Spreading Behavior of Optically Active Macrocycloamides Consisting of Helical Chiral Units at the Air−Water Interface and the Formation of Langmuir−Blodgett Films

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Abstract: The spreading behavior of a new type of chiral compound, namely a series of optically active macrocycloamides ((*P*)-(−)-**1**, (*P*,*P*)-(+)-**2**, (*P*,*P*,*P*)-(+)-**3**, and (*P*,*P*,*P*,*P*)-(+)-**4**) consisting of the helical chiral unit 1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarboxylate, and dianiline derivatives, on the water surface was investigated by measuring surface pressure (π)−area (A) isotherms, with the aim of producing a new type of chiral Langmuir−Blodgett film. Among the four compounds investigated, (*P*)-(−)-**1** and (*P*,*P*)-(+)-**2** formed condensed monolayers. Moreover, the monolayer of (*P*)-(−)-**1** could be successively transferred onto solid supports by both downward and upward strokes, yielding Y-type LB films. An optically active LB film based on helical chirality was produced for the first time. The properties of the chiral LB film are discussed.

Introduction

The Langmuir−Blodgett (LB) technique can provide organized molecular assemblies with well-defined molecular orientation and an ordered layer structure similar to that of biological membranes.[1] In a classical concept, amphiphilic molecules having a polar headgroup and a long hydrophobic tail can form a stable monolayer and LB multilayers. However, molecules without long hydrophobic chains such as porphyrins,[2] phthalocyanines,[3] and calixarenes[4] were also shown to form stable LB films. Recently, LB films composed of chiral molecules have been studied from the aspect of molecular recognition in biomembrane systems. The formation of chiral LB assemblies is desired from the standpoint of designing an organized molecular assembly system capable of discriminating chiral substrates or biomaterials.[5]

Arnett [6] and co-workers extensively studied chiral molecular recognition in monolayers of amino acid derivatives using surface pressure−area measurements and surface shear viscosities from the viewpoint of the effect of stereochemistry on the molecular aggregation in monolayers. Pathirana[7] et al. elucidated the recognition of enantiomeric molecules of carvone, an odorant, by chiral phospholipid monolayers by monitoring changes in the surface pressure−area isotherms. They employed mainly surfactants that have a chiral carbon center (tetrahedral chirality).

Aside from tetrahedral and axial chiralities, helical chirality has attracted much attention; however, to our knowledge, there is no report on the LB film consisting of a helical chiral unit. In our previous studies,[8,9] we prepared a chiral polymer LB film containing axially chiral binaphthalene, and detected enantioselective recognition by the optically active substrate by monitoring the potential of an electrode modified with the chiral polymer LB monolayer. Our group[10] recently reported an efficient synthesizing method for various optically active macrocycloamide compounds using the helical chiral unit, 1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarboxylate, and dianiline derivatives. As a basic approach to create a new type of chiral LB film, we here describe the spreading behavior of a series of macrocycloamides consisting of the helical chiral unit and the first success in the formation of a new optically active LB film based on helical chirality.

Experimental Section

A series of optically active macrocycloamides ((*P*)-(−)-**1**, (*P*,*P*)-(+)-**2**, (*P*,*P*,*P*)-(+)-**3**, and (*P*,*P*,*P*,*P*)-(+)-**4**) and *racemic*-**1** (Chart 1) were synthesized by reacting 1,12-dimethylbenzo[*c*]phenanthrene-5,8-

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† Faculty of Pharmaceutical Sciences.

