Stirring Effects on the Spontaneous Formation of Chirality in the Homoassociation of Diprotonated *meso*-Tetraphenylsulfonato Porphyrins

Raimon Rubires, Joan-Anton Farrera, and Josep M. Ribó*[a]

Abstract: Homoassociates of the achiral title porphyrins in acid solutions show spontaneous symmetry breaking, which can be detected by circular dichroism (CD). The CD spectra are due to differential scattering and differential absorption contributions, the relative significance of which is related to the shape and size of the homoassociate. When an earlier model, designed for the association of these diprotonated porphyrins (*J* aggregates with the geometry of stepped sheets of intramolecular-stabilised zwitterions), was applied to an exciton-coupling point-dipole approximation, the folding of the one-dimensional homoassociates explained the CD signals detected. An effect of the vortex direction, caused by stirring or rotary evaporation, upon the exciton chirality sign was detected. In the case of H_2TPPS_3, the number of experiments performed gave a statistical significance to this effect. This vortex effect can be attributed to enhancement of the chirality fluctuations that originate in the diffusion-limited aggregation to high-molecular-weight homoassociates. In this sense, the phenomenon could be general for supramolecular systems that are obtained under kinetic control, and its detection would be possible when inherent chiral chromophores were being generated in the association process.

Keywords: aggregation · asymmetric amplification · chirality · circular dichroism · exciton coupling · porphyrinoids

Introduction

Chiral-symmetry-breaking processes can be detected in the formation of heterophases. In some cases, autocatalysis leads to high enantiomeric excesses; for example, in the crystallisation of sodium chlorate, 1,1′-binaphthyl and some amino acids.[1] In such cases, stirring affects the growth of the parent nucleation centres and the chain transmission; this leads to the formation of new nucleation centres and can thus enhance the enantiomeric-excess values.

Forty years ago, it was reported that the *J* aggregates of achiral cyanine dyes show induced circular dichroism (CD).[2] In 1976, Hondo and Hada reported that the *J* aggregates of 1,1′-diethyl-2,2′-cyanine iodide or chloride show induced CD, the sign of which depends on the direction of stirring.[3] However, later reports criticised this finding and attributed the CD detected in the cyanine aggregates to linear dichroism (LD) contributions.[4] A recent paper has reported spontaneous chirality in the formation of *J* aggregates of achiral benzoimidocyanines and the authors concluded that LD does not contribute to CD.[5]

Since it is accepted that aggregation and self-assembly play an important role in the origin of life,[6] the little attention generated by these reports on the CD of amphiphilic *J* aggregates is surprising. They could be used as models for the symmetry-breaking processes that lead to optically active systems in primitive biosphere models. Furthermore, the optical properties of the *J* aggregates of these dyes suggest potential applications for their chiral phases.

Ohno et al. have reported the detection of stirring-induced CD in *J*-aggregate solutions of the diprotonated tetrasodium salts of *meso*-tetrakis(4-sulfonatophenyl)porphyrin.[7] However, these results are difficult to reproduce and to interpret. Here we report the spontaneous formation of chirality and that the CD spectra are not only due to differential-absorption contributions. We studied the nature of the detected CD for all 4-sulfonato-substituted tetraphenylporphyrins, their relation to the structure of these aggregates and the effects of stirring during sample preparation on the CD spectra.

The structure of the *J* aggregates of the water-soluble diprotonated porphyrins tested (see Figure 1) arises from the intermolecular association between the positively charged porphyrin ring and negatively charged sulfonato groups; this results in the formation of "polymerised" zwitterions.[8] The quasiplanar structure of the diprotonated porphyrin and the

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[a] Prof. Dr. J. M. Ribó, Dr. R. Rubires, Dr. J.-A. Farrera
Departament de Química Orgànica, Universitat de Barcelona
c/ Martí i Franquès 1, 08028 Barcelona (Spain)
Fax: (+34) 933-397878
E-mail: jmr@qo.ub.es

Supporting Information for this article is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the author: Table with the first series of experiments (91) on H_2TPPS_4-f, H_2TPPS_4, H_2TPPS_3 H_2TPPS_{2O} and H_2TPPS_{2A}. Tables with the chirality signs at the B_H, B_J and Q bands of all compounds and experiments. Example of the evolution of a metastable solution.

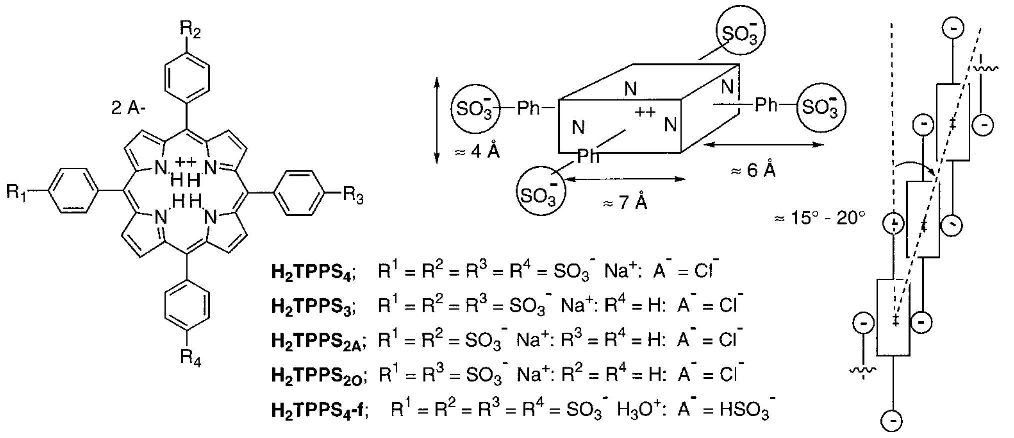

Figure 1. *Meso*-sulfonatophenyl porphyrins. The angle between the "polymerised" chain alignment and the porphyrin plane is shown right.

deformation of the porphyrin ring, with two opposed NH groups above and below the porphyrin plane, facilitate this homoassociation. These *J* aggregates give UV/Vis spectra with strong, red-shifted *B* (Soret) and *Q* bands[7–9] of ≈488 nm and 705 nm, respectively (called here the B_J and *Q* bands). Moreover, at high degrees of association, a blue-shifted *B* band also appears at ≈420 nm (called here the B_H band) due to *H* aggregation.

Results and Discussion

Fresh, unstirred solutions of homoassociates of the diprotonated porphyrins, prepared by acidification of the free base porphryrins (see Experimental Section), only showed weak CD signals, if any. However, after a few hours, CD signals were detected at the wavelengths corresponding to the absorption maxima of the homoassociates. The intensity of the CD signals increased over time. This increase was very strong during the first few days, but after 2–3 months showed asymptotic behaviour. For the same porphyrin, the ellipticity values of old unstirred solutions were about one order of magnitude higher than those of 3–7 day-old unstirred solutions (see, for example, Figure 2a). In these solutions, the increase in ellipticity occurred together with an increase in homoassociate at the expense of nonassociated porphyrin. The high increase in ellipticity and the disappearance of nonassociated monomer (≈435 nm) are shown in Figure 2a.

