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VIP Macroscopic Chirality

Spectroscopic Visualization of Vortex Flows Using Dye-Containing Nanofibers**

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A vortex is a recognized example of macroscopic chirality[1] and one possible origin of chiral symmetry-breaking in nature.[2–8] Compared with, for example, rheometric shear flows,[9] vortices are complex, involving many locally different fluidic flows. Upon mechanical rotary stirring of a fluid in a cuvette, a tight, torsional flow is generated at the rotary center, while the peripheral part of the vortex involves a loose, spiral flow (Figure 1b, left). This intriguing situation prompted us to investigate whether or not vortex flows can be rendered spectroscopically. It is known that certain achiral entities form optically active assemblies in fluids upon rotary stirring.[4–8] Kaizu and co-workers[5a] and Ribó and co-workers[5b,c] have reported pioneering examples in which electrostatic J-aggregates of 4-sulfonylphenylporphyrin derivatives, prepared in aqueous media upon rotary stirring, are optically active. They claimed that hydrodynamic selection of either the right- or left-handed helical conformation of the aggregates is responsible for the optical activity. In fact, the formation of helical ribbons in a stirred solution has recently been confirmed.[5c] If such dye-containing assemblies are flexible and can readily change their conformation while flowing, they can be used as probes for spectroscopic rendering of locally different fluidic flows in a vortex. However, even if the stirring direction is reversed, the reported assemblies do not invert their chiroptical sense once it has been selected.

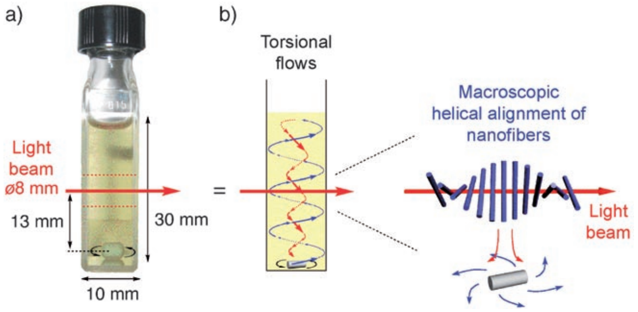

Figure 1. a) A sample solution for bottom rotary stirring in a 10×10×40-mm^3 quartz optical cell containing a ∅2.0×5.0-mm^3 teflon-coated magnetic stirring bar. For CD spectroscopy, an ∅8.0-mm beam of circularly polarized light was allowed to pass through the sample solution 13 mm above the center of the stirring bar. b) Schematic illustrations of torsional flows generated upon bottom counterclockwise (CCW) rotary stirring and accompanying macroscopic helical alignment of nanofibers.

Recently, we reported that zinc porphyrin dendrimer **1** (Scheme 1) forms a J-aggregate through π-stacking interactions, which is promoted by the formation of hydrogen bonds at its carboxylic acid side groups to give a supramolecular polymer. Furthermore, when spin-coated from solution, this J-aggregate forms a chiroptically active film whose sense is selected by the spinning direction.[7] Since this assembly differs from the reported examples in that it is devoid of any electrostatic interactions, we expected it to be flexible enough to change its conformation in response to the local flows of a vortex. Indeed, the J-aggregate of **1** can be used to visualize vortex flows spectroscopically, but by a different mechanism from our initial expectation. Herein, we highlight an interesting possibility that in a vortex, nanofibers of **1** temporarily align like mesogenic molecules in a cholesteric liquid-crystalline mesophase.[10,11]

Self-assembly of **1** to give a J-aggregate (Scheme 1) occurs much more efficiently in benzene and toluene than in halogenated solvents like $CHCl_3$ and CH_2Cl_2, which were mostly used for our previous study.[7] For example, a benzene solution of **1** (6.0×10^{-6} M) at 20 °C displayed an intense red-shifted Soret absorption band at 452 nm (S_{III}, Figure 2a) along with a blue-shifted minor band at 413 nm (S_I) characteristic of zinc porphyrin J-aggregates. Dynamic light scattering

