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Circular Dichroism and UV−Visible Absorption Spectra of the Langmuir−Blodgett Films of an Aggregating Helicene

Colin Nuckolls,[#] Thomas J. Katz,*,[#] Thierry Verbiest,*,[§] Sven Van Elshocht,[§] Hans-Georg Kuball,*,[‡] Stefan Kiesewalter,[‡] Andrew J. Lovinger,[†] and André Persoons[§]

Contribution from the The Department of Chemistry, Columbia University, New York, New York 10027,
Laboratory of Chemical and Biological Dynamics, K. U. Leuven, Celestijnenlaan 200D,
B-3001 Heverlee, Belgium, FB Chemie, Universität Kaiserslautern, 67653 Kaiserslautern, Germany, and
Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974

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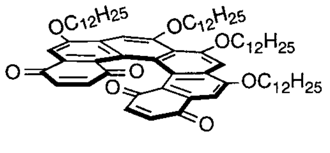
Abstract: Nonracemic helicene **1** forms high-quality Langmuir−Blodgett (LB) films, in which the molecules are organized in parallel columns with their edges exposed to the surface. Evidence for the edge-on exposure is the molecular area of a monolayer on water and, as determined by X-ray diffraction, the similarity of the interlayer spacings of multilayers to the diameters of the molecular columns that constitute nonracemic **1** in bulk. Evidence of the organization into parallel columns includes the linear dichroism of the films and the 180° periodicity with which rotating the films varies the amounts by which plane polarized light is rotated, the intensities of the second harmonics generated, and the films' degree of anisotropy. The circular dichroisms of a 10-layer LB film could be resolved from the effects of linear dichroism and linear birefringence. The CD and UV−vis absorption spectra of the films are similar to those of solutions in which the molecules are aggregated, not isolated. The measurement of a CD spectrum for a monolayer, carried out easily for nonracemic **1**, is unprecedented.

Introduction

Like planar aromatic molecules surrounded by aliphatic side chains, the helical aromatic molecule **1** in nonracemic form self-aggregates into what is believed to be a long corkscrew-shaped assembly, both in alkane solutions[1] and as the pure material.[2] In solution, the aggregation enhances circular dichroisms and the rotation of plane polarized light. It shifts the UV−vis absorption spectrum and the fluorescence emission spectrum. In the pure material, it leads to the formation of liquid crystalline fibers comprised of hexagonally arrayed columns of helicenes with aligned helix axes (**2**, the side chains have been deleted for clarity, and the first helicenes are arbitarily shown to be in the same rotational phase).



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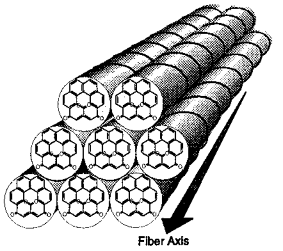

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The intermolecular forces presumed to be the basis for the organization of the planar discotic analogues into columns in solution[3] and in pure materials[4] are also thought[5] to account for why the molecules organize themselves into Langmuir−Blodgett (LB) films comprised of aligned columns of disks oriented with their edges on the substrate.[6−9] This orientation

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[#] Columbia University.

[§] K. U. Leuven.

[‡] Universität Kaiserslautern.

[†] Bell Laboratories.

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[8] Substituted truxenes and benzenes: (a) Maliszewskyj, N. C.; Heiney, P. A.; Blasie, J. K.; McCauley, J. P., Jr.; Smith, A. B., III *J. Phys. II* **1992**, *2*, 75. (b) Albrecht, O.; Cumming, W.; Kreuder, W.; Laschewsky, A.; Ringsdorf, H. *Colloid Polym. Sci.* **1986**, *264*, 659. (c) Reference 5b.