After approximately two weeks, the magnetically stirred solutions showed ellipticity values of the same order as three-month-old unstirred solutions (see, for example, Figure 2b). Here the ellipticity increase cannot be attributed simply to the increase in homoassociate, as it can for the unstirred solutions, since the stirring maintains the amount of homoassociate at the same order of magnitude.

This type of experiment has the difficulty that the acidification is performed in relatively highly concentrated solutions, so that aggregation occurs suddenly, that is, to a large extent and in an uncontrolled manner. To overcome this, we have performed other types of experiments, in which acidification was performed in very dilute solutions so that aggregation did not occur, and these solutions were then concentrate by rotary evaporation (see Experimental Section). The rotary evaporated solutions show ellipticity values of the same order as old, unstirred solutions and, once they have been allowed to stand, they only showed small changes, if any, in their CD spectra. The rotary evaporation method for preparation of homoassociates allows experiments to be performed in which the effect of stirring on the formation of chirality is shown. Figure 2c shows that the ellipticity values of a recently prepared concentrated solution (20 mL) of H_2TPPS_4-f increase following dilution (to 500 mL) and rotary evaporation back to 20 ± 2 mL (see Experimental Section).

Comparison of the ellipticity values of porphyrins shows an order according to the number of 4-sulfonatophenyl substituents (Figure 3). Probably, the degrees of freedom for intermolecular interactions between the sulfonato groups and the

Abstract in Catalan: *En solucions àcides, aquestes porfirines aquirals formen homoassociats que presenten trencament de simetria espontani, el qual hom detecta per DC. Els espectres de DC són deguts al conjunt de contribucions de dispersió diferencial i d'absorció diferencial, la importància relativa de les quals depèn de la mida i forma dels homoassociats. Segons un model publicat anteriorment per a l'associació d'aquestes porfirines diprotonades, llurs J agregats són zwitterions estabilitzats intermolecularment per formació de tires de porfirines escalonades. L'aplicació de l'aproximació punt-dipol del model d'acoblament excitònic a aquestes estructures explica el DC per la formació de colzes en els homoassociats monodimensionals lineals. Agitant o rotoevaporant hom detecta un efecte de la direcció del vòrtex en el signe de la quiralitat. En el cas de* H_2TPPS_3 *el nombre d'experiments efectuats dòna significat estadístic a l'efecte observat. Aquest efecte de la direcció del vortex podria esser atribuïble a una amplificació de les fluctuacions de quiralitat que es produeixen durant l'agregació limitada per difussió cap a homoassociats d'alt pes molecular. En aquest cas, el fenòmen podria ser general en la formació sota control cinètic d'homoassociats d'alt pes molecular, i detectar-lo fora possible quan, com en el cas que hom presenta, els cromòfors generats en el procés d'associació fossin inherenment quirals*

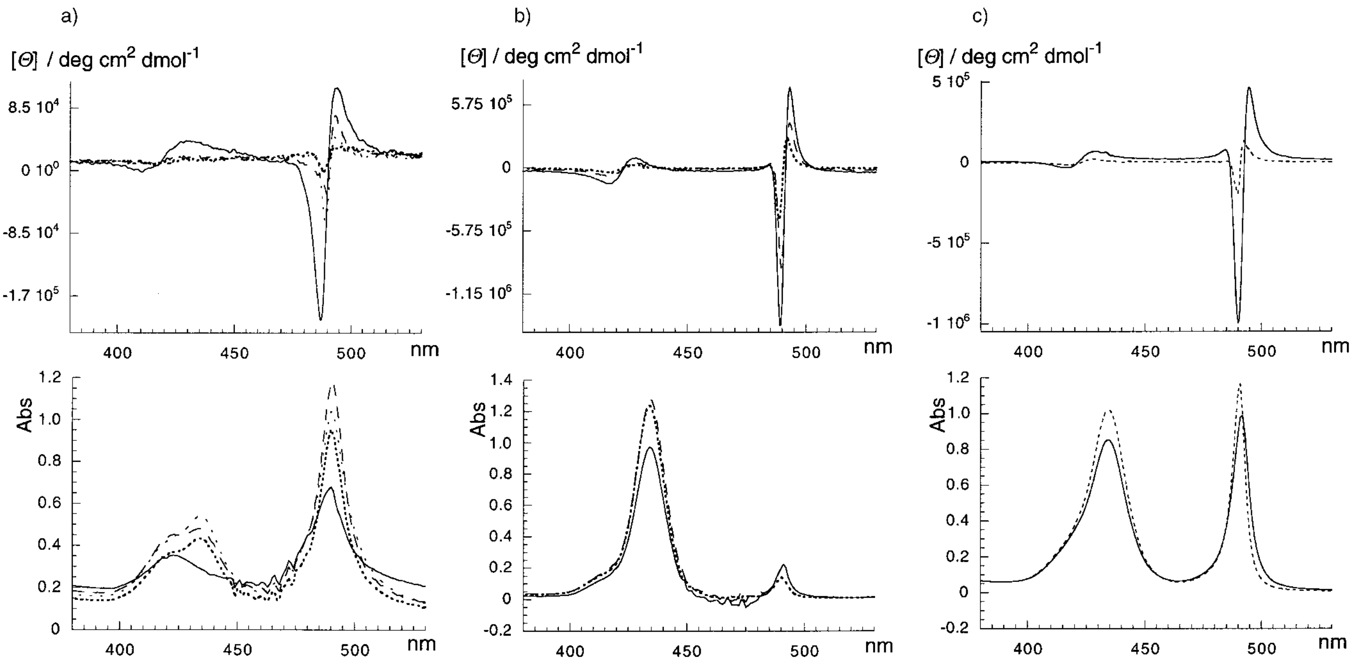

Figure 2. CD (top) and UV/Vis (bottom) spectra of unstirred and stirred solutions of the title porphyrins: a) unstirred H_2TPPS_3: (•••••) freshly prepared, (----) after 2 days, (–––) after 7 days, (——) after 2 months. b) ACW magnetically stirred H_2TPPS_4: (----) after 4 days, (–––) after 20 days, (——) after 1 month. c) ACW rotary evaporated H_2TPPS_4-f: (–––) freshly unstirred solution, (——) after dilution to 500 mL and rotary evaporation to the initial volume.

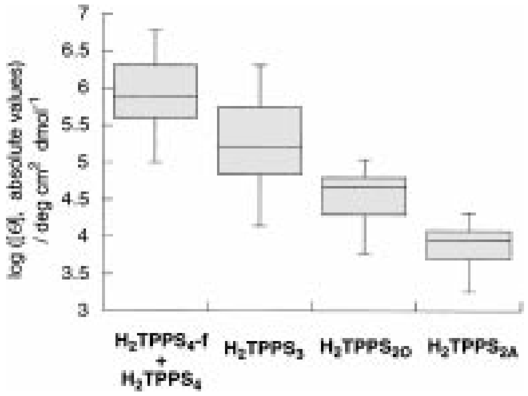

Figure 3. Box diagram of the module of the ellipticity ([Θ]) values for stirred (magnetically and rotary evaporated) solutions of diprotonated *meso*-sulfonatophenyl porphyrins (see also Table S1 in the Supporting Information). The ellipticity values are those of the most intense signal (B_J transition) and are calculated on the basis of the total porphyrin concentration.

central dicationic ring influence the degree of formation of chirality.