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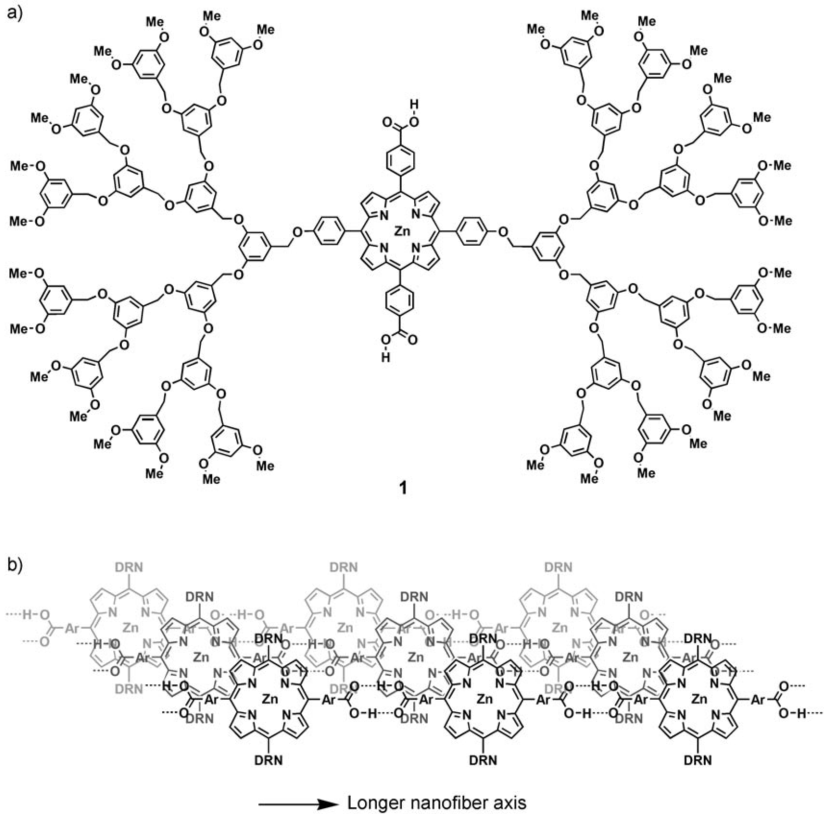

Scheme 1. Structural formulas of a) dendritic zinc porphyrin **1** and b) a J-aggregated form of its hydrogen-bonded supramolecular polymer (nanofiber). DRN represents a dendritic wedge.

(DLS) analysis showed that the benzene solution ([**1**] = 9.1 × 10^{-5} M) contains self-assembled objects whose dimensions range from 23 to 1520 nm with an average radius of 225 nm.[12] The TEM image of an air-dried sample of the benzene solution deposited on a specimen grid covered with a thin carbon support film displayed 10–20-nm-wide discrete nanofibers with a very high aspect ratio (Figures 3 a and b). The height profile of the nanofibers determined by AFM revealed a uniform thickness of 3 nm (Figures 3 c and d), thus indicating that the nanofibers are bundles of a limited number of polymer chains of **1** (Scheme 1 b). The nanofibers dissociated very slowly. For example, upon five-fold dilution of a benzene solution of **1** (3.0 × 10^{-5} M), spectral change that accompanied the disassembly of **1** took place only very sluggishly to reach a plateau after one day.[12]

Our experimental setup allows linear dichroism (LD) and circular dichroism (CD) spectroscopies,[12] which yield information about the orientation and helical deformation, respectively, of nanofibers of **1**. The spectrometers were equipped with a 10 × 10 × 40-mm^3 quartz optical cell in which sample solutions (3 mL) were mechanically stirred using a ∅2.0 × 5.0-mm^3 teflon-coated magnetic stirring bar at the bottom of the cell, 13 mm below the center of a ∅8.0-mm-wide polarized beam of light (Figure 1 a). To vary the position of rotary stirring, the CD spectrometer was equipped with a movable mechanical stirrer connected to a ∅8.0 × 1.0-mm disk-shaped glass fin through a glass shaft.[12]