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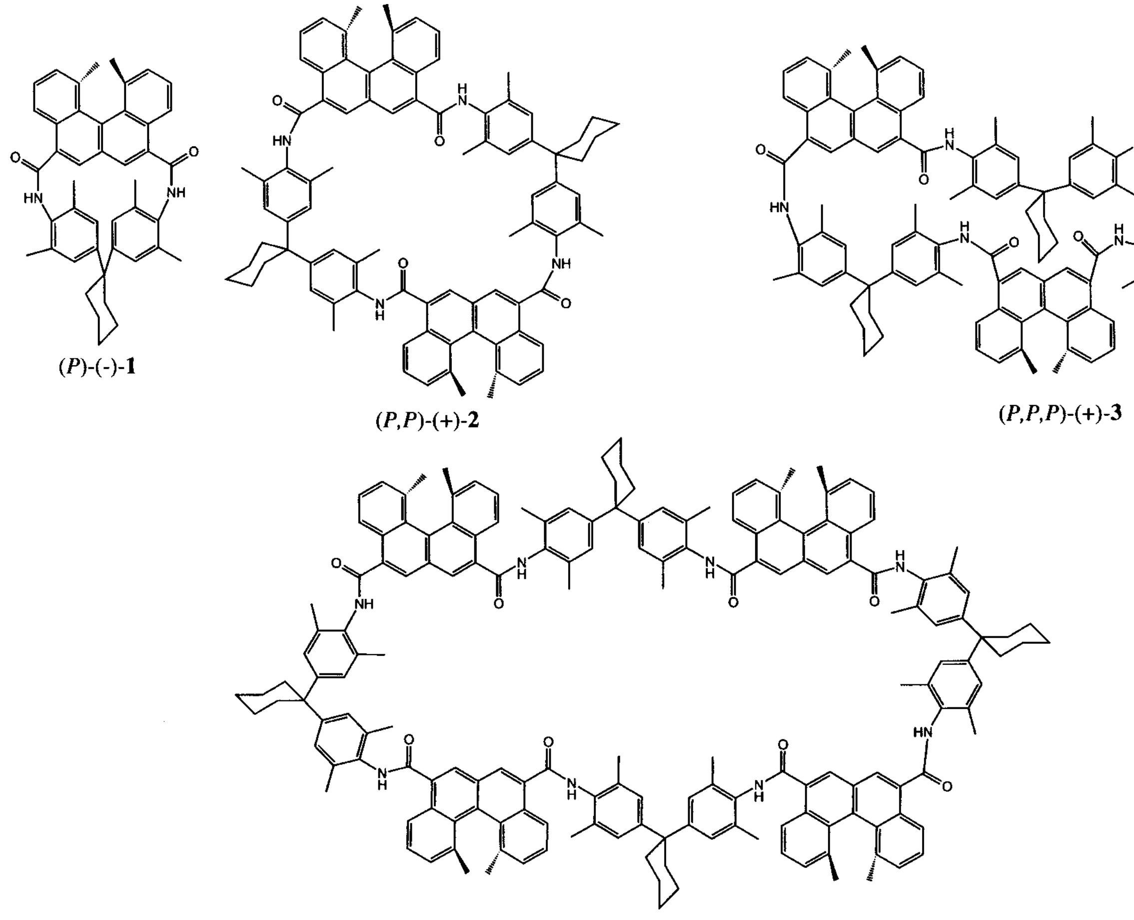
Chart 1: Structure of Macrocycloamides


(*P*)-(-)-**1**

(*P*,*P*)-(+)-**2**

(*P*,*P*,*P*)-(+)-**3**

(*P*,*P*,*P*,*P*)-(+)-**4**

dicarboxylate with a dianiline spacer, using the same method as that described in a previous paper.[10]

Measurement of surface pressure−area (π−A) isotherms and monolayer deposition were carried out at 20 °C with use of an automatic Langmuir trough (Kyowa Kaimen Kagaku HBM-AP) equipped with a Wilhelmy balance. The four chiral compounds were spread from a 1 mM chloroform solution on a pure water (Milli-Q II, Millipore) surface for the measurement of π−A isotherms. The quartz slides on which LB multilayers were deposited were cleaned in boiling *concentrated* HNO_3, washed with pure water, and made hydrophobic with octadecyltrichlorosilane.