With respect to the results previously reported for $TPPS_4$[7] these experiments show two principal differences: a) in some cases, the CD signals did not correspond to bisignate dichroic peaks and b) the correspondence between stirring or rotary evaporation direction and the chirality sign was very low. For some compounds, in particular for H_2TPPS_4, a nonstatiscal distribution of the chirality signs was detected even for the unstirred solutions (see Supporting Information).

Types of CD signals: The CD signal for the *B* transition of the *J* aggregate ($B_J \approx 488$ nm)[10] was more intense than the other signals, that is the *Q* band ($Q \approx 705$ nm) and the *B* band of the *H* aggregates ($B_H \approx 420$ nm). H_2TPPS_4-f, H_2TPPS_4, and H_2TPPS_3 gave a similar pattern of CD spectra, and only very weak CD signals, if any, were detected at the wavelength corresponding to their monomer transitions (Figures 2 and 4). This suggests that the supramolecular structure of these homoassociates does not incorporate a monomer.[11] In contrast, the CD spectra of H_2TPPS_{2A} and, to a certain extent, those of H_2TPPS_{2O} can only be interpreted by assuming that the monomer *B* transition is also CD active and that the broad pattern of their signals is different from those of the other diprotonated porphyrins (see Figure 4).

A comparison of the CD spectra reveals that two types of signal were detected: a) bisignate bands that cross the wavelength of the corresponding *Q*-, B_J- or B_H-band absorption maxima at zero ellipticity and b) single absorption bands with maxima at these wavelengths (Figure 5). In many experiments the CD signals reflect the varying contribution of each band type.

The single CD bands often appear in solutions with a high degree of association and their intensity could be related to an increase in aggregation. This points to CD spectra with variable contributions of differential absorption and differential scattering.[12] The differential scattering contribution to CD has been extensively discussed in the case of biopolymers and biological organelles.[13] Bisignate CD bands are caused by the differential absorption of two near-to-degenerate transitions.[14] The differential-scattering contribution of these degenerate transitions gives a single CD band, because both transitions contribute with the same sign.[13c] Comparison of CD spectra (≈300) reveals the ellipticity sign of the differential scattering with respect to those of the differential-absorption contribution. According to the accepted nomen clature of positive exciton chirality for negative short wavelength and positive long wavelength Cotton effects, and vice versa,[14b,c] the results show that, for the B_J and Q transitions, a negative differential-scattering ellipticity contribution corresponds to positive exciton chirality and, in the case of the H transition, a positive differential-scattering contribution corresponds to a positive exciton chirality, and vice versa (see Figure 5).

The relative signs of the exciton chirality for the B_H, B_J and Q transitions were the same, with only a few exceptions in which the CD spectra changed to all three bands having the same chirality sign when solutions were left to stand (see example in the Supporting Information). This is discussed below in relation to the chromophore interaction and the structure of the homoassociate.

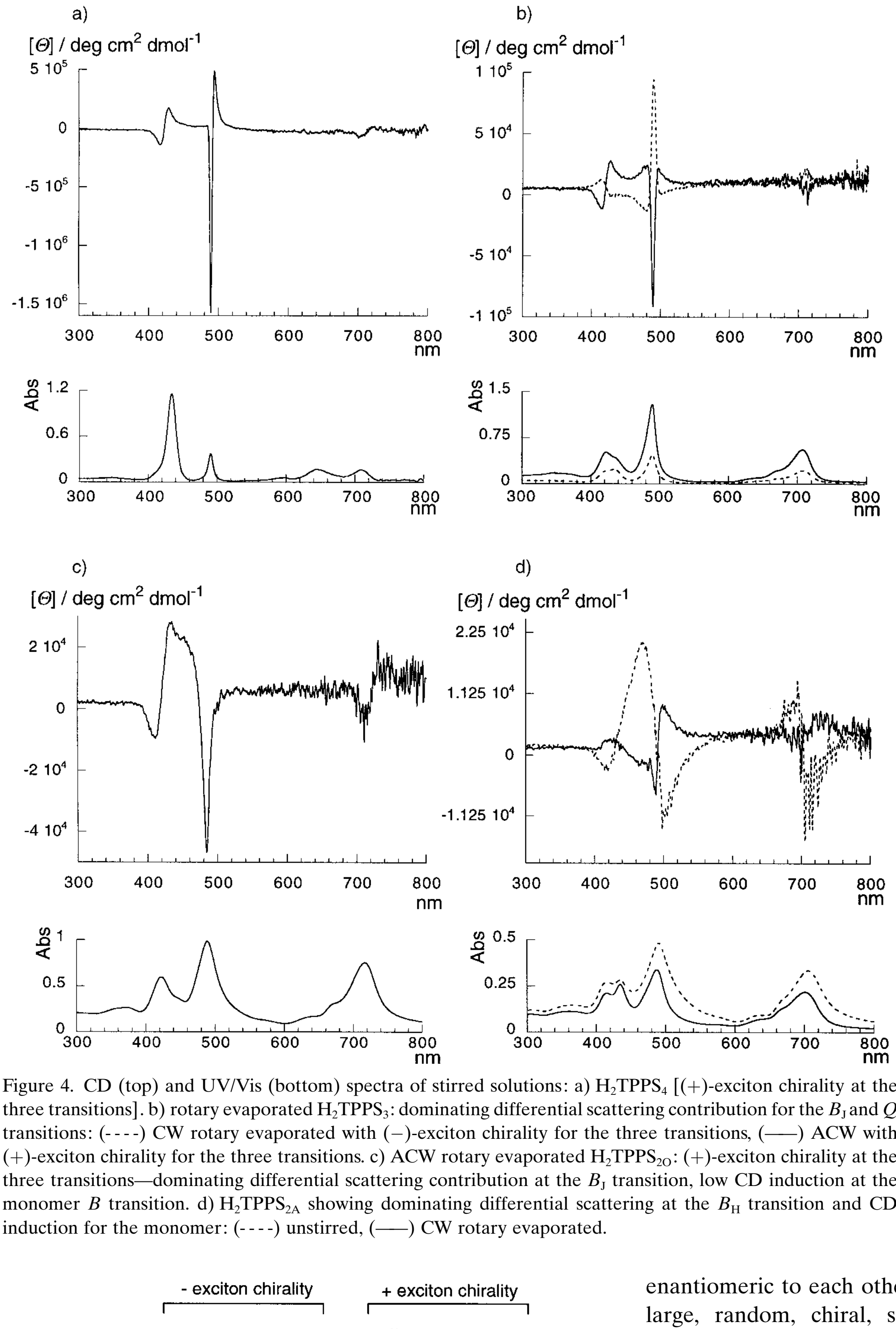

Figure 4. CD (top) and UV/Vis (bottom) spectra of stirred solutions: a) H_2TPPS_4 [(+)-exciton chirality at the three transitions]. b) rotary evaporated H_2TPPS_3: dominating differential scattering contribution for the B_J and Q transitions: (----) CW rotary evaporated with (−)-exciton chirality for the three transitions, (——) ACW with (+)-exciton chirality for the three transitions. c) ACW rotary evaporated H_2TPPS_{2O}: (+)-exciton chirality at the three transitions—dominating differential scattering contribution at the B_J transition, low CD induction at the monomer B transition. d) H_2TPPS_{2A} showing dominating differential scattering at the B_H transition and CD induction for the monomer: (----) unstirred, (——) CW rotary evaporated.