While a benzene solution of **1** (6.0 × 10^{-6} M) without stirring was CD silent, it became optically active upon mechanical stirring (Figure 2 b). For example, when stirred at 1350 rpm in a clockwise direction (CW), the sample solution displayed intense CD bands at the Soret absorption bands owing to J-aggregated **1** [413 (−14 mdeg), 449 (138 mdeg), and 455 nm (−156 mdeg)]. While very weak CD bands were observed in the Q-band region (530–610 nm), no chiroptical activity emerged at the absorption band of non-assembled **1** (428 nm; S_{II} in Figure 2 a). In sharp contrast to the previous examples,[5] reversal of the stirring direction resulted in perfect inversion of the CD spectral sign (Figure 2 b). Furthermore, when the stirring was stopped, the sample solution lost the optical activity. As shown in Figure 2 c, the nanofiber showed a quick chiroptical response to the change in stirring conditions. We also found that the CD intensity increases sigmoidally with increasing rotating speed of the stirrer.[12] In contrast, an ester derivative of **1**, which exists as a monomer in benzene,[7] did not show any chiroptical response upon rotary stirring.[12]

We initially thought that the observed chiroptical activity must be due to the helical twisting of the individual nanofibers of J-aggregated **1** in the vortex flow. However, we later noticed, through a discussion with Meijer and Meskers,[13] that the effect might be due to macroscopic chiral alignment of the nanofibers (Figure 1 b) upon rotary stirring. A similar phenomenon is known for cholesteric liquid crystals, where mesogenic molecules are helically aligned and exert a macroscopic CD effect.[10,11] However, in nonconstraint fluids, such a possibility has been considered unlikely. In order to assess this macroscopic CD effect, compound **1** was dip-coated from its benzene solution (9.1 × 10^{-5} M) on a 0.12–0.17-mm-thick glass plate. The dip-coated thin film showed linear dichroism (LD) activity, the spectral sign of which was inverted by rotation of the sample by 90° relative to the beam of light (Figure 4 a).[14] This finding indicates that the nanofibers are preferentially oriented along the dipping direction. Then, this nanofiber-coated glass plate was placed over another similarly prepared plate and subjected to CD spectroscopy. Quite interestingly, when the films were overlapped such that their oriented directions were at a 45° (ϕ) angle, a distinct chiroptical response (Figure 4 b, red solid curve) appeared, the spectral shape of which is virtually identical to that observed for the stirred solution of J-aggregated **1** (Figure 2 b). When the dihedral angle for overlap (ϕ) was changed from 45° to −45°, a spectral inversion took place (Figure 4 b, blue). In contrast, when ϕ was adjusted to 0° or 90°, no clear chiroptical activity was detected (Figure 4 b, solid and dashed black, respectively). The angle dependency of the chiroptical feature indicates that the observed activity does not arise from the molecular level

