Supramolecular Chemistry

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# Macroscopic Origin of Circular Dichroism Effects by Alignment of Self-Assembled Fibers in Solution**

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We report herein an unexpected circular dichroism (CD) effect observed for a dilute solution of an achiral oligo(*p*-phenylene vinylene) derivative, **A-OPV3** (Scheme 1) in dodecane ($c = 5 \times 10^{-5}$ M). This effect likely originates from macroscopic phenomena during the self-assembly process of **A-OPV3** into fibers after slow cooling from 363 K to 293 K at a rate of 60 K h$^{-1}$ (Figure 1a). To our surprise, the CD response increased in intensity after shaking the fully transparent, nonviscous solution. To shed light on this observation, we studied the self-assembly of **A-OPV3** in more detail. Upon cooling the **A-OPV3** solution from 363 to 293 K, a typical blue shift of the absorption maximum to $\lambda = 407$ nm with a shoulder at $\lambda = 475$ nm is observed. This finding indicates that at high temperature the molecules are molecularly dissolved, while at low temperature they are self-assembled into fibers (Figure 1b).[1] However, at low temperatures, a small response in the linear dichroism (LD) spectrum is observed, which increased slightly after shaking (Figure 1c). LD and CD are absent at higher temperatures. The atomic force microscopy (AFM) images of dried drop-cast solutions of these self-assembled systems on mica showed large bundles of long fibers (Figure 1d).

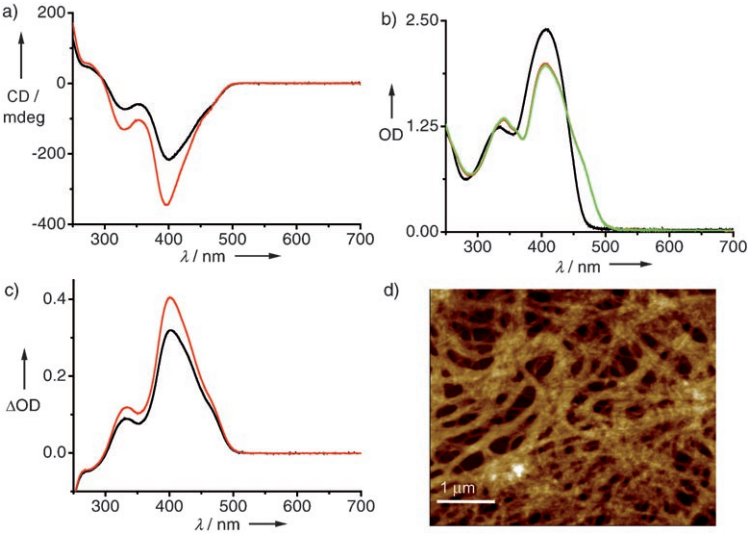
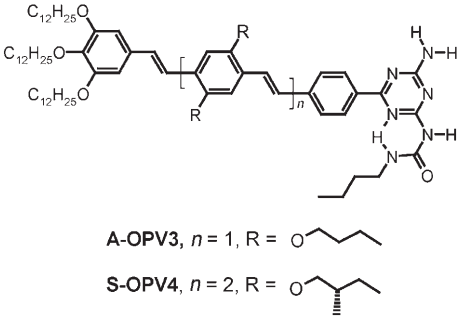



***Figure 1.*** a) CD spectra at 293 K of an **A-OPV3** solution in dodecane after cooling from 363 K at 60 K h$^{-1}$ (black) and after shaking the solution (red).[2] b) Absorption spectra at 363 K (black), at 293 K after cooling (red), and after shaking (green; 1 cm cuvette, $c = 5 \times 10^{-5}$ M) c) LD spectra of an **A-OPV3** solution after cooling (black) and after shaking (red; $c = 5 \times 10^{-5}$ M, $T = 293$ K) d) AFM image of **A-OPV3** on mica drop cast from a dodecane solution ($c = 1 \times 10^{-5}$ M).




***Scheme 1.*** The molecular structures of **A-OPV3** and **S-OPV4**.

The three spectra (UV/Vis, CD, and LD) are almost identical in shape (Figure 1a–c). However, when monitoring the spectra during the temperature-induced self-assembly process (absorption and CD intensity at $\lambda = 475$ nm and the LD intensity at $\lambda = 400$ nm), the absorbance changes first, while the LD and CD signals arise together at lower temperatures.[2] Because **A-OPV3** molecules form fibrous aggregates with a length that increases upon lowering the temperature, this behavior indicates that a certain fiber length is needed to induce the LD and CD effects. Hence, the increase in the LD is most likely associated with the (partial) alignment of the **A-OPV3** fibers in solution arising from convective flow, which is caused by temperature differences in the cuvette.[3] Additional measurements show that the alignment is less significant when a smaller cuvette (0.1 vs. 1 cm) is used,[2] that is, when the flow pattern is altered. The flow pattern induced by shaking might enhance the alignment

