

Reversible Mechanical Induction of Optical Activity in Solutions of Soft-Matter Nanophases

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Abstract: Nanophases of J-aggregates of several achiral amphiphilic porphyrins, which have thin long acicular shapes (nanoribbons), show the immediate and reversible formation of a stationary mechano-chiral state in the solution by vortex stirring, as detected by their circular dichroic signals measured by 2-modulator generalized ellipsome-

try. The results suggest that when a macroscopic chiral force creates supra-molecular chirality, it also creates an

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enantiomeric excess of screw distortions, which may be detected by their excitonic absorption. An explanation on the effect of the shear flow gradients is proposed on the basis of the orientation of the rotating particles in the vortex and the size, shape, and mechanical properties of the nanoparticles.

Introduction

The formation of chiral-shaped inorganic nanophases by an initial induction with chiral organic compounds is being studied in the formation of inorganic biological structures (e.g., micro-shells).^[1] This constitutes, in fact, the basis of a new emerging field aimed at the biomimetic preparation of

novel chiral nanostructures and materials starting from achiral materials.^[2]

The action of the mechanical forces originated by flows on chemical phenomena are generally considered to be undetectable and not significant, in spite of their accepted important role in some topics, for example, protein folding.^[3] However, the role of chiral flows (stirring vortices) in the irreversible induction of chirality during the self-assembly of achiral building blocks has been previously reported.^[4] These scarce previous experimental results correspond to aggregates of the diprotonated 5-phenyl-10,15,20-tris(4-sulfonatophenyl)porphyrin (H₂TPPS₃; Scheme 1) obtained in a stirring vortex,^[4a-d] dendrimer aggregates obtained by spin-coating,^[4e] and the aggregates of diprotonated *meso*-tetraphenylporphyrin obtained in a centrifugal liquid membrane cell.^[4f] Nevertheless, these reports have not led to the development of new chiral methodologies. All these previous reports describe experimental systems containing the porphyrin chromophore, as it seems to be an ideal chromophore probe for the detection of chirality by CD spectroscopy because of its high oscillator strength and degenerate transitions.^[5] The difficulty in these types of studies is to ascertain whether or not the experimental optical polarization corresponds to CD [or circular birefringence (CB)] or to other anisotropies of the sample, that is, linear dichroism (LD) and linear birefringence (LB) contributions.^[6] In the case of particles in solution, the measurement of the optical polarization properties has the additional difficulty that the natural convection flows may lead to an average orientation of

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stant of the probes (k_v) was individually calculated for each tip before the experiments using the thermal-noise method,^[17a] and their tip radius was measured using the SPIP reconstruction software (Image Metrology, Hørsholm, Denmark), and a SiO₂ test grating with nanometrically sharp spikes (TGT 1, NT-MDT, Moscow, Russia). Then, the sample was imaged, and only aggregates placed in a direction parallel to the main cantilever axis were indented. This is an important fact because the aggregates are only 35 nm–60 nm wide, and during the indentation process, the tip can slip a certain distance as F increases as proposed previously.^[17b] Then, indenting the aggregates which are parallel to the cantilever ensures that the eventual slipping process will take place on top of the aggregate, as shown in Figure 7.

F is calculated as:

$$F = k_v \times \Delta_z \quad (1)$$

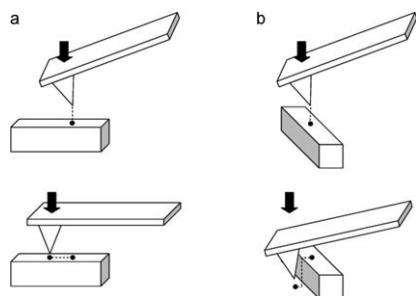


Figure 7. Aggregate indentation by the AFM probe. a) Aggregate parallel to the main cantilever axis, where the slipping process takes place on the aggregate. b) Aggregate perpendicular to the cantilever main axis. As F value increases, the probe tip can lose contact with the aggregate.

where Δ_z is the cantilever deflection, defined as:

$$\Delta_z = \Delta V/S \quad (2)$$

where ΔV is the increment in photodetector vertical signal as the tip contacts the sample, and S is the sensitivity, which is the slope of the contact region of a force curve performed on a rigid sample.

The sample penetration (δ) arising from the exerted F value is evaluated as:

$$\delta = z - \Delta_z \quad (3)$$

where z represents the piezo-scanner displacement in the axis perpendicular to the sample plane. After puncturing the aggregates, a topographic image was captured in order to ensure that the force curve was performed on the aggregate, and that it was plastically deformed.

Mechanical Resistance Measurements

Force spectroscopy is being used to assess the force needed to break a variety of structures (yield threshold, F_y), mainly organic monolayers and bilayers.^[17c] The breakthrough event is detected as a sudden jump in the contact region of the force curves, corresponding to the tip penetrating the sample.^[17d] The HOPG substrate used in these experiments is virtually undeformable under the range of vertical forces exerted by the tip, so the experimental δ value in force curves, in which sample breakthrough is detected, corresponds to the thickness of the aggregates. To ensure that the force curves were performed on the desired structures, AFM topographic images were recorded before and after the indentations.

The Young's modulus (E) can be expressed as

$$E = \left(\frac{F}{A}\right) \left(\frac{L_o}{\Delta L}\right) \quad (4)$$

where A is the area of contact, L_o is the initial length of the material, and ΔL represents the total amount of extension or compression. Being an elastic constant, E can only be calculated as long as the elastic limit of the material is not surpassed, that is, before any plastic deformation.

Several attempts have been done to calculate the E value for nanometrically thin structures,^[17e] and is always limited by the major contribution of the substrate mechanical properties.^[17f] To overcome this problem, Chadwick^[17g] developed a model which takes into account the thickness of a soft sample deposited on a hard substrate:

$$E = \frac{3}{2\pi} \left(\frac{Fh}{R\delta^2}\right) \quad (5)$$

where R is the probe radius, and h is the film thickness. More details about the experimental applicability of this model can be found elsewhere.^[17h] The elasticity modulus E was calculated according to Equation (5). To do that, only the elastic region of force curves exerted on the desired particles was considered, and reported E values were calculated by averaging several force curves performed in one particle, different particles on the same deposition sample, and several samples from different preparation batches.

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