UV−visible spectra and fluorescence spectra were measured with a Hitachi U-3000 UV−visible spectrophotometer and a Hitachi 850 spectrofluorophotometer, respectively.

Time-resolved emission spectra were measured by a single-photon counting method with an argon ion laser (Spectra-Physics, BeamLok 2060-10-SA), a pumped Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, 1.5 ps fwhm) with a pulse selector (Spectra-Physics, Model 3980), a third harmonic generator (GWU-23PS), and a streakscope (Hamamatsu Photonics, C4334−01).

Results and Discussion

Monolayer Behavior on the Water Surface. Optically active macrocycloamides that have various ring sizes (Chart 1) were spread from a chloroform solution on the water surface to measure the π−A isotherms at 20 °C (Figure 1). It is of interest that all of the π−A isotherms show a relatively steep rise in surface pressure and have a high collapse pressure despite the absence of a long alkyl chain that is considered to be necessary for stable monolayer formation. In our previous work,[11] we showed that polyacrylamides form a stable monolayer even on polymer materials, where the hydrogen bond based on the amide structure is an important factor for self-assembly. A similar interpretation also applies in the present case: The macrocycloamide molecules form a monomolecular layer on the water surface and not a crystal due to hydrogen bonding by the amide group. The isotherm apparently varies with the size of the macrocycloamide; the surface area shifts toward larger surface area with increase in the number of condensed rings and the collapse pressure decreases with increasing ring size. This

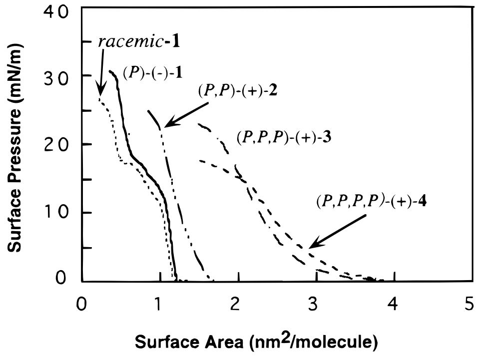


Figure 1. Surface pressure−area isotherms of macrocycloamides at 20 °C.

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Chart 2: CPK Model of (*P*)-(−)-**1** at Face-On Orientation

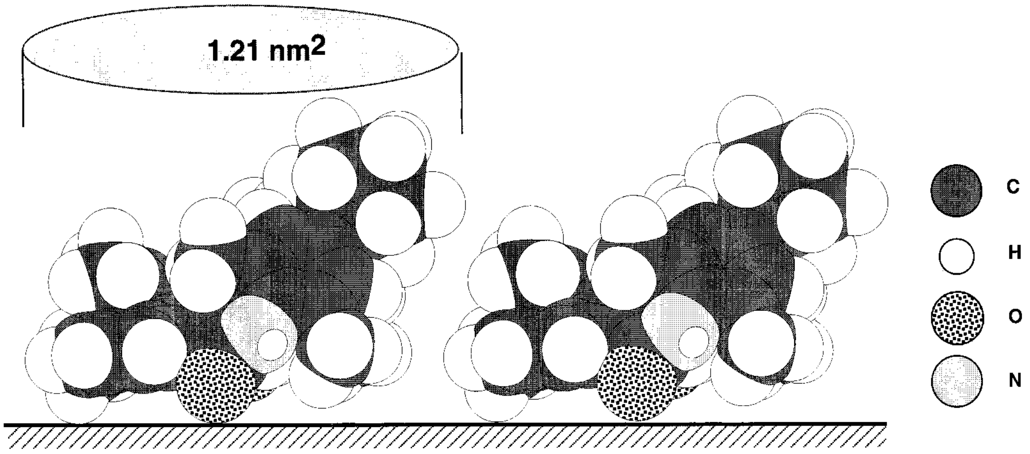
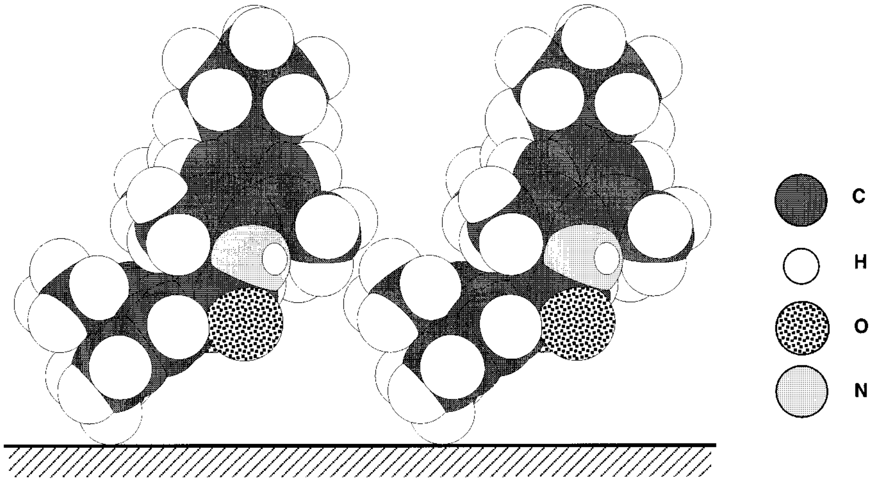