Comparison of the CD spectra for the same compound reveals differences that cannot be attributed to different enantiomeric excesses. Rather it shows the different relative contributions from differential scattering and differential absorption and also different relative intensities between transitions. That is, comparison of CD spectra of reversed signs shows that the molecules from which corresponding spectra were generated were never enantiomeric to each other. This is the expected result for a large, random, chiral, supramolecular structure obtained through a diffusion-limited process; the exact mirror image (virtual enantiomer) can never be obtained.[15] With respect to the definitions of chirality for these systems that are given by the authors of ref. [15], the handedness reported here corresponds to the "natural enantiomers". CD spectra can come from a "racemic" mixture of natural enantiomers with different size and shape. For example, in a 1:1 mixture of natural enantiomers, one with dominating differential scattering and the other with dominating differential absorption, the CD will not be zero. In three experiments (see Supporting Information) we detected CD spectra, which can be understood according this explanation.

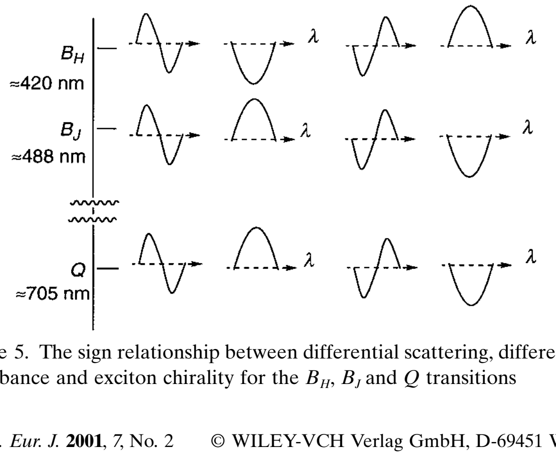

Figure 5. The sign relationship between differential scattering, differential absorbance and exciton chirality for the B_H, B_J and Q transitions

The relationship between stirring direction and chirality sign: In a first series of experiments, the direction of stirring did not have any significance to the sign of the induced chirality with respect to the unstirred solutions (except for H_2TPPS_3, for which see Supporting Information). In some compounds, this could be attributed to an inadequate number of experiments. However, in the case of H_2TPPS_4, in contrast with previously reported results,[7] the negative exciton-chirality sign could not be obtained even with a relatively high number of experiments (27). Furthermore, for this compound, the ellipticity values of stirred and nonstirred solutions were also of the same order.

Unstirred solutions of H_2TPPS_3 showed a distribution (5/4) of the sign of the exciton chirality that agrees with that expected for spontaneous induction. The stirring experiments show chirality signs 5(+)/4(−) for the clockwise (CW) direction and 8(+)/2(−) for the anticlockwise (ACW) direction. However, when we submitted some of these solutions to a second rotary evaporation, that is, fresh dilution and rotary evaporation in the same direction as for the first rotary evaporation, the significance of the ACW stirring was maintained [5(+)/1(−) to 4(+)/2(−)] and the CW stirring resulted in a change of the chirality sign [4(+)/3(−) to 1(+)/6(−)]. This suggests that there is a stirring-direction effect on the chirality sign; CW for (−) and ACW for (+).

Therefore, we performed a second series of experiments in order to detect the effect of the stirring direction on the chirality sign. We took as our target the case of H_2TPPS_3. We did not take into account the compounds H_2TPPS_4, H_2TPPS_{2A}, H_2TPPS_{2O} and H_2TPPS_4-f: H_2TPPS_4, because we assumed that other chirality induction effects were acting; H_2TPPS_{2A} because of its CD spectra, and probably the structure of its *J* aggregate,[8b] which show significant differences from those of the other tested diprotonated porphyrins; H_2TPPS_{2O} and H_2TPPS_{2A} because the hydrophobic phenyl groups also give intermolecular association[8b] (which probably results in the formation of micelles including "monomeric" porphyrin, as suggested by their CD spectra); and H_2TPPS_4-f because of the different equilibria implied in the formation of the homoassociate (H_2SO_4 segregation compared to NaCl segregation for the rest of the diprotonated porphyrins). We performed some of the experiments by applying simultaneous parallel rotary evaporations in both rotation directions. Here, the effect of CW compared with ACW rotary evaporation was more evident than in experiments not performed in simultaneous parallel mode. This suggests that many unidentified experimental factors influence the formation of chirality and remained uncontrolled under our experimental conditions. When the experiments were performed in simultaneous parallel mode and by the same operator, the differences between these unidentified factors decreased. We identified one of the experimental factors that influence the chirality in the final volume of the rotary evaporated solutions. Owing to the large initial volume, the final volume (20 mL in a 1 L round bottom flask) was only estimated. In spite of the fact that an additional control was performed (UV/Vis spectra of the final solution) a difference of ± 2 mL was unavoidable. Below 14 mL, the viscosity of the sample and the small amount of solution cause a change in the vortex of the solution from being in the same direction as the rotary evaporator rotation to a more complex movement that basically corresponds to its being in the opposite direction to the rotation of the flask.[16] The effect of this change in the vortex was studied in experiments where rotary evaporation was performed to ≈25 mL, then, after recording its CD spectra, the same solution was rotary evaporated to 10 ± 2 mL. In all these experiments (5), which led to a marked increase in homoassociation as a consequence of the increased concentration, a decrease in the ellipticity of the B_J transition was recorded (see, for example Figure 6a). In one experiment (see Figure 6b), even the exciton-chirality sign for B_J changed besides the change to dominating differential scattering for B_H. This effect of the change of the vortex (on going from 25 mL to 10 mL by rotary evaporation) is clear for fresh solutions but not for old ones. Old, unstirred solutions (> 3 months old) did not show significant changes in the CD spectra when they were subjected to the above experiment.

We could also detect that the addition of a higher ratio of sulfuric acid (see Experimental Section) results, at least for H_2TPPS_3, in a better correlation between vortex direction and chirality sign.

