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On the Mechano-Chiral Effect of Vortical Flows on the Dichroic Spectra of 5-Phenyl-10,15,20-tris(4-sulfonatophenyl)porphyrin J-Aggregates

Zoubir El-Hachemi,[a] Oriol Arteaga,[b] Adolf Canillas,*[b] Joaquim Crusats,[a] Carlos Escudero,[a] Reiko Kuroda,[c, d] Takunori Harada,[c] Mònica Rosa,[a] and Josep M. Ribó*[a]

Abstract: Phase-modulated ellipsometry of the J-aggregates of the title porphyrin shows that the material gives a true CD signal. This confirms that there is a real chiral transfer by mechanical forces, mediated by shear gradient flows, from the macroscopic to the electronic transition level. Dislocations in the structure of the aggregate could justify the formation of chirality at the level of the electronic transitions once the mesophases can be sculptured by hydrodynamic gradient flows.

Keywords: chirality · circular dichroism · porphyrinoids · self-assembly

Introduction

It has been reported that diprotonated porphyrins self-assemble into J-aggregates with spontaneous breaking of mirror symmetry.[1] To date, these reports lack definitive proof of the absence of CD artifacts in the dichroic spectra.[2,3] Moreover, in the case of the diprotonated 5,10,15,20-tetrakis-(4-sulfonatophenyl)porphyrin ($H_4TPPS_4^{2-}$) the aggregation process shows a strong statistical bias towards one chirality sign, which makes it necessary to rule out the existence of CD artifacts in these reports. Measurements on the homo-associates of $H_4TPPS_4^{2-}$ using the methodology reported herein unambiguously show that their chiral signal really corresponds to "true" CD contributions[4] and that their CD spectra do not show important differences to those recorded in conventional instruments.[5]

In the case of the title porphyrin $H_4TPPS_3^{-}$ (Scheme 1) it has been statistically shown that a stirring vortex can select the resulting chirality sign of its emerging circular dichroism (CD).[1a–c,e] Two other reports on different systems, which, however, both share the presence of *meso*-substituted porphyrins as the target chromophore, have also shown the effect of the direction of chiral shear gradients upon the sign of the dichroic spectra.[1f,6]

Chiral gradient flows were recently reported[1e] to lead to ordered folded structures in the J-aggregates of $H_4TPPS_3^{-}$ (helices; see, for example, the AFM image in Scheme 1). In the absence of laminar gradients (quiescent solutions), Brownian dynamics lead to irregularly folded structures. Therefore, in this system, the effect of a chiral gradient flow would be to drive the transition towards the more stable folded *meso* forms, thereby producing more regular structures and enantiomeric excesses of the folding sign (*P* or *M*).

Recent reports[7,8] describe a fast and reversible effect of the vortex flow direction on the dichroic sign observed in solutions of supramolecular systems forming nanofibers. This effect is attributed to the detection of the macroscopic chirality of the vortex flow through the alignment of fiber-like mesophases, which would lead to a CD artifact. In spite of the absence of measurements of second-order contribu-

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[a] Dr. Z. El-Hachemi, Dr. J. Crusats, Dr. C. Escudero, M. Rosa,
Prof. Dr. J. M. Ribó
Departament de Química Orgànica
Universitat de Barcelona
c. Martí i Franquès 1, 08028 Barcelona, Catalonia (Spain)
Fax: (+34) 933-397-878
E-mail: jmribo@ub.edu

[b] O. Arteaga, Dr. A. Canillas
Departament de Física Aplicada i Òptica
Universitat de Barcelona, Martí i Franquès 1
08028 Barcelona, Catalonia (Spain)
Fax: (+34) 934039219
E-mail: acanillas@ub.edu

[c] Prof. R. Kuroda, Dr. T. Harada
ERATO-SORST Kuroda Chiromorphology Team
4–7–6 Komaba, Meguro-ku, Tokyo (Japan)

[d] Prof. R. Kuroda
Department of Life Sciences
Graduate School of Arts and Sciences
University of Tokyo
3–8–1 Komaga, Meguro-ku, Tokyo (Japan)

