Macroscopic Chirality

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Alignment by the Convective and Vortex Flow of Achiral Self-Assembled Fibers Induces Strong Circular Dichroism Effects

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alignment · circular dichroism · convective flow ·
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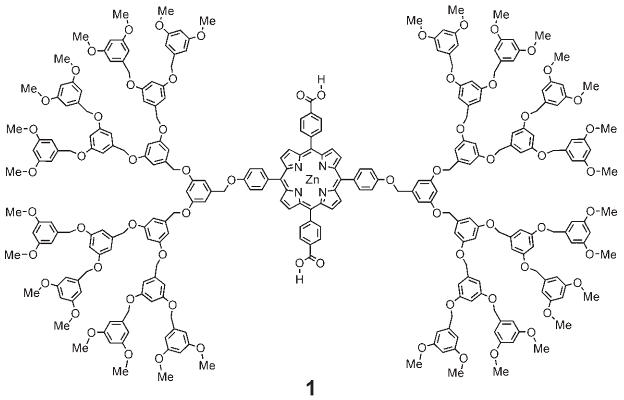
It is well known that upon association or aggregation, some molecules (chiral or achiral) spontaneously form chiral supramolecular systems in which enantiomeric structures condense separately.[1] An excess of one of the enantiomers may be obtained, although with an unpredictable sign, as the consequence of spontaneous symmetry breaking under nonequilibrium conditions.[2] This spontaneous induction of optical activity from achiral entities has attracted much attention in relation to the origin of chirality in nature. Examples of chiral symmetry breaking have mostly been reported in the context of crystallization.[3] In this case, stirring can lead to an enantiomeric excess, but there is no chirality sign selection, and the actual handedness of crystals produced in a single experiment is unpredictable.[4] In the field of aggregation and growth processes, representative examples have been published in which large electrostatic assemblies, formed in aqueous media by cyanine dyes and porphyrin derivatives, adopt helical architectures whose handedness is selected accidentally in the initial stage of self-organization.[5] Again, the handedness of the emerging chirality is unpredictable.

In striking contrast to these observations, Kaizu[6] and coworkers and Ribó et al.[7] reported that a macroscopic chirality factor, the spinning direction of vortex stirring initially applied to a solution, selects the chirality of a supramolecular structure; consequently, the symmetry breaking can be biased. Electrostatic J-aggregates of sulfonylphenylporphyrin derivatives prepared in aqueous media under rotary stirring are optically active, and even if the stirring direction is reversed, the supramolecular homoassemblies[7] do not invert their chiroptical sense. The authors interpreted their observations in terms of hydrodynamic and steric effects acting during the growth of the assemblies.

Recently, Aida and co-workers[8] reported that spin-coated films of dendritic zinc porphyrin (**1**) J-aggregates chiroptically "remember" the spinning direction in the solid state, that is, in optically active films in which either of the two enantiomeric forms is selected by the spinning direction. The optical activity of the films is temperature-independent and is preserved up to the melting point of the J-aggregates.



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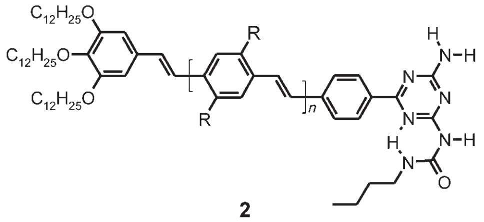

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A breakthrough is presented in two recent studies by the groups of Aida [9] and Meijer[10] They reason that, if the supramolecular assemblies obtained under vortex flow were flexible and readily changed their conformation while flowing, they might be suitable as probes for reversible chiroptical rendering of different local fluidic flows.

Their work also points out that caution is needed to interpret circular dichroism (CD) spectra in the presence of (partial) alignment arising from flow or boundary conditions. The nonmolecular contributions to CD arising from solute alignment are to be considered artifacts; however, if correctly interpreted, they can give important information on the macroscopic chiral arrangement of supramolecular assemblies. Although the artificial appearance of CD in aligned

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systems has been considered previously,[7,11] the reports by the Aida and Meijer groups describe in detail the origin of CD in achiral systems in which the solute self-assembles into anisometric aggregates that are able to orient in response to fluidic flows.