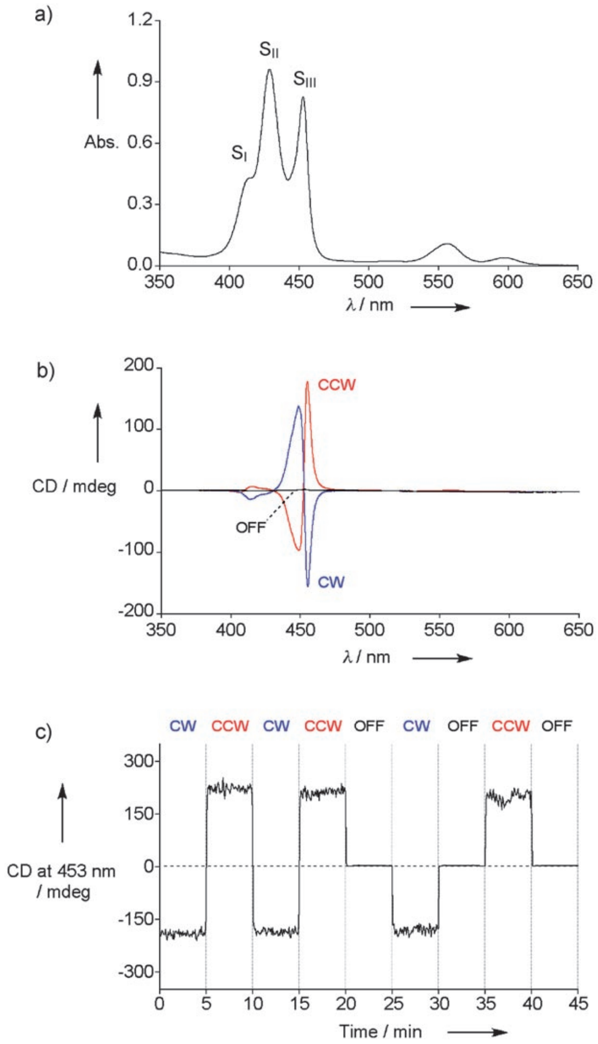

Figure 2. Absorption and circular dichroism (CD) spectra of a benzene solution (3.0 mL) of **1** (6.0×10^{-6} M) in a $10\times10\times40$-mm^3 quartz optical cell. a) Absorption spectrum at 20 °C. b) CD spectra at 20 °C upon bottom rotary stirring at 1350 rpm in clockwise (CW; blue curve) and counterclockwise (CCW; red curve) directions using a $\varnothing 2.0\times5.0$-mm^3 teflon-coated magnetic stirring bar, and without stirring (OFF; black curve). c) Change in CD intensity at 453 nm in response to a stepwise variation of the stirring conditions at 20 °C.

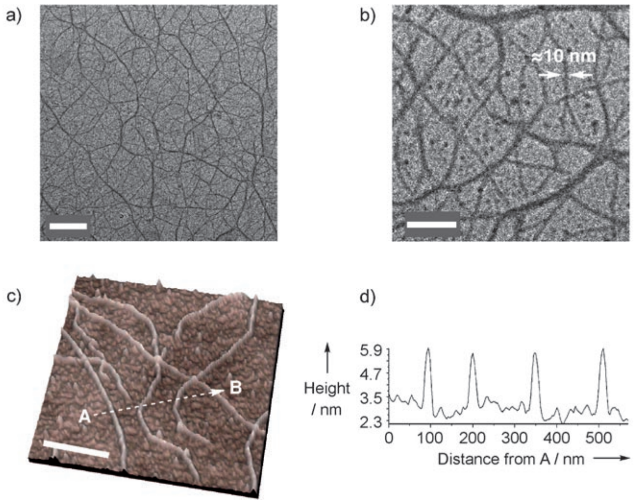

Figure 3. a) and b) Transmission electron micrographs of an air-dried sample of a benzene solution of **1** (10^{-5} M) deposited on a specimen grid covered with a thin carbon support film. Scale bars: a) 500 nm, b) 100 nm. c) AFM image (scale bar: 200 nm) of an air-dried sample of a benzene solution of **1** (10^{-5} M) deposited on a mica substrate and d) its height profile along the arrow from A to B.

but is a macroscopic CD effect originating from the twisted overlapping geometry of the oriented films.[15]