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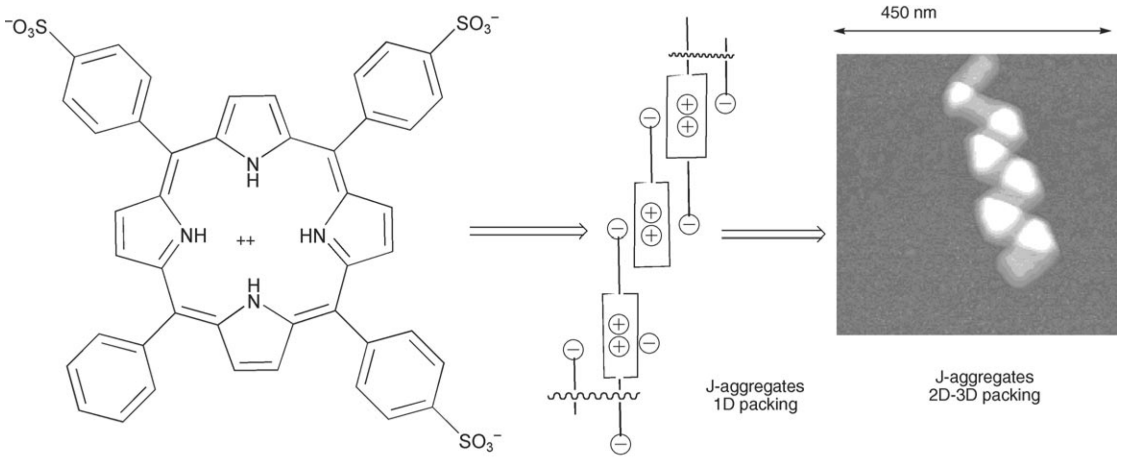
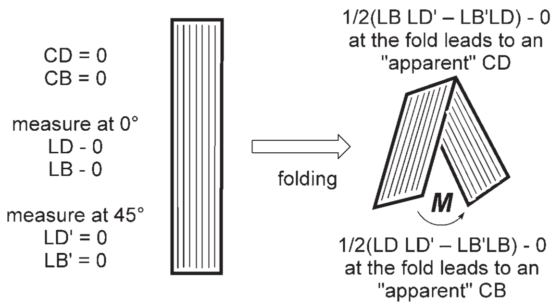


Scheme 1. $H_4TPPS_3^-$ and its J-aggregate structure.

tions to the spectra, this is a reasonable and non-controversial explanation. One may be tempted to extrapolate this finding to previous reports[1a–c,e,f,6] of similar effects. However, here we report that, in the case of $H_4TPPS_3^-$ J-aggregates, the dichroic signals correspond to CD contributions and that therefore, the effect of a vortical flow (i.e. of a chiral shear gradient) is to select the chirality at a molecular level.

Results and Discussion

When we compare the shape of the $H_4TPPS_3^-$ J-aggregate mesophases in Scheme 1[1c,e] and the second-order contributions shown in Scheme 2, the structure of folded helicoidal ribbons suggests the presence of such CD artifacts. However, it should be noted that the second-order contributions giving rise to CD or optical rotatory dispersion (CB) artifacts as a consequence of the folding (along with a preferred orientation of the long ribbons in the solution) would actually be the sign of the folding sense (*P* or *M*), that is, the sign of the chiral shape of the nano-object (Supporting Information). Our previous reports[1a–c,e] on $H_4TPPS_3^-$ J-aggregates demonstrated that the shear gradient acts from the macroscopic level down to tenths and hundredths of nanometers, the level of the chirally shaped particles. Nevertheless, chiral transfer to the level of the electronic transition of the J-aggregate can only be demonstrated if the reported dichroic signals correspond to genuine CD contributions. To clarify this, we measured the dichroic spectra of transparent films of $H_4TPPS_3^-$ J-aggregates at the level of second-order linear contributions by using phase-modulated ellipsometry (PME)[9] (see Experimental Section). As direct examination of their solutions is complicated by experimental difficulties,[10] we studied the transparent films obtained by simply casting the solutions on quartz substrates.[11] In a conventional instrument these films show CD spectra with no significant differences to those of their solutions (see examples in the Supporting Information). This allows us to qualitatively extrapolate the dichroic measurements of the films to those of their solutions. To avoid salt deposits (which interfere with the light scattering), we studied films of the sulfonic acid species of $H_4TPPS_3^-$ J-aggregates, which we obtained in ultra pure water as previously reported.[1e,11]