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is adopted even when the molecules are not amphiphilic and even when hydrophobic side chains in the Langmuir films would have to be submerged in water.[10] We consider below whether the analogies between planar discotics and helical molecule **1** would extend to stable LB films being formed by **1** and whether such thin films would be highly optically active. We show that the films do form, and we analyze their absorption spectra, circular dichroism spectra, and optical activities. Although some points are made about the nonlinear optical properties, a separate paper considers these properties in depth and also analyzes, by means of atomic force microscopy, how the films are organized.[11]

Experimental Section

The LB films were prepared in a KSV minitrough from (+)-**1** that was >98% optically pure.[1] The subphase was Millipore ultrapure water. The monolayers of **1** were transferred by the horizontal lifting method to optical quality glass or quartz plates that were silanized with octadecyltrichlorosilane to make them hydrophobic. The transfer ratio was 1.09 to glass and 1.05 to quartz, showing that the layers transferred were single and transferred completely. The high quality of the films is also attested to by the intensities of the second harmonics increasing in proportion to the square of the number of layers.[11,12]

UV−vis absorption spectra were recorded on a Perkin-Elmer Lambda 19 UV−vis spectrometer, polarized UV−vis spectra on a Varian Cary 2200 spectrometer, circular dichroism spectra on a JASCO 720 spectrometer and a Jobin Yvon Mark IV dichrograph, and optical rotations on a JASCO Dip 1000 polarimeter. A plate holder allowed the samples to be rotated through 360° at 30° increments. The light transmitted by samples irradiated with plane polarized light and rotated in 7.5° steps about an axis parallel to the propagation direction was analyzed by de Sénarmont's method[13,14] to determine its ellipticity and the amount by which its azimuth was rotated.

X-ray diffractograms of Ni-filtered Cu Kα radiation were recorded in the reflection geometry at 0.25−1° 2Θ/min.

Results and Discussion

Formation and Structure of Langmuir−Blodgett Films. Dextrorotatory **1**,[1] almost surely of the *P* configuration,[15] as a 2×10^{-4} M solution in chloroform was spread onto a water surface at 20 °C, and after the chloroform had evaporated, the surface was compressed at a rate of 0.02 nm^2/molecule min. Figure 1 shows that the surface pressure rises sharply when the area is decreased below ca. 0.9 nm^2/molecule, and that the area collapses when the pressure increases to 42 mN/m. The well-defined collapse implies that a monolayer is formed, and the area per molecule implies that in the monolayer the molecules are oriented with their edges, rather than their faces, on the surface. Thus, the area found above (0.9 nm^2) is consistent with the 1.33 nm^2 area calculated for the molecule assuming that the side chains are extended and the view is from an edge. (Calculated areas are usually somewhat larger than those found by compressing Langmuir films, presumably because side chains fold and interdigitate[7b,8a,9d] and cores tilt.[16]) If the view were from a face, the area calculated (assuming the side-chains to be extended) would be ca. 12 nm^2.[17] That the molecules of **1** orient themselves edge-on to the surface agrees with numerous analyses cited above of discotic molecules that in bulk organize themselves in columns and in Langmuir and Langmuir−Blodgett films orient themselves perpendicular to the substrate. Moreover, the way planar discotic molecules arrange themselves perpendicular to the surface is in parallel columns, which makes their films anisotropic,[7b,f,9e,f,18] and if the molecules of **1** organized themselves similarly, their films would be anisotropic too.

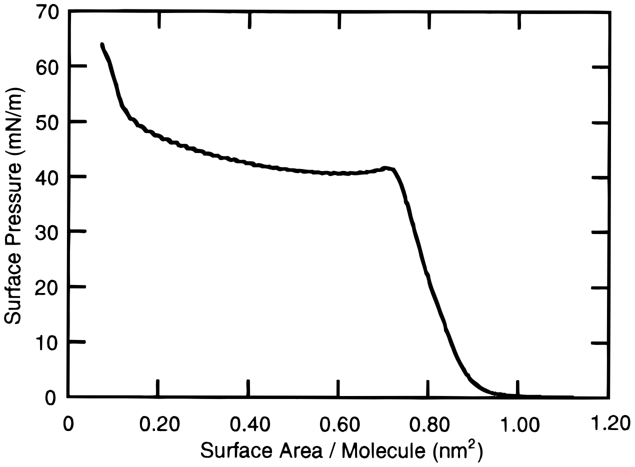

Figure 1. Surface pressure as a function of molecular area for films of nonracemic **1** on water at 20 °C.