Chart 3: CPK Model of (*P*)-(−)-**1** at Edge-On Orientation



implies that the monolayer becomes unstable with increase in the molecular size. (*P*)-(−)-**1** and (*P*,*P*)-(+)-**2** form condensed monolayers whereas (*P*,*P*,*P*)-(+)-**3** and (*P*,*P*,*P*,*P*)-(+)-**4** show the formation of expanded monolayers. The isotherm of *racemic*-**1** shows a similar behavior to that of (*P*)-(−)-**1**; however, the surface area is smaller and the collapse pressure is lower, indicating that the racemic monolayer is relatively unstable compared with (*P*)-(−)-**1**.

The most well-defined condensed monolayer was obtained with the smallest macrocycloamide, (*P*)-(−)-**1**. The $\pi-A$ isotherm shows a steep rise in surface pressure and a plateau region of the surface pressure, which corresponds to a phase transition. Extrapolation of the steeply rising part of the $\pi-A$ curve to zero pressure gives the average surface area occupied by molecule in the monolayer on the water surface. On the basis of this value, the molecular orientation and the molecular packing state in the condensed monolayer are discussed. The surface area of (*P*)-(−)-**1** was estimated to be 1.21 and 0.78 nm^2/molecule for the monolayer before and after the phase transition, respectively. As the most probable molecular orientation, the face-on orientation is shown in Chart 2, where a relatively hydrophilic dimethylbenzo[*c*]phenanthrene amide plane faces the water subphase and the hydrophobic diphenylcyclohexane spacer group orients toward the air phase. The value of 1.21 nm^2 is consistent with the cross section calculated from the CPK model based on the face-on orientation (Chart 2). Upon further compression of the monolayer, the isotherm shows a phase transition resulting in a more compact form having an area of 0.78 nm^2/molecule. Although the phase transition is not clear in the present study, the transition from the face-on orientation to the edge-on orientation (Chart 3), where the phenanthrene amide plane is detached from the water surface, can be considered. We conclude that the condensed monolayer after the transition was not transferred onto a solid support as will be described hereafter.

The surface areas of (*P*,*P*)-(+)-**2**, (*P*,*P*,*P*)-(+)-**3**, and (*P*,*P*,*P*,*P*)-(+)-**4** were estimated to be 1.42, 2.71, and 2.95 nm^2 and their collapse pressures were determined to be 24.7, 23.0, and 17.8 mN/m, respectively. It is difficult to estimate the orientation of (*P*,*P*)-(+)-**2**, (*P*,*P*,*P*)-(+)-**3**, and (*P*,*P*,*P*,*P*)-(+)-**4** at the water−air interface because there are several hydrophilic planes and hydrophobic parts in these molecules.