Scheme 2. Second-order contributions of the linear anisotropies (in a special case of the absence of CD and CB contributions), which in a conventional CD (CB) instrument may lead to apparent CD (CB) measurements.

Figure 1 and Figure 2 show CD and CB as well as the corresponding artifacts from representative samples of $H_4TPPS_3^-$ J-aggregates (for a pair of enantiomorphic samples prepared by the same procedure but with different stirring directions,[1e] see Supporting Information). In all the samples tested the CD artifact contribution to the CD signal

Abstract in Catalan: *Les mesures mitjançant el·lipsometria de fase modulada indiquen que els J-agregats de la porfirina del títol mostren senyals de DC vers. Aquest resultat confirma que els gradients de flux de cisalla, originats per forces mecàniques, poden induir la transferència de quiralitat des de nivell macroscòpic al de transició electrònica. Aquesta formació de quiralitat a nivell de transicions electròniques podria ser deguda a les dislocacions generades pels gradients hidrodinàmics del flux, els quals podrien esculpir les mesofases de J-agregat.*

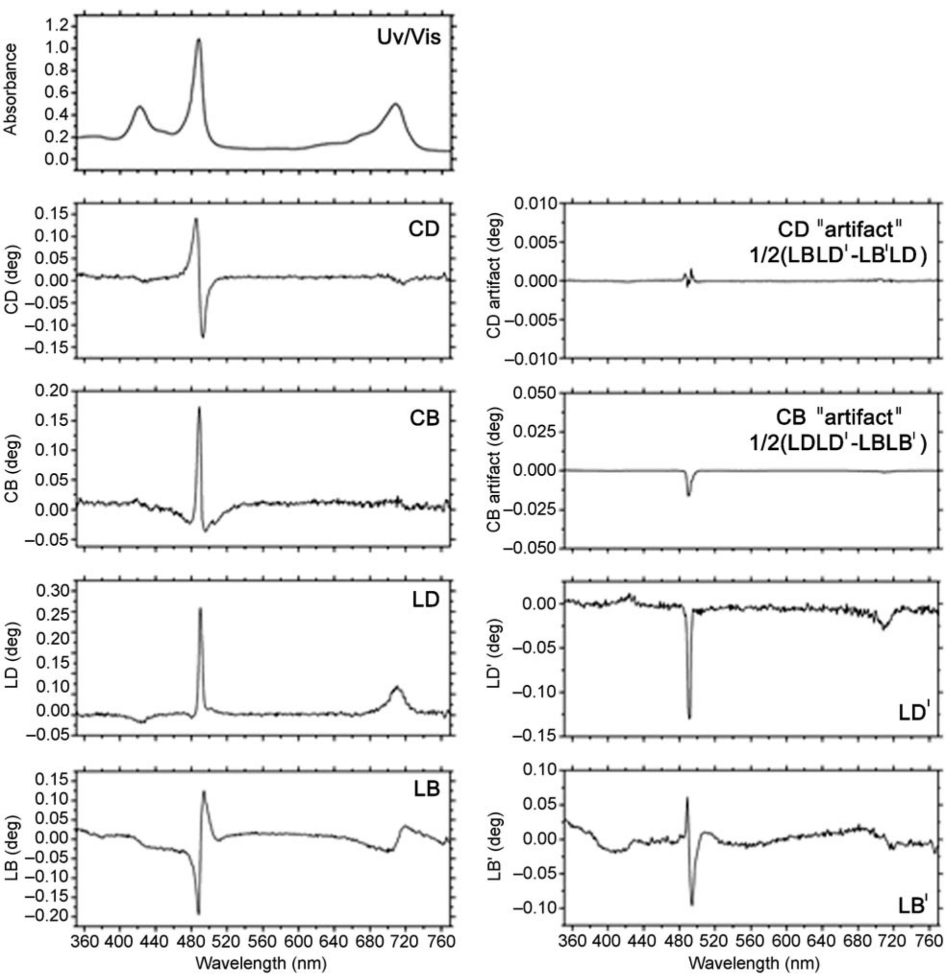


Figure 1. UV/Vis absorption and CD spectra measured by phase-modulated ellipsometry of a J-aggregate sample of $H_4TPPS_3^-$. LD, LD′, LB, and LB′ are measured along the laboratory axis for an arbitrary orientation of the sample and do not correspond necessarily to its maximum value. 1/2(LBLD′-LB′LD) and 1/2(LDLD′-LB′LB) artifact spectra are calculated from the observed spectra.

was low, such that the spectra recorded with the conventional instrument and by PME are not significantly different. We conclude that there is chiral transfer to the level of the electronic transitions via the macroscopic forces of stirring, mediated by hydrodynamic flow shear gradients. This still does not explain the underlying hydrodynamic mechanisms in detail, although gradient shears in interfaces are probably the acting force [solid/liquid (flask or substrate wall and solution) in refs. [1a–c,e,6], liquid/liquid (two immiscible solvents) in ref. [1]]. We are indeed faced with a mechanochiral effect that shows how a macroscopic force (solution stirring) transfers chirality through multiple scale lengths down to the molecular level. In the remainder of this paper we discuss the structural issues that justify such a transfer of chirality down to the level of electronic transitions.