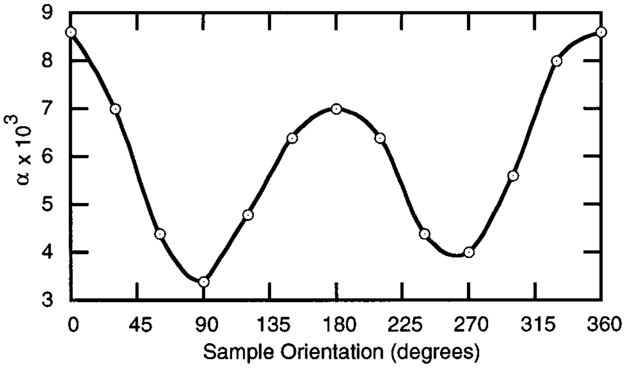

Figure 2. The amount by which a 10-layer LB film of (+)-**1** on quartz rotates the plane of polarization of an 8 mm light beam at the Na D-wavelength (589 nm) as a function of the angle through which the sample is rotated about the normal to the film's plane.

Evidence that the films are indeed anisotropic is presented in Figures 2 and 3. Figure 2 shows how rotating a 10-layer

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(10) Reference 6a and references therein.

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(12) The variation in the maximum second harmonic signal intensity, measured as in ref 11, fits, with $R = 99.9\%$, the equation, second harmonic intensity $= 0.513n^2 + 0.471$. (Verbiest, T.; Van Elshocht, S.; Kauranen, M.; Persoons, A. Unpublished results.)

(13) Briegleb, G.; Kuball, H.-G. *Z. Phys. Chem. N. F.* **1965**, *45*, 339.

(14) Kiesewalter, S. Ph.D. Dissertation, University of Kaiserslautern, 1998.

(15) The CD spectrum of a dilute solution in dodecane (see Figure 4) resembles that of a related (*P*)-(+)-[6]helicenebisquinone of known absolute configuration (Katz, T. J.; Liu, L.; Willmore, N. D.; Fox, J. M.; Rheingold, A. L.; Shi, S.; Nuckolls, C.; Rickman, B. H. *J. Am. Chem. Soc.* **1997**, *119*, 10054).

(16) Jákli, A.; Müller, M.; Krüerke, D.; Heppke, G. *Liq. Cryst.* **1998**, *24*, 467 and references therein.

(17) The area with edge on the surface was calculated as the packing distance of a typical discotic liquid crystal (ca. 3.8 Å) and the average (ca. 35 Å) of the length (44 Å) and width (27 Å) of helicene **1**.[2] The area of the face is the product of the length and width.

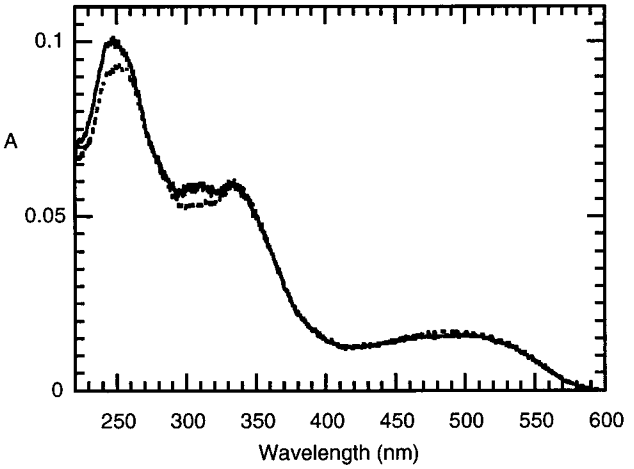

Figure 3. UV−vis absorption spectra of a 10-layer LB film of (+)-**1** on quartz for a 3 mm × 5 mm light beam polarized parallel (−) and perpendicular (···) to an axis in the sample rotated 30° from the short axis of the substrate.

