces so as to obtain reliable measurements.

Surface functionalization: Cleaved mica surfaces were functionalized with 3-aminopropyltriethoxysilane (Aldrich 99%). The procedure involved different steps: First, 100 μ l of the functionalizing reagent, which had been previously filtered, was dissolved in a mixture of 20 ml ethanol/water 10:1. Immediately after the preparation of this solution (<10 s), the freshly cleaved mica surface was immersed in it for 1 minute. Next, the mica surface was withdrawn from the solution, thoroughly rinsed with an ethanol/water 10:1 mixture, and then dried under a N₂ (99.99% purity) stream. After this treatment, a near-to-continuous island-shaped monolayer of the 3-aminopropyltriethoxysilane molecule, with a clean background free of particles or any other possible contamination was always observed on the mica surface.

Sample deposition procedure: Suspensions of the aggregate (in acidic media) were deposited onto the aminosilane-modified 0.5 cm square-sided mica surface resulting in attachment between the aggregated structures (sulfonato anions) and the mica substrate (protonated amino groups). Simple deposition procedures lead mostly to microdrops of concentrate gel, which show a smooth surface as a consequence of the van der Waals interaction between the tip and the gel surface. In fact, appropriate procedures taking into account the colloidal character of the solution (e.g. the favorable effect of the ionic strength in the flocculation) lead to representative samples of the solution particles. It is worth to notice here that most of the particles appear in groups as expected for the flocculation of sols and gels (see Fig. S2). The aggregates have a polyelectrolyte nature, and in spite of adhering to the positively charged AFM mica by a strong electrostatic interaction this can only be achieved after overcoming the stability of the particles in colloidal solution. Thus, owing to the colloidal behavior of these porphyrin mesophases two different procedures were developed for the sample deposition:

(a) Two drops (~100 μ l) of the aggregated porphyrin solution were deposited onto the modified-mica surface. After being in contact at room temperature for one minute, the sample was rinsed during 10 seconds with a jet of deionized Milli-Q water directed to the surface with a squeeze bottle. According to this procedure dispersed particles are deposited on the surface. A random search for particles and high resolution imaging of some of them, gives images as those of Fig. 2: such dramatic helical ribbons can be estimated to be about 5-10 % of the present particles.

(b) Three drops (~150 μ l) of the aggregated porphyrin solution were deposited onto the modified-mica surface for 2 hours. In order to avoid the influence of the hydrodynamic conditions on the adsorption process, the washing stage was performed as follows: After the deposition time, the sample solution was carefully aspirated with a Pasteur pipette and then subsequent cycles of depositing-aspiring with 2-3 drops of MilliQ water were applied (equilibrated 4 times during 20 min with 18.2 M Ω cm⁻¹ Milli-Q water and finally rinsed as above). Finally, the sample was dried under a N₂ (99.99%) stream and imaged immediately afterwards. In this way, the gel drops were flocculated by the long contact with the mica surface and resulted in groups of bundles of colloidal particles, as expected for a flocculation process (see Fig. S2, which is a typical example of the obtained images; see main text). In this respect, the shape and type of the colloidal particles in solution correspond to those of Fig. S2.

The sense of the folding of the helicoidal ribbons of H₂TPPS₃⁻ (e.g. in Fig. 2 of the communication) was determined by AFM section analysis.

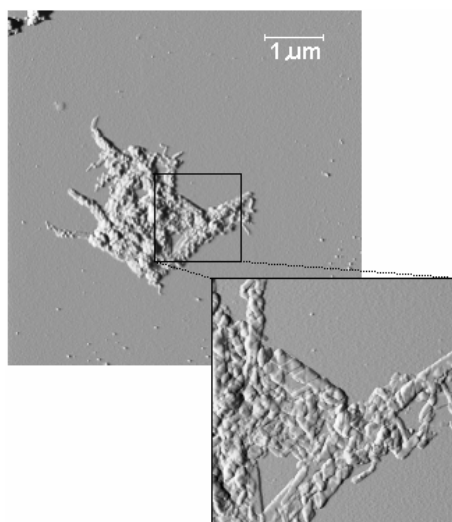


Fig. S2. AFM feedback amplitude signal of $\text{H}_2\text{TPPS}_3^-$ showing several bundles of folded strips, which appear in aggregated solutions obtained by rotary evaporation after flocculation of the gel drops ($\sim 3 \mu\text{M}$ of porphyrin, $\text{NaCl} \sim 0.34 \text{ M}$, $\text{pH} \sim 1.7 \text{ H}_2\text{SO}_4$, see the general procedure followed for the aggregation experiments described in the previous pages), $[(5.7 \times 5.7) \mu\text{m}^2, \text{Z scale: } 0.3 \text{ V}; \text{inset } (1.5 \times 1.5) \mu\text{m}^2, \text{Z scale: } 0.2 \text{ V}]$.

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