The excited state of the electronic transition of the J-aggregate corresponds to a Frenkel exciton, the coherent length of which, is about 25–45 porphyrin units.[12] The length of the porphyrin building block is about 20 Å, and the porphyrin alignment in the one-dimensional J-aggregated chain forms an angle with the growing axis of about 40°[12] (or lower according to other reports).[13] This leads to lengths of about 35–70 nm; the same order as those of the chirally shaped foldings. Therefore, the dichroic response is probably that of an inherent chiral chromophore.[14] An important aspect of the $H_4TPPS_3^-$ J-aggregate mesophases is their bilayer character and flexibility, because the interface between the two monolayers is bounded by hydrophobic forces.[1e] The folding "deformation" thus needs only small energy inputs. For a discussion of the entropy driven process leading to folded *meso* forms as a more stable form, see reference [1e]. The structural changes necessary to achieve the folding probably also result in conformational changes in the porphyrin building blocks that make them chiral.[15] In the case of a solid phase consisting of achiral building blocks, a chiral elemental cell is not a necessary condition for optical chirality, because chiral dislocations can also cause optical activity. In this respect, screw dislocations are chiral at the electronic level[16] and an enantiomeric excess of them, such as those produced by the folding in the current case, would explain the chirality of the material. There are two examples of chirality originating from screw dislocations in the field of physics, which we summarize below.

The first example begins with an almost 50-year-old report on the preparation of optically active chiral thin films from isotropic materials (CaF_2 and MgF_2) by oblique chemical vapor deposition (CVD) on a flat substrate revolving about its normal as an axis (macroscopic chirality).[17] The resulting material is a helicoidal bianisotropic medium, that is, parallel ordered homochiral nano-helices, whose chiral sign depends on the rotary direction during preparation. Today the preparation of such sculptured nanoscopic structures for chiroptical applications is a widely studied topic, and one which is already yielding commercial applications.[18] Reports of the ellipsometric measurement of these materials confirm that they show optical rotation.[19] In summary, the displacement of the crystal planes, due to the rotating CVD target, generates chiral dislocations in the growing fluoride crystal that lead to a chiroptical response. Since