LB film on quartz varies the amount by which the film rotates the plane of polarization of 589 nm ("D-line") light. Similarly, when a 7-layer LB film of nonracemic **1** on glass is irradiated with 1064 nm light, rotation about the surface normal varies the intensity of the generated second harmonic in the same way.[11] Figure 3, the polarized UV−vis spectra of a 10-layer LB film on quartz, shows that the film is linearly dichroic, the optic axis being oriented 30° from the short axis of the substrate. This linear dichroism was independently analyzed by measuring the amount by which dichroic absorption rotates the polarized light's azimuth, a method that is much more sensitive than polarized light absorption spectroscopy.[19] The degree of anisotropy[20] R is 0.024 for the absorption at 250 nm and 0.026 for the absorption at 306 nm. The experiments show that the films have 2-fold axes of symmetry, which suggests that the molecules assemble into the parallel columns characteristic of LB films of the related planar molecules.[21]

This organization is demonstrated by Atomic Force Microscopic images.[11] X-ray diffraction analysis also provides evidence. The diffraction from 5-layer and 10-layer LB films of the nonracemic helicene on glass shows layer spacings of ca. 4.6 ± 0.2 nm, almost equal to the diameters of the columns (4.2 nm) that constitute the bulk material.[2] The layer spacing suggests that the columns of helicene molecules in the LB films may be packed tetragonally or possibly skewed from parallelism in adjacent layers, whereas in the pure material, they are packed on a hexagonal lattice.[22,23] The absence of additional peaks, in particular higher order reflections corresponding to the 4.6 nm spacing, implies that this ordering of the columns is imperfect. We also noted that *no* crystallographic X-ray diffraction peaks could be recorded from 5-layer LB films on glass of the racemic helicene **1**, a material that does not form visible fibers and whose LB films on AFM analysis show only short unaligned columns.[11]

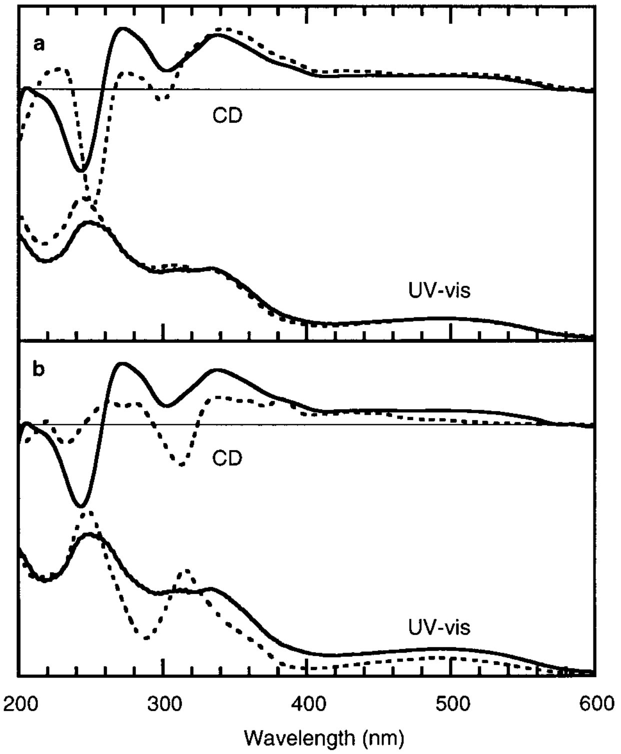

Figure 4. CD and UV−vis spectra of (+)-**1** (a) as a 10-layer film (solid line) and as a 2.5×10^{-2} M solution in dodecane (dashed line) and (b) as a 10-layer film (solid line) and as a 1.0×10^{-4} M solution in dodecane (dashed line). Intensities are scaled to match. The light beam is 8 mm in diameter.

Circular Dichroism and UV−Vis Absorption Spectra of Langmuir−Blodgett Films and Solutions of Nonracemic 1 Compared. Figure 4 compares the circular dichroism (CD) and UV−vis absorption spectra of (+)-**1** as a 10-layer LB film on a quartz plate with the CD and UV−vis absorption spectra of (+)-**1** dissolved in dodecane at a concentration of either 2.5×10^{-2} (Figure 4a) or 1.0×10^{-4} M (Figure 4b). Note that the displayed CD spectrum of the film is the average of 12 spectra measured by the CD spectrometer as the sample was rotated through succesive 30° increments about an axis parallel to the light beam. It should therefore be free of artifacts due to linear effects arising from the anisotropy of the film,[24] a point that, as described further below, was double-checked and confirmed. The significant observation is that the spectra in Figure 4a are similar while those in Figure 4b are different. Since in the more concentrated solution of Figure 4a the

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(21) For the planar discotics, this assembly is consequent on the transfer to the substrate, and it occurs even for the horizontal lifting method used here. (a) Reference 9e. (b) Schwiegk, S.; Vahlenkamp, T.; Xu, Y.; Wegner, G. *Macromolecules* **1992**, *25*, 2513.