LB Film Formation. Among the chiral cycloamide compounds, the monolayer of the smallest cycloamide (*racemic*-**1** and (*P*)-(−)-**1**) could be transferred onto solid supports by both downward and upward strokes at a deposition pressure of 10 mN/m. The transfer ratio of the upward stroke for (*P*)-(−)-**1** was almost unity, while that of the downward one decreased as the deposition proceeded. This is because the interaction between hydrophobic interfaces is not sufficient to keep the deposition ratio constant. However, the total average transfer ratio up to 80 layers was maintained at 0.8, suggesting that a fairly uniform LB film was prepared. It was difficult to keep the monolayer of (*P*)-(−)-**1** constant at pressures over 15 mN/m and the monolayer could not be deposited onto a solid support.

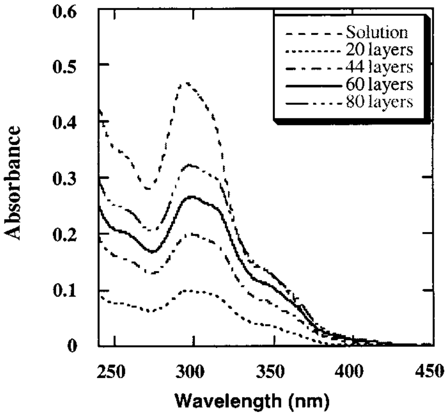


Figure 2. UV absorption spectra of (*P*)-(−)-**1** in chloroform solution (1.5×10^{-5} M) and in LB films.

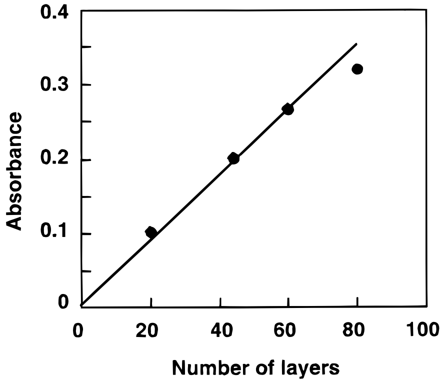


Figure 3. Plots of the absorbance at 297 nm of (*P*)-(−)-**1** in LB films as a function of the number of layers.

After the phase transition, which is ascribed to a change from the face-on to the edge-on orientation, the condensed monolayer collapsed.

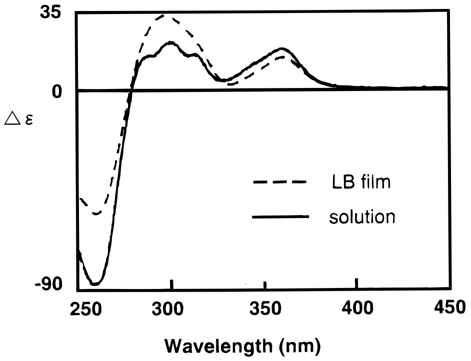


Figure 4. CD spectra of (*P*)-(−)-**1** in chloroform solution (1.5×10^{-5} M) and in LB films with 22 layers.

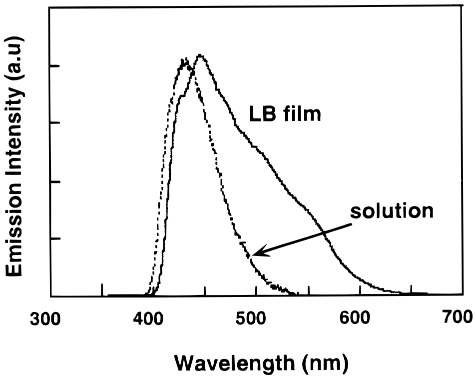


Figure 5. Fluorescence spectra of (*P*)-(−)-**1** in chloroform solution (1.5×10^{-5} M) and in LB films with 22 layers.