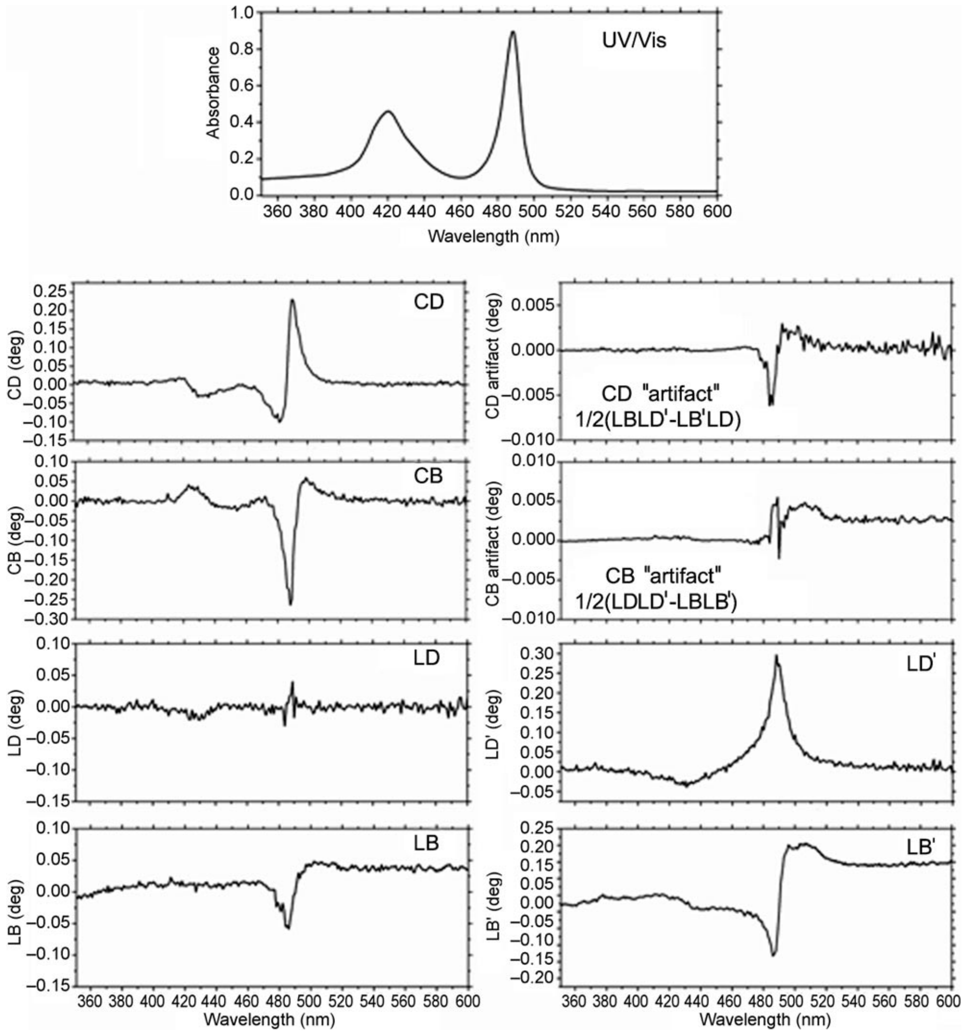


Figure 2. Dichroic spectra measurements (PME) of $H_4TPPS_3^-$ J-aggregates of a sample at the very end of the hierarchical aggregation of the system. LD, LD′, LB, and LB′ are measured along the laboratory axis for an arbitrary orientation of the sample. 1/2(LBLD′-LB′LD) and 1/2(LDLD′-LB′LB) artifact spectra are calculated from the observed spectra.

the distances between dislocation centers are in the Ångstrom range, electronic perturbations are likely. However, this cannot be the same as the macroscopic arrangement reported in reference [8] (a similar alignment to that in Scheme 2). In this macroscopic example there is no contact interface between the active layers and therefore no electronic perturbations can occur. Consequently, such folding can only show a CD artifact due to a combination of linear contributions.

The second example involves an elegant experiment reported by Rikken et al. on the electro-magnetochiral effect brought about by charge-carrier scattering mechanisms.[20] When straight bismuth wires are subjected to torsional deformation, the sign of the magnetoresistence depends on the direction of torsion. Here the screw dislocation creates chiral scattering centers, which scatter the charge carriers (made chiral by the magnetic field). Annealing of the chiral, conductor wire, (i.e., a repairing action against dislocations) leads to the disappearance of the effect.