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obtained by the convective flow. Furthermore, LD and CD spectra of aligned **A-OPV3** films show effects very similar to those observed in solution.[2] Consistent with the LD of aligned films and the convective nature of the flow in the heated cell, the LD measurements show that the **A-OPV3** fibers in solution orient preferentially in the vertical direction.[4] The apparent CD effect can thus be interpreted in terms of an artifact resulting from LD in the partially aligned solution together with the inherent optical imperfections of the CD instrument, namely linear birefringence (LB) in the photoelastic modulator and/or other optical elements.[5] These imperfections cause a contamination of the pure left (right) circular polarized light with a horizontal (vertical) linear polarized component, which is then selectively absorbed by the partially aligned **A-OPV3** fibers. Consistent with this interpretation, the apparent CD effect arising from alignment caused by convective flow (which is in the vertical direction) always shows the same sign. The sign of the apparent CD effect from the aligned film of **A-OPV3** can be inverted by rotating the film over 90° relative to the propagation direction of the light beam. The maximal artifical CD contribution can, in this first approximation, not be larger than the flow-induced LD, so that only CD effects larger than the LD should be considered for molecular structural interpretations.

As the result of discussions with Aida and co-workers,[6] we were introduced to the large Cotton effects in CD that occur in stirred solutions of aggregates of dendritic zinc porphyrins. For these systems, the sign and intensity of the signal is proportional to the direction and speed of the vortex flow created in the cuvette. To discriminate this type of vortex flow from the convective flow described above, we decided to stir the aligned achiral **A-OPV3** solution first clockwise and then counterclockwise (Figure 2). Stirring of the slowly cooled solution results in extraordinary, large bisignate CD effects, with the zero-crossing at the maximum absorption and for which the sign is affected by the stirring direction, in full agreement with the results of Aida and co-workers.[2,7] After removing the vortex flow, the CD effect reverts to that observed for the aligned **A-OPV3** solution.[2] The shape of the CD spectrum induced by stirring is very different from that of the spectrum induced by convective flow discussed above, which suggests a different origin for the stirring-induced effect.

The CD effects caused by vortex flow in the cuvette can be explained by considering two aligned **A-OPV3** films[2] that are rotated with respect to each other. Bisignate CD effects,

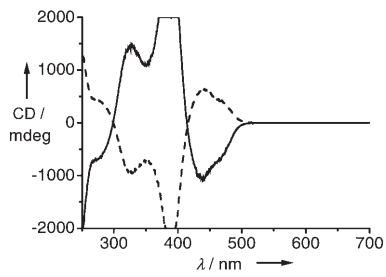


***Figure 2.*** CD measurements of a previously cooled (self-assembled) **A-OPV3** solution stirred clockwise (——) and counterclockwise (-----; $c = 5 \times 10^{-5}$ M, $T = 293$ K).

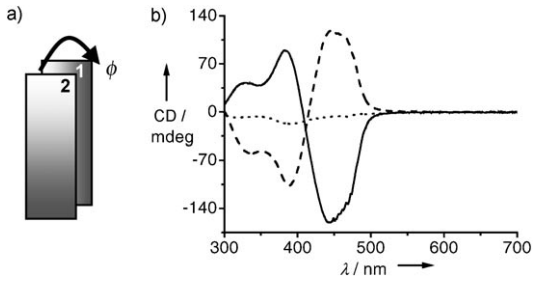


***Figure 3.*** a) Schematic picture of the angle $\phi$ between film 1 and film 2. b) Results of the orientation study of aligned films of **A-OPV3** for $\phi = -45°$ (——), $\phi = 45°$ (-----) and $\phi = 90°$ (•••••).

whose sign and intensity depend on the angle of rotation of film 2 (Figure 3), are obtained; these effects are very similar to those induced by stirring. For dye-doped cholesteric liquid crystals, macroscopic chirality can induce artificial CD effects, which can be explained by considering a two-layer sample. With the first layer showing LB and the second layer showing LD′ at $\pm 45°$ with respect to the first layer, large apparent circular dichroism is observed, which is essentially a cross product of the LB and LD′ in the two layers.[8,9] Similarly, in the case of **A-OPV3**, the CD signal originates on the macroscopic length scale and is determined by the relative orientation of the second layer ($\pm 45°$).[8,9] The observed bisignate CD effects for stirred solutions of **A-OPV3** can now be explained by the vortex flow aligning the fibers in the front and back of the cell at different angles with respect to the vertical direction and with the LB of the front and the LD′ of back side of the cell combining to an apparent CD contribution. The LD spectrum of the fibers is monosignate (Figure 1c) so that the LB spectrum, which is the Kramers–Kronig transform of the LD spectrum, is expected to be bisignate with a zero-crossing near the maximum of the LD intensity. For the combination of LB and LD into the artificial CD contribution, a bisignate spectral signature is expected, consistent with the experiment.[10] These experiments allow us to asses three different contributions to the observed CD effects of **A-OPV3** in a stirred solution. The first results from the macroscopic helical arrangement of the assemblies induced by the helical flow pattern in the sample cell, leading to a bisignate CD effect originating from the combined LB and LD′ optical responses of the **A-OPV3**. Furthermore, there can be a minor contribution arising from LD of the **A-OPV3** and birefringence in the optical system, similar to the monosignate CD effect under convective flow (see above). Lastly, there might be a contribution from stirring-induced chirality on the molecular level, for which a bisignate spectral shape is also expected, but we disregard this option, because the observed CD effect appears and disappears very rapidly when turning the stirring on and off.