A series of experiments on H_2TPPS_3 in sulfuric acid were conducted in which the effect of change of vortex direction was avoided by rotary evaporation down to a slightly higher final volume. These resulted in a high significance of the stirring direction with respect to the chirality sign (see Table 1

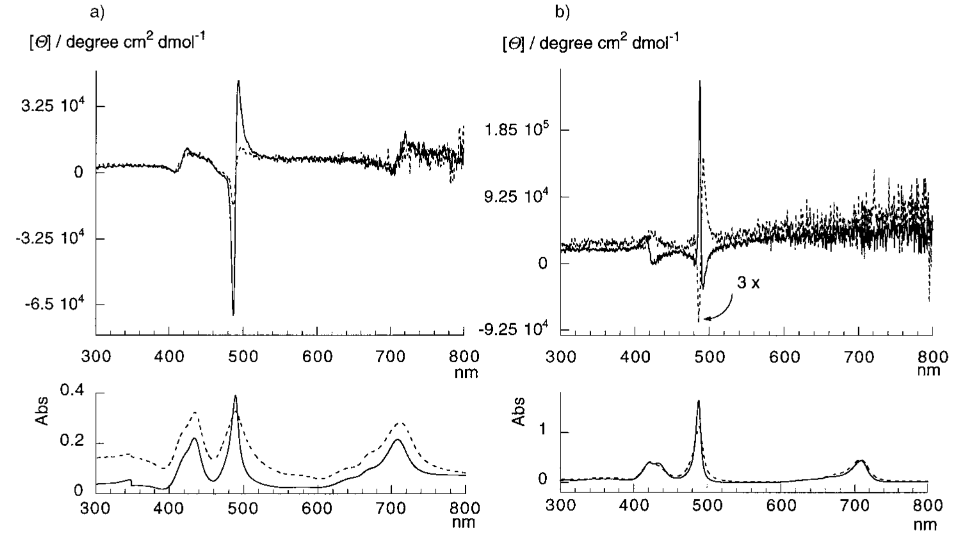

Figure 6. CD (top) and UV/Vis (bottom) spectra showing the effect of rotary evaporation to below the volume limit where the vortex of the solution changes direction: a) ACW rotary evaporated H_2TPPS_3 solution. b) CW rotary evaporated H_2TPPS_3 solution. (——) 30 mL final volume, (- - - -) 12 mL final volume.

Table 1. Sign of the CD exciton chirality for the B_J transition[a] in rotary evaporated solutions of H_2TPPS_3. The experimental conditions of this series of experiments differ from those of first series of experiments (see Supporting Information) in that the second rotary evaporation experiments were performed after dilution to the initial conditions.

	CW			ACW			Totals	Unstirred		
	+	nd	−	+	nd	−		+	nd	−
first evaporation	5	0	15	18	0	3	41			
second evaporation	1	0	19	19	0	2	41			
								6	0	7
totals	6	0	34	37	0	5	82	6	0	7

[a] + (−) is for a bisignate signal − /0/ + (+ /0/ −), on going from low to higher wavelenghts, or for the corresponding differential scattering contribution; nd is for CD not detected. Measurements were performed 48 h after preparation of the solution.

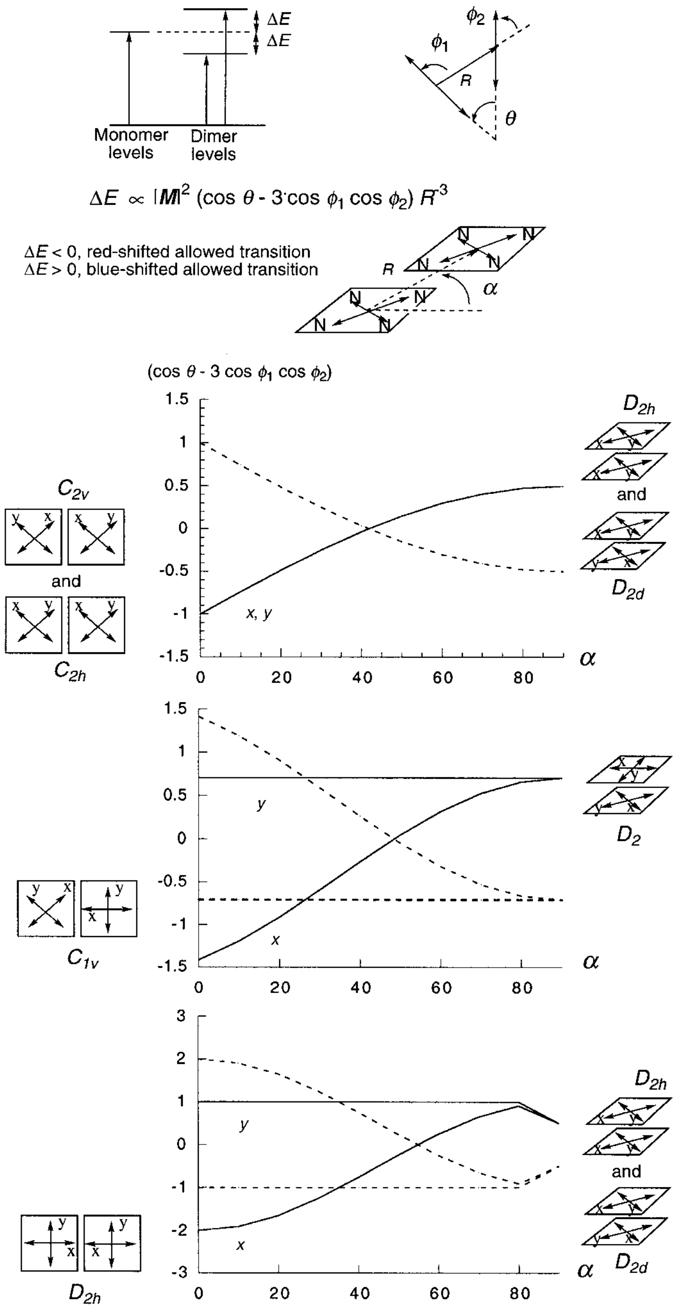

Figure 7. Point-dipole approximations of the exciton coupling models of two interacting porphyrin rings in edge-to-edge and face-to-face arrangements for several orientations of the degenerate pairs of transition dipole moments: (——) allowed transitions, (- - - -) forbidden transitions.

and Figure 7). The expected chirality sign was obtained in 80 % of the first rotary evaporation experiments and in 93 % of the second, that is, in 87 % of the whole set of experiments. This illustrates how the experiments could be optimised to obtain high correlation between chirality sign and vortex direction. Since the addition of acid and NaCl was not necessary for the second rotary evaporation, effects, other than those caused by stirring, on the symmetry breaking (such as the history of the free base sample) probably disappear.

These results point towards a relationship between stirring and the formation of chirality, which is not easy to detect as other effects can induce a change in the chirality sign of the symmetry-breaking process.