In our opinion the significant issue for the effect of stirring on chirality[1,2] is that a chiral flow is capable of sculpting nanoparticles, that is, it can potentially manipulate the shape of soft–matter nano-objects. Detection of this phenomenon by CD or CB would be a consequence of the former process.

Concluding Remarks

The recent reports hypothesizing the existence of stirring-induced CD artifacts in certain supramolecular systems when measured in conventional CD instruments[7,8] (in contrast with the reports of refs. [1a–c, e, f, 6]) correspond to systems, in which there is a reversible and fast change in the dichroic spectra associated with the direction of a swirling vortex (CD-silent systems in quiescent solutions). Taking into account the results reported here, in our opinion it is not clear whether or not in these systems the swirling vortex leads to a dichroic signal due exclusively to a CD artifact. The answer to such an intriguing question requires advanced CD methods specifically adapted to the evaluation of optical activity parameters in strongly oriented soft-matter supramolecular systems, which are not possible with commercially available instrumentation. New efforts in this direction (notably by Kuroda's group) using novel chiroptical spectrophotometers that are capable of measuring macroscopic anisotropies to obtain true CD in solid-state specimens are underway. Nevertheless, we have herein unambiguously shown that in the case of the aggregates of the title compound, the swirling-selected dichroic signal that emerges during the mirror-symmetry breaking process corresponds to CD contributions and, hence, that vortical flows can indeed select the chirality at the molecular level.

Experimental Section

General: For the preparation of the title porphyrin and for precautionary notes on the use and manipulation of the sodium-cation-free zwitterionic porphyrins (e.g. adsorption on glass surfaces) see reference [11]. For experimental details on the porphyrin preparation and AFM imaging of their J-aggregates see references [1c,e].

Films were prepared in silica-fused plates by slow casting of solutions ($H_4TPPS_3^- \approx 1.10^{-4}$ м: 4×50 μL: final spot diameter ≈15 mm) of the J-aggregates. To diminish anisotropies only films with absorbance values between 0.5 and 1.1 were used for the phase-modulated ellipsometry (PME) measurements. The UV/Vis and CD spectra (Jasco 810) of the initial solutions and of the films were recorded prior to the PME measurements. The samples did not suffer photochemical transformations during the measurements.

Phase-modulated ellipsometry (PME): The change of the polarization state of a light beam when it interacts with a sample can be described by a matrix of 16 elements, which is called the Müller matrix. All useful Müller matrix elements can be determined in a direct way by using ellipsometric techniques.

$$
e^{-Ae}\left\{\begin{array}{cc}
1+1/2(LD^2+LD'^2) & -(LD'\cos 2\theta + LD\sin 2\theta) \\
-(LD'\cos 2\theta + LD\sin 2\theta) & \begin{array}{c}[1+1/2(LD'^2-LB^2)]\cos^2 2\theta \\ +[1+1/2(LD^2-LB'^2)]\sin^2 2\theta\end{array} \\
CD+1/2(LB'LD-LBLD') & LB\cos 2\theta - LB'\sin 2\theta \\
LD'\sin 2\theta - LD\cos 2\theta & \begin{array}{c}CB+1/2(LD^2-LB^2-LD'^2-LB'^2)\ \sin 4\theta \\ +(LDLD'+LBLB')\cos 4\theta\end{array}
\end{array}\right.
$$

$$
\left.\begin{array}{cc}
CD+1/2(LD'LB-LBLD') & LD'\sin 2\theta - LD\cos 2\theta \\
-LB\cos 2\theta + LB'\sin 2\theta & \begin{array}{c}-CB+1/2(LD^2+LB^2-LD'^2-LB'^2)\ \sin 4\theta \\ +(LDLD'+LBLB')\cos 4\theta\end{array} \\
1-1/2(LB^2+LB'^2) & -(LB\sin 2\theta + LB'\cos 2\theta) \\
-LB\sin 2\theta + LB'\cos 2\theta & \begin{array}{c}1+1/2(LD'^2-LB^2)\sin^2 2\theta + 1/2(LD^2-LB'^2)\cos^2 2\theta \\ -2(LDLD'+LBLB')\sin 4\theta\end{array}
\end{array}\right\}
$$

Scheme 3. The Müller matrix for a general sample with mixed anisotropies (CD, CB, LD, LB, LD′, and LB′) for which *θ* is the rotation angle of the sample.