With the above observations in mind, we carried out LD spectroscopy of the stirred solution of J-aggregated **1** to investigate if its chiroptical activity (Figure 2b) likewise originates from a special macroscopic alignment of the nanofibers in torsional flows (Figure 1b). While the sample solution ($[\mathbf{1}]=6.0\times10^{-6}$ M), although it contains the long nanofibers, was LD silent without stirring, it turned LD active upon rotary stirring.[12,16,17] The spectral shape was virtually identical to that observed for the dip-coated thin film of the nanofibers, but the spectral sign was independent of the stirring direction (clockwise or counterclockwise, Figure 5a). Since the spectral sign is the same as that of the film sample with its oriented direction parallel to the vertical axis of the linearly polarized incident light (Figure 4a, solid curve), it is likely that the nanofibers preferentially align perpendicular to the rotary direction. Nevertheless, considering that the fluidic situation in a vortex may change locally, we carried out LD spectroscopy with optical cells selectively masked at the vertical center or at the margins (Figure 5). Quite interestingly, while the LD sign observed through the central slit of the masked cell (Figure 5b) was identical to that of the entire solution (Figure 5a), the LD spectrum observed through the margins (Figure 5c) was opposite in sign to the others.[12] These observations suggest that the preferential alignment of the nanofibers flowing at the center of the vortex is different from that at the periphery. Considering the hydrodynamic model of a vortex of fluids generated in a cuvette (Figure 1b, left),[12] this possibility may be realistic. Thus, rotary stirring of the solution at the bottom of the cuvette gives rise to a tight, downward torsional flow toward the rotary center because of a centripetal force. Stirring at the bottom also generates a relatively loose upward spiral flow at the periphery of the vortex arising from the collision of fluid molecules with the side wall of the cuvette. Accordingly, the nanofibers flowing above the rotary centers tend to align perpendicular to the rotary direction, while they align parallel to the rotary direction in the periphery of the vortex.

Such locally varied fluidic situations can temporarily give rise to a macroscopic helical alignment of the nanofibers along the beam of light for CD spectroscopy (Figure 1b, right), potentially leading to a chiroptical response of the solution. Obviously, a change in rotary direction of the solution can result in quick switching of the handedness of the helical nanofiber array and therefore in a reversal of its chiroptical response (Figures 2b and c). To further support this possibility, we stirred the sample solution from the upper side of the cell, since the handedness of the torsional flow