(22) Tetragonal packed columns of a discotic triphenylene (reference 7c) and a discotic copper phthalocyanine (reference 9b) have previously been analyzed. The columns of other triphenylenes have been found to be spaced more widely in their LB films than in the bulk materials (refs 7b and 7f).

(23) The spacing analyzed by X-ray diffraction from the hexagonal lattice of the bulk material is 3.6 nm.[2]

(24) (a) Kuball, H.-G.; Schönhofer, A. In *Circular Dichroism: Principles and Applications*; Nakanishi, K., Berova, N., Woody, R., Eds.; VCH: New York, 1994; Chapter 4. (b) Schönhofer, A.; Kuball, H.-G. *Chem. Phys.* **1987**, *115*, 159. (c) Nordén, B. *Acta Chem. Scand.* **1972**, *26*, 1763. (d) Tunis-Schneider, M. J. B.; Maestre, M. F. *J. Mol. Biol.* **1970**, *52*, 521. (e) Cornell, D. G. *J. Colloid Interface Sci.* **1979**, *70*, 167.

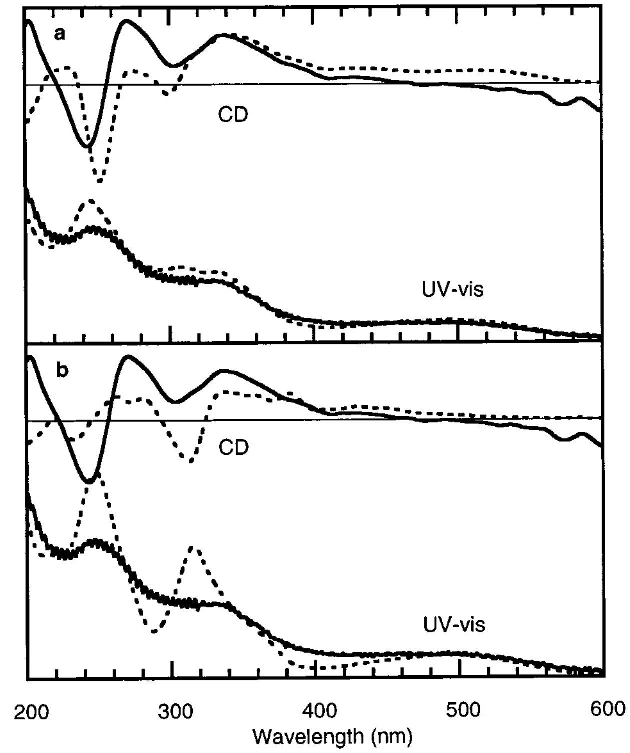

Figure 5. CD and UV−vis spectra of (+)-**1** (a) as a 1-layer film (solid line) and as a 2.5×10^{-2} M solution in dodecane (dashed line) and (b) as a 1-layer film (solid line) and as a 1.0×10^{-4} M solution in dodecane (dashed line). Intensities are scaled to match. The light beam is 8 mm in diameter.

molecules of **1** are aggregated, whereas in the more dilute solution of Figure 4b they are not,[1] the implication is that the molecules in the LB film are aggregated much as they are in the more concentrated solution. This observation agrees with and even magnifies similar ones made for a number of phthalocyanines, whose LB films display UV−vis absorption spectra resembling those of solutions of aggregated molecules, but which unlike the LB films of nonracemic **1** also display recognizable peaks characteristic of the monomers.[3a,9e,18d,e,25] It also agrees with the observation that the sheared films of a propeller-shaped polycyclic aromatic molecule display UV absorption spectra resembling those of solutions of its aggregates, not monomers.[26]

Unprecedented, however, are the similarities displayed in Figure 5. This compares the CD and UV−vis absorption spectra of (+)-**1** in dodecane as aggregates (Figure 5a) and as monomers (Figure 5b) with those of (+)-**1** as a *monolayer* on quartz. (Again the CD spectrum of the film is the average of 12 measured as the sample was rotated through successive 30° increments.) The conclusion again is that the spectra of the film resemble those of the aggregates in solution, not of the monomers in solution. The implication is that since the molecules comprising the LB monolayer are organized in sheets that are only one molecule thick, an account for the spectra in solution would require the aggregates to be clustered in at most two dimensions, and probably only one. That is, like the columnar structures formed by triphenylenes in hexadecane,[3b,c] the aggregates of nonracemic **1** in dodecane solution are likely to be comprised of columns of helicene molecules.