In particular, Aida and co-workers reported that while a hydrocarbon solution of achiral **1** without stirring was CD-silent, it became optically active upon mechanical rotary stirring (Figure 1).[9] When stirred in a clockwise direction (CW), the sample solution displayed intense CD signals at the Soret absorption bands arising from J-aggregated zinc porphyrin, while no chiroptical activity emerged at the absorption band of unassembled molecules. Notably, reversal of the stirring direction resulted in perfect inversion of the sign of the CD response, and when rotary stirring was stopped, the sample solution lost its optical activity. Hydrocarbon solutions of the achiral oligo(*p*-phenylene vinylene) derivative **2** investigated by Meijer and co-workers also result in a strong bisignate CD effect whose sign is affected by the stirring direction.[10]

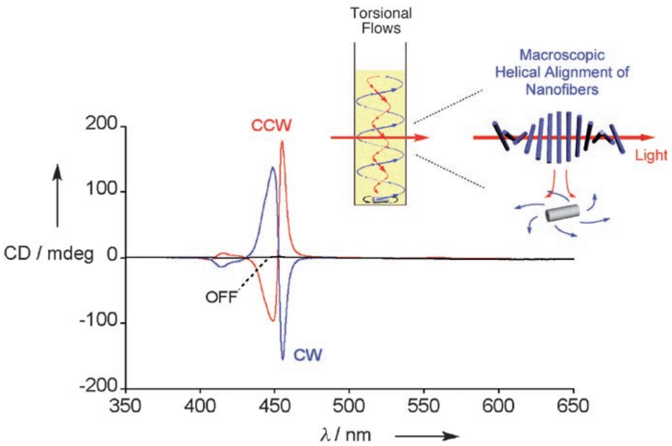

Figure 1. Circular dichroism (CD) spectra of a benzene solution of assemblies of **1** upon rotary stirring in clockwise (CW, blue curve) and counterclockwise (CCW, red curve) directions, and without stirring (OFF, black curve). The inset shows a schematic illustration of torsional flows and macroscopic helical alignment of nanofibers generated upon counterclockwise rotary stirring. Reproduced from reference [9].

In both studies, the observed bisignate CD effect for stirred solutions of **1** and **2** is explained by the vortex-flow macroscopic alignment of the nanofibers (Figure 1, inset) in the front and back of the cell at different angles with respect to the vertical directions. A similar phenomenon is known for cholesteric liquid crystals, in which mesogenic molecules are helically aligned and exert an apparent macroscopic CD effect originating from the combined linear dichroism (LD) and linear birefringence (LB) optical responses of the liquid-crystal layers.[12] Aida and Meijer confirmed the similar origin of the CD effect in the stirred solutions by preparing dip-coated thin aligned films of **1** and **2**, which showed LD and LB. Interestingly, when two films of **1** or **2** were overlaid such that their oriented directions were at a 45° angle, a distinct chiroptical response appeared, the spectral shape of which is virtually identical to that observed for the corresponding stirred solution of **1** or **2**. When the dihedral overlap angle was changed from 45° to −45°, a spectral inversion took place. The angle dependence of the chiroptical feature indicates that the observed chiroptical activity is not present at the molecular level but is instead a macroscopic CD effect originating from the twisted overlapping geometry of the oriented films. These experiments indicate that the major contribution to the strong bisignate CD signals is the helical arrangement of assemblies induced by the helical flow.