To determine optical effects such as circular dichroism (CD), optical rotatory dispersion (CB), linear birefringence (LB, LB′), and linear dichroism (LD, LD′) from measurements of elements of the Müller matrix, it is necessary to model the optical properties of the samples in terms of these effects. For an experiment in which the transmission-mode is perpendicular to the incidence beam (this is the usual optical configuration for recording circular dichroic spectra), the correspondence between Müller matrix elements and CD, CB, LD, LB, LD′, and LB′ given in Table VI of reference [3a] seems the most general and accurate approach. This form allows the description of complex systems having both linear and circular anisotropies, and can be easily derived to a simpler form when dealing with specimens with small anisotropies.

The correspondence we use considers second-order linear terms, not usually taken into account by commercial spectropolarimeters, and which sometimes may create significant apparent CD contributions.[3a] However second-order chiral anisotropies, quadratic terms which involve both linear and chiral anisotropies, and any higher order contributions are not taken into account in our approach. Thus, using the same notation as in reference [3a], we formularize the optical sample as indicated in Scheme 3, in which *θ* is the rotation angle of the sample. This approximation is based on the fact that the anisotropies measured are always small (typically all of them are <0.01 rad), so that a first-order approximation of their trigonometric functions can be used. Since anisotropies are proportional to sample thickness, the accuracy of the approximation was assured by keeping film thickness as low as possible. Note that for a highly birefringent (dichroic) system, such a quarter-wave-plate (polarizer) this matrix does not offer a correct description of its optical behavior.

Measurements: Measurements were performed with a home-made spectroscopic phase modulated ellipsometer working in perpendicular incidence transmission mode with the PMSA arrangement. Seven Müller matrix elements were determined by harmonic irradiance analysis using a phase-sensitive detection method.[9] At this moment, for our experimental setup, these measurements require four different optical configurations, in which the sample is azimuthally rotated by 45° from an initial arbitrary position. CD, CB, LD, LB, LD′ and LB′ spectra were computed by using the correspondence described in Scheme 3.

Note that the current paper focuses on CD measurements of the sample at a particular orientation, and on the artifacts that may be mixed in the CD signal. We are aware that we don't completely evaluate some macroscopic anisotropies such as LD and LB since we do not determine their maximum values. These data are also of interest for the study of the structure of the J-aggregates and will be treated in a subsequent paper.

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[1] a) J. M. Ribó, J. Crusats, F. Sagués, J. M. Claret, R Rubires, *Science* **2001**, *292*, 2063–2066; b) R. Rubires, J-A. Farrera, J. M. Ribó, *Chem. Eur. J.* **2001**, *7*, 436–446; c) J. Crusats, J. Claret, I. Díez-Pérez, Z. El-Hachemi, H. Garcia-Ortega, R. Rubires, F. Sagués, J. M. Ribó, *Chem. Commun.* **2003**, 1588–1589; d) P. Chen, X. Ma, P. Duan, M. Liu, *ChemPhysChem* **2006**, *7*, 2419–2423; e) C. Escudero, J. Crusats, I. Díez-Pérez, Z. El-Hachemi, J. M. Ribó, *Angew. Chem.* **2006**, *118*, 8200–8203; *Angew. Chem. Int. Ed.* **2006**, *45*, 8032–8035; f) S. Wada, K. Fujiwara, H. Monjushiro, H. Watarai, *J. Phys. Condens. Matter* **2007**, *19*, 375105(12).