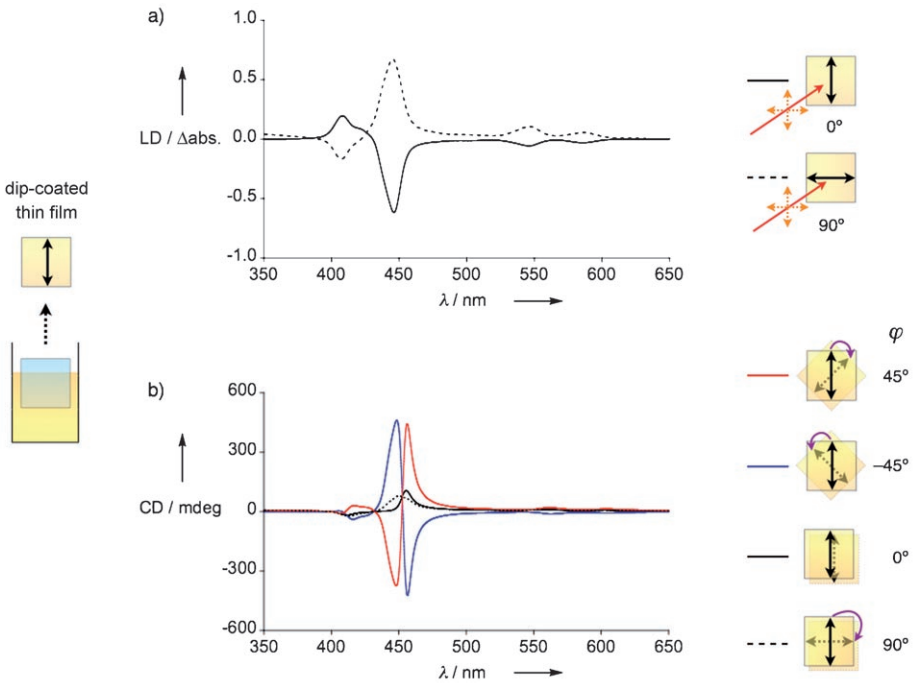

Figure 4. a) Linear dichroism (LD) spectroscopy of an oriented thin film of nanofibers of **1**. The oriented direction of the film was placed at a 0° (solid) or 90° (dashed) angle relative to the vertical axis of linearly polarized incident light. b) Circular dichroism (CD) spectroscopy of overlapping samples of two oriented thin films of nanofibers of **1**. The second film was placed over the first one such that their oriented directions were at an angle ϕ of 45° (red), −45° (blue), 0° (solid black), or 90° (dashed black). The films were prepared by dip-coating of a benzene solution of **1** (9.1×10^{-5} M) at 20 °C on a 0.12–0.17-mm-thick glass plate.

generated by top stirring is opposite to that generated by bottom stirring when their rotary directions are identical. Thus, the sample solution was stirred at 600 rpm in a CW direction using the disk-shaped glass fin 13 mm above the center of the light beam. As expected, the observed CD spectrum was a mirror image of that recorded with CW stirring at the bottom of the cell (Figure 6 a). While keeping the same rotating speed and direction, we moved the glass fin toward the lower side of the cell (Figure 6 b). The CD response became larger until the rotating fin approached a position 8 mm above the center of the light beam, after which point it began to decrease. However, after the fin passed through the light beam, the CD response inverted its sign and became larger as the fin approached the bottom of the cell. These observations appear to support the hypothesis that the stirred solution of J-aggregated **1** exerts a predominantly macroscopic CD effect while the contribution of a molecular-level CD effect, if any, must be negligible.

The present study shows an interesting possibility that upon rotary stirring, long nanofibers in fluids can temporarily align helically at the macroscopic level (Figure 1 b, right). Since the nanofibers contain J-aggregated dye units (Scheme 1 b), torsional flows in the generated vortex can be chiroptically visualized by this macroscopic helical alignment. While some optically active J-aggregated dyes are known to form in vortex flows,[5,6] they are fundamentally different from our system in that their optical activity, once achieved, is hardly erased without dissociation. Furthermore, no inversion of the chiroptical sense occurs upon reversal of the stirring direction. The phenomenon observed with nanofibers of J-aggregated **1** is known for cholesteric liquid crystalline materials and involves a macroscopic helical alignment of mesogenic molecules. However, in our system such a macroscopic helical alignment occurs in nonconstraint, fluid media without any assistance of rheometric flows. Subjects that deserve further study involve rational understanding of this interesting macroscopic phenomenon with a variety of dye assemblies with different dimensions and physical and mechanical properties.[18]