Meijer and co-workers point out another possible source of apparent CD in solutions of achiral assemblies. In the temperature-induced self-assembly of achiral **2**, LD and CD signals appear, even in unstirred solutions, when the assemblies reach a certain length; these optical responses, which are enhanced by shaking the solutions, are a consequence of partial alignment of the fibers owing to convective flow (Figure 2). This explanation seems reasonable for the emergence of LD, but why do CD signals appear in the absence of an asymmetric force such as stirring? The CD signal is an artifact resulting from the LD of the partially aligned assemblies combined with the inherent optical imperfection of the CD instrument. The incident light is not completely right or left circularly polarized but is contaminated by linearly polarized components (horizontal and vertical in the two opposite circularly polarized components) that are absorbed differentially by the partially aligned systems.

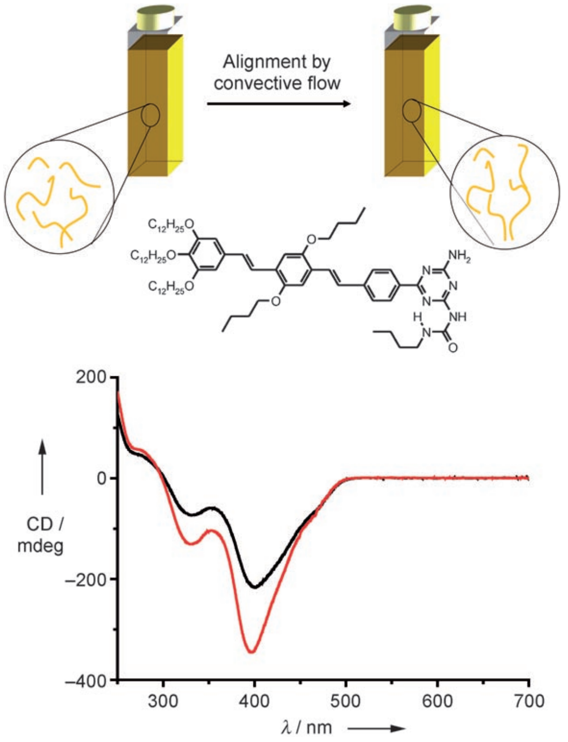

Figure 2. CD spectra of a solution of **2** in dodecane after cooling (black) and after shaking the solution (red). Reproduced from reference [10].

These studies by the groups of Aida and Meijer show that supramolecular assemblies can be partially oriented in fluid, nonviscous media by convective flow, shaking, or stirring, and that this partial orientation induces an artificial contribution in the circular dichroism spectra of achiral assemblies. The shape, sign, and intensity of the CD effect depend on the linear dichroism and the linear birefringence that arise during alignment. It is clear that the alignment of supramolecular assemblies in dilute solutions can create artifacts in the chiroptical properties of the system, which should be clearly differentiated from the effects originating from chirality at the molecular scale. The results of their research are therefore significant for anyone working on self-assembly systems in which (partial) alignment arising from boundary conditions and flows may be common. In the past, little attention has been paid to these effects, and several pieces of data in the literature are known to be questionable, if not incorrect, as no care has been taken to prevent or control the CD artifacts. The studies by the groups of Aida and Meijer have the merit of presenting simple and elegant experiments on achiral, self-assembling molecules, thus demonstrating the important role of alignment for chiroptical responses.

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[11] See, for example: G. Gottarelli, G. P. Spada, E. Castiglioni in *Molecular Gels: Materials with Self-Assembled Fibrillar Network* (Eds.: R. G. Weiss, P. Terech), Springer, Dordrecht, **2006**, chap. 13.

[12] Many papers deal with contamination of CD from LD and LB or apparent CD originating from LD and LB; see, for example: F. D. Saeva, P. E. Sharpe, G. R. Olin, *J. Am. Chem. Soc.* **1973**, *95*, 7656; B. Nordén, *J. Phys. Chem.* **1978**, *82*, 744; Y. Shindo, M. Nishio, S. Maeda, *Biopolymers* **1990**, *30*, 405; R. Kuroda, T. Harada, Y. Shindo, *Rev. Sci. Instrum.* **2001**, *72*, 3802; Y. Shindo, Y. Ohmi, *J. Am. Chem. Soc.* **1985**, *107*, 91; F. Livolant, M. F. Maestre, *Biochemistry* **1988**, *27*, 3056.