In the case of H_2TPPS_4 (see Supporting Information), the clear deviation of its symmetry breaking from statistical behaviour must be related to some uncontrolled induction effect. We performed second rotary evaporation experiments for six pairs [CW 6(+) and ACW 6(+)] of H_2TPPS_4 solutions. The results were 1(+)/5(−) for CW stirring and 5(+)/1(−) for ACW stirring. This confirms that the stirring direction has an induction effect on the chirality sign, but that there are also other induction effects. These induction effects could be caused by, for example: a) chiral effects in the preparation of the sample, b) the history of the sample and c) chiral contamination originating in the laboratory. We believe that the first and third reasons can be ruled out, because different vessels and slightly different procedures were tested but no significant differences were detected. With respect to the history of the sample, it is significant that the free bases also aggregate. In fact, $TPPS_{2O}$ and $TPPS_{2A}$ give, respectively, J and H homoassociates that, in some cases, have CD spectra.[17] However, in the case of the free base $TPPS_4$ we did not detect CD spectra under several different sets of experimental conditions. With respect to chiral contamination, we verified the absence of optically active substances, but the presence of contamination by low-UV/Vis-absorbing chiral objects, such as bacteria or traces of biopolymers, cannot be ruled out. The detection by CD of chiral heteroassociates of soluble porphyrins, such as those described here, with DNA and polypeptides has been reported.[18] In these cases, the CD is induced through the perturbation of the monomeric chromophore in association with a chiral matrix; however, in our case, it would be due to induction during the process of obtaining a high-molecular-weight chiral homoassociate (CD is detected for the homoassociate-absorbing bands), that is, to induction caused by traces of a chiral contaminant when a chiral supramolecular structure of the homoassociate is generated. Chiral heteroaggregates of H_2TPPS_4 with α-helical polyglutamic acid (1:10) have been described and show similar CD spectra that those described here.[19]

We performed 18 experiments with H_2TPPS_4, the solutions of which were obtained from a $TPPS_4$ sample prepared by following a different synthetic work-up from that used for the first series of experiments. In this case, the results point to statistical symmetry breaking for the unstirred solutions

[2(+)/2(−)] and to sign induction for the rotary evaporated solutions of 4(+)/3(−) for CW stirring and 6(+)/1(0) for ACW stirring. The current preparation of $TPPS_4$[8b] involves filtration through infusorial earth (Celite 535). This was avoided in this new work-up and suggests that contamination with infusorial earth induces chirality. This contamination was not present in the other porphyrins because, in spite of being obtained by following the same work-up as for $TPPS_4$, they were submitted to a final purification by column chromatography. This was not necessary for $TPPS_4$.

However, when we attribute an induction effect to the infusorial earth contamination, we attribute the induction to chiral objects rather than to chiral molecular systems. A chiral object would act at the mesoscale level. If we assume that the formation of chiral supramolecular aggregates of the diprotonated porphyrins tested here occurs through kinetically controlled processes, that is, the diffusion-limited formation of large random structures,[15] then symmetry breaking is possible. However, the weak chiral forces that act during stirring or growth upon chiral objects, must act upon these kinetically controlled processes.[6b, 20] We believe that this is only possibility at the mesoscale level.

Probably, the chirality detected corresponds to a low enantiomeric excess of chiral chromophores, but CD is detected because of the strong rotational strengths of the inherent chiral chromophores. Thus, a model of an inherent chromophore that is in agreement with the previously proposed structure of the homoassociates[8c] and the results reported here would explain the CD detected.

Structure of the homoassociates versus choromophore coupling: The exciton-coupling model in its simple exciton point-dipole form[14] has been used by many authors to relate the UV/Vis spectra of porphyrin dimers, oligomers and heterodimers to their structure.[21] Although, in the case of porphyrins, it has been claimed that the transition-monopole treatment gives better predictions than the point-dipole treatment,[22] we assume that the intense spectral shifts caused by the aggregation of the porphyrins reported here ensure that a simple model would be sufficient for a qualitative explanation.

The *B* band of porphyrins shows two degenerate perpendicular transitions B_x and B_y (with the porphyrin plane as *xy* plane). According to Gouterman's four-orbital porphyrin model, these transitions are aligned with the opposite nitrogen atoms.[23] When we considered the case of porphyrin dimerisation with porphyrin planes parallel to each other: an edge-to-edge (*J*-aggregate-like) or a face-to-face (*H*-aggregate-like) dimer, there were three possible orientations of the pairs of transition dipoles (Figure 7). In the case of the face-to-face dimer, all possible relative orientations of the transition dipole result in two degenerate, allowed blue-shifted transitions. This agrees with the experimental CD spectra of the B_H band (bisignate differential-absorption contributions). However, for edge-to-edge dimerisation only the $C_{2h}-C_{2v}$ arrangement, which corresponds to the geometrical arrangement of the *J* aggregates,[7, 8] is in agreement with the experimental CD spectra of the B_J absorption, that is, two degenerate bands for the allowed red-shifted transition.

However, this dimer model does not account for the chirality of system. Therefore, the same arguments as for the dimer should be applied to *J*-oligomers of similar geometry. A collective exciton-coupling model cannot be applied to these one-dimensional homoassociates; the chromophore interaction between neighbours is much more intense than the rest of the interactions. In the case of the one-dimensional 180° association (Figure 8), the interactions between neighbouring rings (1-to-2) must be higher than the 1-to-3 interactions, because of the dependence of the interaction energy on R^{-3} (Figure 7). According to the geometry of the association,[8] and assuming standard interatomic distances ($R_{12} \approx 10$ Å and $R_{13} \approx 20$ Å), the 1-to-2 interaction is eight times higher than the 1-to-3 interaction. The 1-to-4 interactions are two orders of magnitude smaller than 1-to-2 interactions. The one-dimensional 180° chromophore interaction model can then be approximated to a porphyrin that only interacts with its two neighbouring porphyrins.

The *J* homoassociation can also show 90° folding due to structural defects in the supramolecular assembly or, as in the case of H_2TPPS_{2A}, because linear 180° arrangements are not possible. The 90° folding shows *P*, *M* chirality (Figure 8) because of the angle of 15°–20° between the chain alignment and the porphyrin plane (see Figure 1). The CD detected in the B_J and *Q* transitions could be attributed to this folding. However, this model only agrees with the experimental data

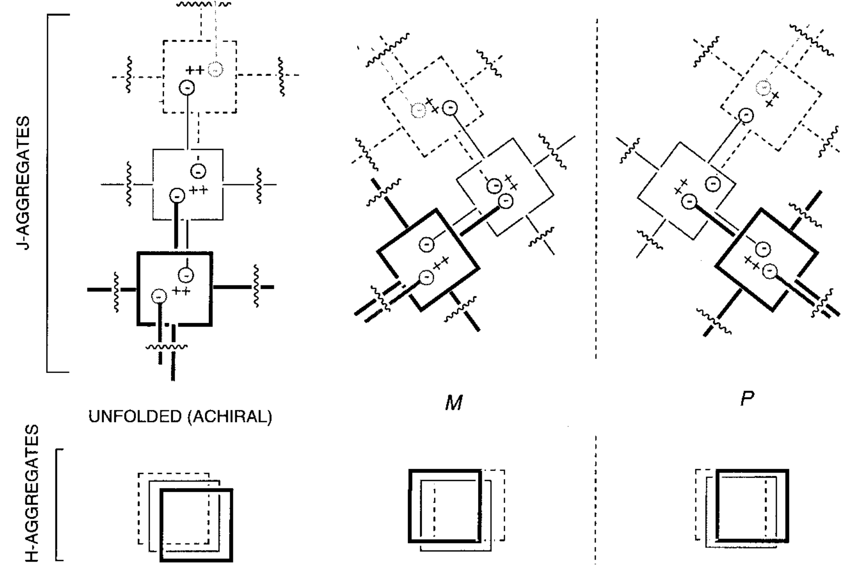

Figure 8. Porphyrin association at 180° and 90°. The latter shows *P*, *M* chirality due to the angle between the chain alignment and the porphyrin plane.

when the absorption spectra of the 180° and the 90° arrangements are very similar, because all diprotonated *meso*-sulfonatophenyl porphyrins, irrespective of the relative positions of their sulfonatophenyl substituents, show similar UV/Vis absorption;[8b] differences between compounds are only detected in the width of the absorption bands.