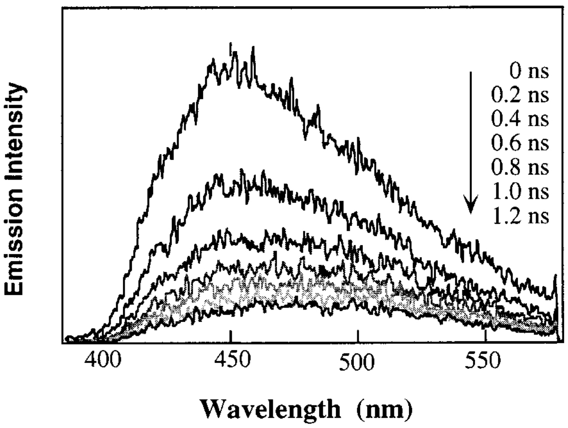


Figure 6. Time-resolved emission spectra of (*P*)-(−)-**1** in LB films.

The UV absorption spectra of (*P*)-(−)-**1** in chloroform solution (1.5×10^{-5} M) and in LB film with various numbers of deposited layers are shown in Figure 2. The absorption of (*P*)-(−)-**1** in the LB films slightly shifted toward the longer wavelength region compared with that of (*P*)-(−)-**1** in solution, indicating some interaction between chromophores due to the close molecular packing in the LB films such as J-aggregates,[12] which are often observed in LB films. Moreover, the absorbance at 297 nm of (*P*)-(−)-**1** in the LB films increases with increasing number of deposited layers. A linear relationship between the absorbance and the number of layers was obtained for LB films with less than 60 layers; however, the absorbance gradually deviated from the line when the number of layers exceeded 60 (Figure 3). This is due to a gradual decrease in the transfer ratio for the downward stroke as the number of deposited layers increased, in contrast to the constant transfer ratio for the upward stroke of almost unity. The formation of optically active LB films based on helical chirality is confirmed by CD (circular dichroism) spectral measurements (Figure 4). The film exhibited the same Cotton effect[13] as the solution, which indicates that the helical chirality in solution is also maintained in LB films. No specific change in the CD spectra of the chiral LB films due to strong coupling between the chiral units was observed. A weak interaction between the molecules as reflected by the following fluorescence measurement results did not appear in this CD spectra.

The fluorescence spectra of (*P*)-(−)-**1** in solution (1.5×10^{-5} M) and in the LB film with 22 layers excited at 297 nm are shown in Figure 5. The fluorescence spectrum of (*P*)-(−)-**1** in the LB film differs from that for the solution. Broad emissions around 500 and 550 nm are observed in the spectrum of (*P*)-(−)-**1** in the LB film other than the monomer emission around 450 nm which is observed in the spectrum of (*P*)-(−)-**1** in solution. These broad emissions that are observed at longer wavelengths than the monomer emission in aromatic compounds are, in general, attributed to excimer species. Time-resolved emission spectra were measured to investigate the dynamic behavior of the excited state of (*P*)-(−)-**1** in the LB film as a preliminary dynamic analysis. The emission spectra changed with the monitoring time (Figure 6). The emission around 450 nm decays faster than that at longer wavelengths, resulting in

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the shift of the emission peak toward longer wavelengths with time. It is not clear what kind of excimer species and what kind of mechanism are involved, from the present study. Further studies based on dynamic analysis are necessary to clarify the behavior of the excited state of (*P*)-(−)-**1** in this chiral LB film.

In conclusion, the properties of the monolayers of a series of optically chiral macrocycloamides containing a helical chiral unit, 1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarboxylate, which spread on the water surface, were investigated with the aim of producing a new type of chiral LB film. Among the four compounds investigated, the monolayer of (*P*)-(−)-**1** could be transferred onto solid supports by both downward and upward strokes, yielding Y-type LB films. An optically active LB film based on helical chirality was produced for the first time. Chiral discrimination by the optically active LB film and application to a chiral sensor device are expected.

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