Since we have studied the self-assembly of the chiral **S-OPV4** in great detail before,[11] we also investigated the influence of shaking, cooling, and stirring on its assembly.[12] This oligomer has one phenylene vinylene unit more than **A-OPV3**, and the stereocenters in the side chains bias the helicity of the chiral stacked fibers. The CD spectrum taken at ambient temperature without stirring (Figure 4a) is free from

  

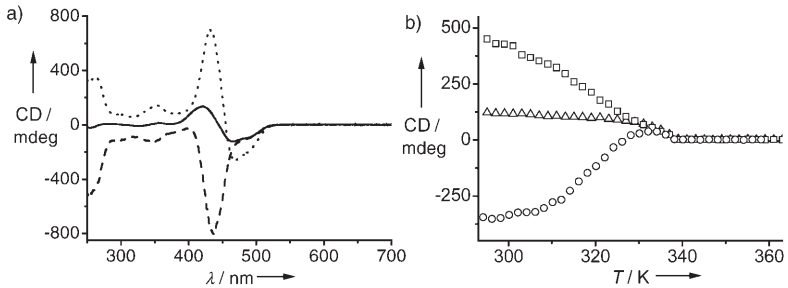


***Figure 4.*** **S-OPV4** dodecane solution (1 cm cuvette, $c = 3 \times 10^{-5}$ M). a) CD spectra at 293 K without stirring (——) and with clockwise (-----) and counterclockwise (•••••) stirring (solution obtained by cooling from 363 to 293 K with 60 K h$^{-1}$ without stirring) b) Temperature-dependent CD measurements at $\lambda = 420$ nm ($-dT/dt = 60$ K h$^{-1}$) without stirring (△) and with clockwise (○) and counterclockwise (□) stirring.

the two types of artifacts discussed above and corresponds to the spectra reported earlier.[1,2] Furthermore, shaking does not affect the CD spectra.[2] Under stationary conditions, no LD effects are present. A CD cooling curve, similar to that reported previously, is shown in Figure 4b; it displays an elongation temperature $T_e$ of 339 K ($c = 2.4 \times 10^{-5}$ M).[1] Monitoring the cooling of the **S-OPV4** solution with linear dichroism shows an increase in LD[2] that starts at 334 K, that is, below the elongation temperature of the self-assembly. Since the size of the **S-OPV4** assemblies is much smaller than that for **A-OPV3**, the **S-OPV4** fibers are less susceptible to the flow patterns created in the cuvette; hence, randomization of the fibers is much faster.[1] Although LD is present during cooling, the CD response at 293 K is only marginally affected (typically by 4%). Previously, we suggested on the basis of AFM data that **S-OPV4** forms bundles of fibers at high concentrations and ascribed the additional increase in CD intensity during cooling to the lateral interactions of the fibers.[1] When this **S-OPV4** solution ($c = 2.4 \times 10^{-4}$ M) is monitored by LD, an increase in intensity occurs at the same temperature as the additional increase in CD. This result suggests that the deviation from the cooperative self-assembly model is probably caused by the formation of bundled fibers that are aligned by the convective flow, as visualized with linear dichroism.[2] Hence, we conclude that for **S-OPV4**, convective flows can also give rise to deviations of the optical spectra; the magnitude is so low that all published data are only marginally influenced by this phenomenon.

Stirring of the **S-OPV4** solutions, on the other hand, again has a significant influence on the CD effect, the sign of which depends on the stirring direction (Figure 4a). The absorption is not affected by the vortex flow.[2] The CD intensity upon stirring is less than for **A-OPV3**, which is probably a result of the different sizes of the assemblies. Furthermore, the CD intensity was also monitored at $\lambda = 420$ nm during cooling, while the **S-OPV4** solution was either not stirred or stirred continuously in a clockwise or counterclockwise direction (Figure 4b). The effect of stirring becomes visible 5 K below the elongation temperature. This behavior again suggests that a certain stack length is needed for the systems to be influenced by stirring and that chirality at the molecular level seems unaffected by the stirring.

In conclusion, we observed that supramolecular assemblies can be partially oriented by convective flow, shaking, or stirring. This partial orientation induces an artificial contribution in the circular dichroism spectra of both chiral and achiral assemblies. The shape, sign, and intensity of the CD spectrum depend on the type of flow, and two different CD effects are observed; one is due to convective flow and is based on linear dichroism, and the other is due to vortex flow patterns and is based on linear dichroism and linear birefringence. 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 length scale. To reduce the flow, we are currently designing a cuvette with improved heat transfer to decrease the temperature gradient. The flow-induced CD, together with hydrodynamic modeling, will be used to study size and shape of the assemblies.

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