The corner ring of a 90° fold, according to the model used in Figure 7 and for the $C_{2h}-C_{2v}$ arrangement, has the same 1-to-2 and 1-to-3 interactions as the 180° arrangement. In consequence, no significant differences in the energy of the B_J transition could be expected between the central ring of a 180° arrangement and the corner ring of a 90° folding. However, in the 90° folding, the two porphyrin rings lying near to a "corner" porphyrin will show a different 1-to-3 interaction from that of a 180° arrangement. The calculation shows that this interaction would only result in a small energy split of the B_x and B_y bands of the B_J absorption.[24] Figure 9 illustrates the differences between the absorption spectra of H_2TPPS_{2O}, which would show a smaller proportion of 90° folding, and H_2TPPS_{2A}, which must be aggregated through 90° folding. The broadening of the band towards low energies agrees with the proposed model. In this sense, it is significant that the width of the B_J absorption band of all diprotonated porphyrins was not dependent solely on the concentration, pH, and so on, but also on the previous stirring process and the history of the solution.

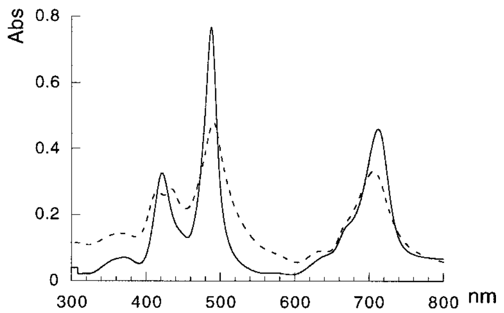

Figure 9. UV/Vis absorption spectra of H_2TPPS_{2O} (——) and H_2TPPS_{2A} (----) in water (2×10^{-5} mol L^{-1}). The differences in the width of the *B* absorption bands could be attributed to the presence of 90° folding in the *J* aggregates.

The explanation for the CD of the B_H band is more speculative, because the geometry of the *H* stacking is not known. However, folding of shifted *H* aggregates would result in chirality (Figure 8).[25]

In conclusion, we can explain the CD reported here by assuming the presence of two exciton chirality axes (*H* and *J*) in the supramolecular structure due to the folding of the one-dimensional *H* and *J* aggregates. The exciton chirality rule, which relates the torsion angle (+ or −) or helicity (*P* or *M*) of two electric-dipole transition moments to the sign of the differential absorption pair of CD Cotton effects, gives a +(−) exciton chirality for +(−) or *P* (*M*) sign. Normally the experimentally detected exciton-chirality signs were the same for both axes. However, for H_2TPPS_3 and H_2TPPS_4, alternated signs between the B_H and the B_J and *Q* transition were detected in some cases (12 out of 263 experiments). These samples were obtained by rotary evaporation, but ageing or dilution and stirring resulted in the reversal of the *H* chirality sign, that is, to the same sign as the *J* chirality (see Supporting Information). This points to a more stable structure with torsion angles of the same sign in both chiral axes. Torsion angles of different sign in the *J* and the *H* direction imply steric hindrance effects.[26]

Differential scattering contributions versus structure of the homoassociate: When the distance between the interacting transition dipole moments is short in relation to the absorption wavelength, the sign of the differential scattering ($s_L - s_R$) depends on the chirality characterised by the relative orientations of the transition dipole moments and the distance vector between centres.[13c] The different relation, for the B_H and the B_J or *Q* transition, between the signs of the differential scattering and the absorption chirality accounts for the presence of two highly differentiated chirality axes; this agrees with their attribution to the *J* and *H* directions of association.

The differential-scattering contribution to CD gives information on the structure of the homoassociates at a higher scale level than that obtained from the differential absorption contribution. Resonance-enhanced scattering and, consequently, differential scattering arise from the alignment between polarisibilities and the growth direction of the aggregate.[12] The relation between absorption and scattering depends on the relation between their cross sections. In the case of self-assembly that results in spheres,[12b] the absorption would be proportional to the volume of the sphere, but the scattering would be proportional to the square of the volume; an increase in the sphere volume would, therefore, result in a greater increase in the scattering. For nonspherical homoassociates, the scattering would be higher when the volume increase occurred in the direction of the transition polarisibility. Then, the detection of differential scattering at the B_H or B_J transitions would be a consequence of the increase in volume in the direction of the *H* or *J* homoassociation. This accounts for some of the differences between porphyrins in their CD spectra; the significance of the contribution of the differential scattering versus differential absorption would depend on the size and shape of the homoassociate. Ageing of the solutions in permanently magnetically stirred conditions normally results in an increase in differential scattering contributions; this can be explained by an increase in the growth selectivity in the direction of the preferred association.[7, 8]

The homoassociates of H_2TPPS_{2O}, H_2TPPS_4 and H_2TPPS_3 are rodlike aggregates, as inferred from depolarised fluorescence studies.[7, 8] Due to the interplay of opposed and adjacent sulfonato groups we should expect *J* homoassociates with less 90° folding and, consequently, greater differences between the long axis (180° alignment between rings) and the short axis (90° alignment) of the rodlike aggregates in the order $H_2TPPS_{2O} > H_2TPPS_4$, H_2TPPS_3. This agrees with the significance of the detected differential-scattering contributions (Table S1 in the Supporting Information corresponds to experiments with dominating-scattering contributions at the

B_J transition of 10/10, 14/27 and 12/29 for H_2TPPS_{2O}, H_2TPPS_4 and H_2TPPS_3, respectively.)

With respect to the B_H transition in the CD spectra in which differential scattering is dominant, the differential absorption contribution reveals the role of the hydrophobic phenyl substituents and the relative position of the 4-sulfonatophenyl substituents. (Note: not all experiments result in the detection of CD for this transition.) The ratio of experiments that give dominating differential scattering for the B_H transition to experiments in which the CD contribution of this transition was 3/27, 4/29, 0/10 and 7/19 for H_2TPPS_4, H_2TPPS_3, H_2TPPS_{2O} and H_2TPPS_{2A}, respectively (see Supporting Information). The high proportion of B_H differential scattering for H_2TPPS_{2A} agrees with the expected structure of the homoassociate, in which *J*-self-assembly (alternating 90° folding) is hindered by the substitution pattern.