[2] Conventional CD spectrometers do not recognize the artifacts that can arise during analysis of media with mixed anisotropies. For example, when two type of linear anisotropies are present the combination 1/2(LBLD′-LB′LD) may be different from zero and erroneously interpeted as a CD signal (see ref. [3]) (LD and LB are the linear contributions at 0° and LD′ and LB′ those at 45°).

[3] a) J. Schellman, H. P. Jensen, *Chem. Rev.* **1987**, *87*, 1359–1399; b) Y. Shindo, M. Nishio, *Biopolymers* **1990**, *30*, 25–31

[4] a) Y. Shindo, *Optical Engineering* **1995**, *34*, 3369–3384; b) R. Kuroda, T. Harada, Y. Shindo, *Rev. Sci. Instrum.* **2001**, *72*, 3802–3810; c) T. Harada, Y. Shindo, R. Kuroda, *Chem. Phys. Lett.* **2002**, *360*, 217–222.

[5] A more detailed analysis on the dichroic spectra of these aggregates taking into consideration other macroscopic anisotropies will be published elsewhere.

[6] T. Yamaguchi, T. Kimura, H. Matsuda, T. Aida, *Angew. Chem.* **2004**, *116*, 6510–6515; *Angew. Chem. Int. Ed.* **2004**, *43*, 6350–6355.

[7] A. Tsuda, Md. A. Alam, T. Harada, T. Yamaguchi, N. Ishii, T. Aida, *Angew. Chem.* **2007**, *119*, 8346–8350; *Angew. Chem. Int. Ed.* **2007**, *46*, 8198–8202.

[8] M. Wolffs, S. J. George, Z. Tomovi, S. C. J. Meskers, A. P. H. J. Schenning, E. W. Meijer, *Angew. Chem.* **2007**, *119*, 8351–8353; *Angew. Chem. Int. Ed.* **2007**, *46*, 8203–8205.

[9] See Supporting Information and: O. Arteaga, Z. El-Hachemi, A. Canillas, *Phys. Stat. Sol. A*, **2008**, *205*, 797–801.

[10] With our instrument, we cannot measure second-order contributions in colloidal solutions because of possible Brownian-rotation orientation of the long particles. Therefore the 0° and 45° measurements can only be performed in solid transparent samples.

[11] For the preparation and experimental details to avoid the neutralization and the absorption on glass of these sulfonic acid species, see: C. Escudero, Z. El-Hachemi, J. Crusats, J. M. Ribó, *J. Porphyrins Phthalocyanines*, **2005**, *9*, 852–863.

[12] M. A. Castriciano, A. Romeo, V. Villari, N. Micali, L. Monsu Scolaro, *J. Phys. Chem. B* **2004**, *108*, 9054–9059.

[13] J. M. Ribó, J. Crusats, J.-A. Farrera, M. L. Valero, *J. Chem. Soc. Chem. Commun.* **1994**, 681–682.

[14] This does not exclude the chiral exciton coupling between transition dipoles due to the 2D/3D packing, which would explain how in this type of aggregates experimental conditions that lead to different particle sizes and shapes also lead to different shape CD spectra (from monosignate to bisignate signals).

[15] Changes in the conformational angles of the *meso*-aryl substituents result in the change of the S_4 symmetry of the diprotonated porphyrin building block in D_2, C_2, or C_1 chiral symmetries.

[16] R. Bausch, R. Schmitz, L. A. Turski, *Phys. Rev. B* **1999**, *59*, 13491–13493.

[17] N. O. Young, J. Kowal, *Nature* **1959**, *183*. 105–105.

[18] a) R. Messer, A. Lakhtakia, *Mater. Res. Innovations* **1999**, *3*, 217–222; b) L. Lakhtakia, *Mater. Sci. Eng. C* **2002**, *10*, 427–434.

[19] see e.g.: P. I. Rovira, R. A. Yarussi, R. W. Collins, R. Messier, V. C. Venugopal, A. Lakhtakia, K. Robbie, M. J. Brett, *Appl. Phys. Lett.* **1997**, *71*, 1180–1182.

[20] G. L. J. A. Rikken, J. Fölling, P. Wyder, *Phys. Rev. Lett.* **2001**, *87*, 236602 (4pp).

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