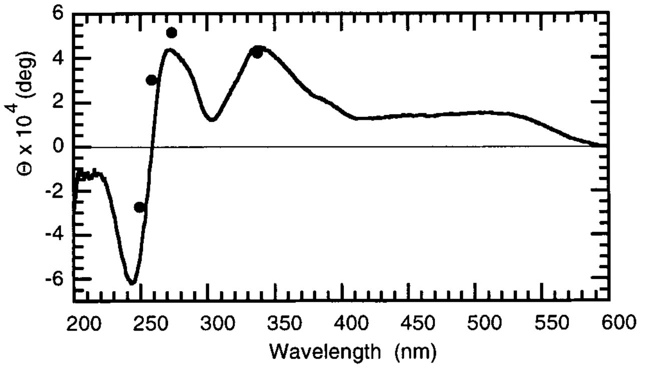

Figure 6. CDs of a 10-layer LB film of (+)-**1**: (—) average, as the sample was rotated, of spectra measured with a commercial dichrograph (the light beam was 5 mm × 10 mm); (●) values measured by the ellipticity of the transmitted light (diameter 5 mm).

While, as described above, the average of the spectra of the LB films in different phases of rotation should be the true CD spectra of the films, we double checked the point because the measured spectra did change, particularly at 303 and 242 nm, when the samples were rotated. The implication is that the unaveraged spectra blend linear and circular effects. The circular dichroisms of the films were therefore derived independently from the ellipticities of transmitted light at four selected wavelengths as measured by de Sénarmont's method.[13,14] As Figure 6 shows, within experimental error the circular dichroisms analyzed by the two methods are the same.

One other point about the CD spectra is notable. The *g* value ($\Delta\epsilon/\epsilon$), ca. 7.5×10^{-3} for the CD at ca. 240 nm, which appears when the molecules aggregate, is similar to that of inherently chiral chromophores,[27] in accord with the proposition that the CD spectrum at this wavelength results from an exciton coupling between transition moments parallel and perpendicular to the helix axis.

It is significant that the CD spectrum of nonracemic **1** as a monolayer (Figure 5) is observed at all. Thus, while there is a previous example in which CD spectra of LB monolayers are recorded—of helical peptides, and this may be the only example[28]—those CD spectra were analyzed by using six plates stacked in series. The CD spectra of LB films of other helical peptides were measured using stacks of 5−20 bilayers, but for a single monolayer, they were too weak to analyze.[29] The CD spectrum of an annealed 40-layer LB film of a chiral phthalocyanine is reported, but not of a thinner film.[9f] Presumably the reason the CD spectrum of the monolayer of **1** is so intense is that the molecules are assembled into columns, in which the CDs are enhanced. This assembly also enhances the specific rotation. Thus the average rotation in Figure 2 is +0.007°, and since the thickness of the 10-layer film determined by AFM is ca. 45 nm (which agrees with the 10 × 4.6 nm according to the X-ray diffraction analysis above), the specific rotation of the film is 146 deg/mm or $[\alpha]_D$ +18000 deg cm^2/10 g. This rotation is much larger than the $[\alpha]_D$ of 678 deg cm^2/10 g of a 2.1×10^{-5} M solution in dodecane (in which the molecules of **1** are unaggregated) and similar to the 15500 deg cm^2/10 g measured for the gel formed when this solution is concentrated to 1×10^{-1} M (in which they are aggregated).[30]

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Conclusions. Like molecules that aggregate into columnar mesophases, nonracemic **1** forms anisotropic LB films whose CD and UV−vis absorption spectra resemble those of solutions of aggregates, not of monomers. The implication is that both in the films and in dodecane solutions, as in the bulk material, the molecules assemble into long columns. The CDs of these corkscrew shaped assemblies are so large they can be measured easily for a monolayer, which is unprecedented.

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