Conclusion

The diprotonated porphyrins tested undergo a spontaneous symmetry-breaking process on forming homoassociates. In some cases, there was induction of chirality—as detected by a high bias from the statistical distribution of the chirality sign. We identified one of the effects that induces chirality as being the vortex direction of stirring. In this respect, we obtained highly significant results for H_2TPPS_3 after optimisation of the stirring/evaporation conditions. This suggests that similar significant relations could be obtained for the rest of the porphyrins that were tested. In the case of H_2TPPS_4, the results suggest that microscopic chiral objects (infusorial earth) also induce chirality in the spontaneous symmetry breaking.

We can rule out the possibility that the weak stirring forces cause energy differences between enantiomers. The chiral vortex can only act at the mesoscale level, that is, upon the kinetically controlled growth of the supramolecular structure. Our results suggest the enhancing effect of stirring upon spontaneous symmetry-breaking processes in the diffusion-limited generation of the high-molecular-weight homoassociates. The intermolecular interactions which resulted in the generation of the chiral cromophore also corresponded to weak forces that are enhanced by cooperativity. These results are, therefore, an example of how weak cooperative forces at molecular level, that is, the forces acting in supramolecular chemistry, can be influenced by weak external forces. There is an indirect effect of the weak forces caused by stirring on the shape of the homoassociates; this can be detected through the contributions of the differential scattering at the *H* and *J* chirality axes. For example, there was a general trend that the change of stirring direction resulted in a decrease in the differential scattering contributions of the B_J transition and an increase in the B_H transition; see, for example, Figure 6. This points to an effect of the vortex direction on the growth of the *H* and *J* chirality axes. We would expect a chiral self-assembling object moving in a vortex to show preferred growth and diminishing directions.

We believe that all these stirring effects belong to the same type as those recently described in the preparation of millimetre scale objects obtained by weak interactions between "monomeric" pieces.[27]

On the basis of thermodynamic reasoning, when the concentration in a solution of one-dimensional, 180° homo-associates increases, stacking of the chains parallel to each other must occur.[28] Assuming that the detected chirality is due to the folding of one-dimensional homoassociates, when folding occurs (as consequence of the substitution pattern on the porphyrin or as a structural defect) there is probably an autocatalytic effect on the direction of folding of the neighbouring chains; folding of the other chains in the same direction would result in better stacking of the homoassociates. This raises fluctuations in the chirality,[15, 29] and stirring would have an effect on the amplification of these fluctuations.

The results reported here suggest that, in supramolecular self-assembly to high-molecular-weight associates, that is, where diffusion-limited growth often occurs, symmetry breaking could be a general phenomenon; this could be chirally induced by weak forces. In this sense, it is significant that symmetry-breaking processes have been observed in the formation of liquid phases, monolayers, and so on.[30] These results, and previously reported results on *J* aggregates of cyanine dyes, would be a consequence of their easy detection through CD, because of the formation of inherent chiral chromophores, which have huge rotational strengths but are probably present in low proportion with respect to the nonchiral associates.

Experimental Section

The sodium salts of the *meso*-sulfonatophenyl porphyrins shown in Figure 1 were prepared and purified as described elsewhere.[8b] The purity of the samples was assessed by HPLC analysis.[8b, 9d] Solutions of the diprotonated porphyrins, except in the case of H_2TPPS_4-f, were obtained by acidification with HCl or H_2SO_4 (see below) of the sodium salts of the porphyrin free bases. H_2TPPS_4-f solutions, that is, bis(hydrogensulfate) diprotonated $TPPS_4$ (metal-cation free), were obtained as a suspension in water ($\approx 5\%$ w/v) by sulfonation of $TPPS_4$ with concentrated H_2SO_4, in the same way as for the preparation of $TPPS_4$ but that the crude of the reaction was repeatedly washed and centrifuged ($3000 \times g$) to pH 2.0. Elemental analysis showed the presence of two moles of sulfate (or hydrogen sulfate) per mole of porphyrin. The diprotonated porphyrin solutions, aggregated or not, are stable for months and can be reversibly converted to their free bases.

UV/Vis spectra were recorded in a Cary–Varian 5E instrument. These spectra were used to estimate the degree of aggregation.[7–9]

Circular Dichroism (CD) and Optical Rotatory Dispersion (ORD) measurements were performed on a Jasco J720 instrument (Pockels' cell).[31, 32] In order to avoid orientation of the aggregates along the walls of the recipient, only long-path cuvettes (1 to 5 cm) were used for the measurements. All solutions gave the same CD spectra when they were recorded by performing a 90° rotation of the cuvette around the incident light. Response times of 2 s were used in all measurements. No significant changes were observed on decreasing the distance between the cuvette and the detector. ORD measurements of the samples that were performed with this instrument gave signals that were in agreement with those expected for the CD signals and did not show significant differences with the measurements obtained with a deviation angle polarimeter (Perkin-Elmer 251MC). Solutions in which the formation of large aggregates was seen gave irreproducible CD spectra. This can be attributed to the fluctuating LD contributions of large mesoscopic aggregates. Coarse filtration resulted in stable CD recordings,[33] which did not change with time as a result of previous shaking of the CD cuvette.

There was only partial formation of homoassociates in the CD solutions studied. This is due to the compromise between visually homogeneous solutions, sufficient homoassociates and low light absorption (Abs < 1.5). In order to avoid differences in the association due to differences in the ionic strength, NaCl (biopolymer free, Sigma) was added to the solutions (except in the case of H_2TPPS_4-f). For the CD tests three types of solution were tested: a) magnetically stirred, b) unstirred and c) rotary evaporated solutions.

Magnetically stirred solutions: A solution of the free base (19 mL, 1.25×10^{-5} M), which had been previously sonicated for 30 min, was stirred magnetically at 600 ± 50 rpm in one spin direction in a flat bottomed cylinder (2.6 cm in diameter with a 1 cm long magnetic stirrer) either clockwise or anti-clockwise, as observed from the top of the cylinder, and NaCl was added slowly (12 h) to give a final concentration of 0.6 M. HCl (1 mL, 0.3 M) was then added slowly. The solution was stirred continuously.

Rotary evaporated solutions: experiments in Table S1 of the Supporting Information: A solution of free base porphyrin (5 mL, 1×10^{-5} M), previously sonicated for 30 min, was diluted to 500 mL in a one litre round bottom flask; NaCl (0.7 g, 2.4×10^{-2} M) and H_2SO_4 (8.3 μL, 96%) were added. Rotary evaporation to a final volume of 20 ± 2 mL was performed in a 55 °C bath at 600 ± 50 rpm in one spin direction (CW or ACW), 25 Torr. Some samples were subjected to a second rotary evaporation process after dilution of the concentrate solution to 500 mL.

Rotary evaporated solutions: experiments in Table 1: The same experiments as above were carried out with H_2SO_4 (14 μL, 96%) and rotary evaporating to a final volume of 25 ± 2 mL.

Unstirred solutions: These were prepared in the same way as the magnetically stirred solutions but without stirring.

These experiments were performed in five different rotary evaporators and in different one litre round bottom flasks. The results of these experiments are shown in Table 1 and in the Supporting Information. Moreover, the chiral induced solutions were observed over time or subjected to additional experiments.

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