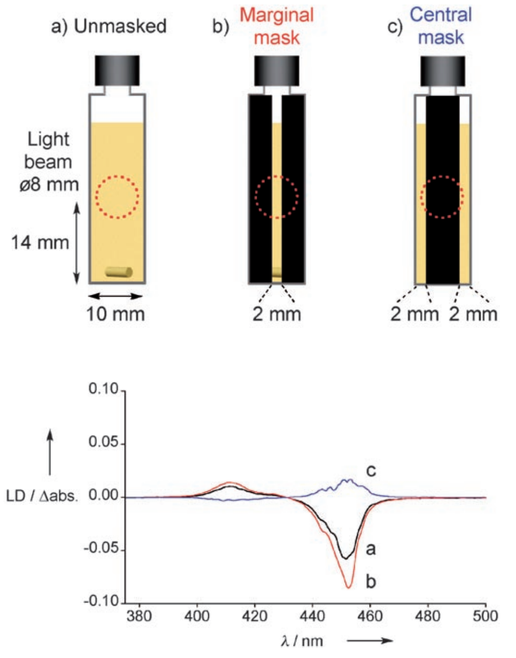

Figure 5. Linear dichroism (LD) spectra of a benzene solution (3.0 mL) of nanofibers of **1** (6.0×10^{-6} M) upon clockwise bottom rotary stirring at 1350 rpm using a ∅2.0×5.0-mm^3 teflon-coated magnetic stirring bar at 20 °C in a $10\times10\times40$-mm^3 quartz optical cell. LD spectra were obtained with cells that were a) unmasked (black), b) masked on the edges with 4-mm-wide black tapes to leave a 2-mm-wide central slit (red), and c) masked at the vertical center with a 6-mm-wide black tape (blue).

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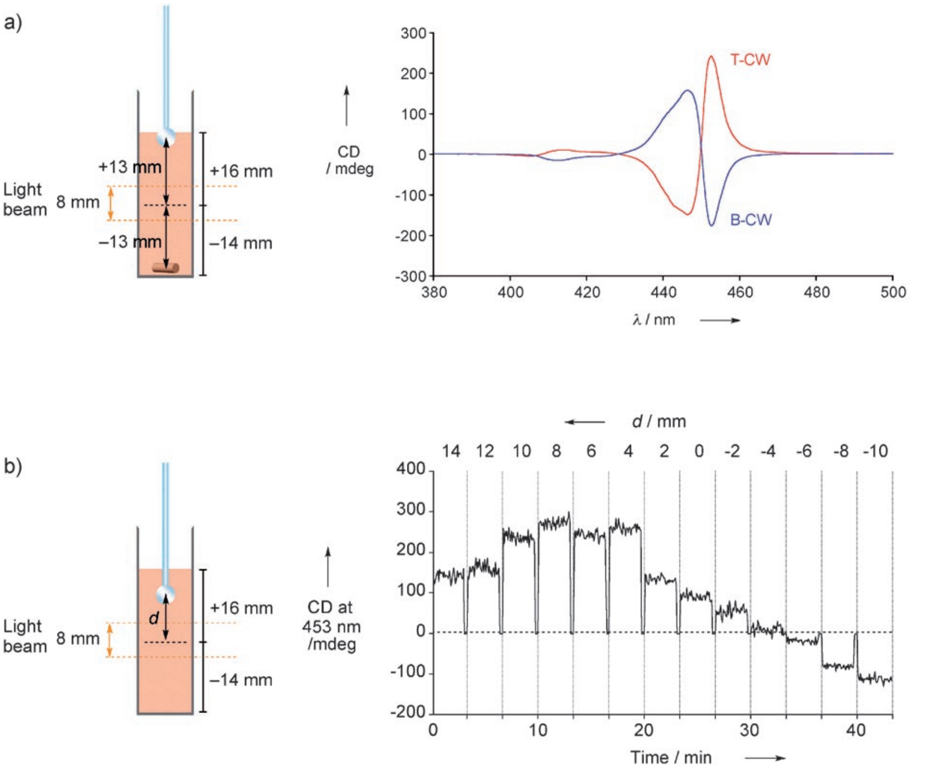

Figure 6. Circular dichroism (CD) spectra of a benzene solution (3.0 mL) of nanofibers of **1** (6.0×10^{-6} M) at 20 °C in a $10\times10\times40$-mm^3 quartz optical cell under different stirring conditions. a) CD spectra upon top clockwise (T-CW) stirring using a ∅8.0×1.0-mm^3 disk-shaped glass fin at 600 rpm (red) and bottom clockwise (B-CW) stirring using a ∅2.0×5.0-mm^3 teflon-coated magnetic stirring bar at 900 rpm. The stirring positions for T-CW and B-CW were 13 mm above and below the center of an ∅8.0-mm-wide light beam, respectively. b) CD intensities at 453 nm upon rotary stirring at varying distances *d* from the light-beam. Whenever the stirring distance was changed, a shutter connected to the CD spectrometer was closed for 20 seconds.

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