

## Chiral Molecular Assemblies from a Novel Achiral Amphiphilic 2-(Heptadecyl) Naphtha[2,3]imidazole through Interfacial Coordination

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**Abstract:** A novel amphiphilic compound 2-(heptadecyl) naphtha[2,3]imidazole (NpImC17) was synthesized, and its coordination with AgNO<sub>3</sub> in situ in the monolayer at the air/water interface and ex situ in the Langmuir–Blodgett (LB) film on solid substrate has been investigated. It has been found that interfacial coordination between NpImC17 and Ag(I) ion occurred both in the monolayer and in the LB film. It is interesting to note that the Ag(I)-coordinated ultrathin film became chiral although the ligand itself is achiral. It was suggested that the chirality of the Ag(I)-coordinated LB film was developed due to the formation of a helical coordination polymer through the interfacial coordination. To the best of our knowledge, this is the first report on the formation of chiral monolayer and LB films from an achiral molecule through interfacial coordination.

### Introduction

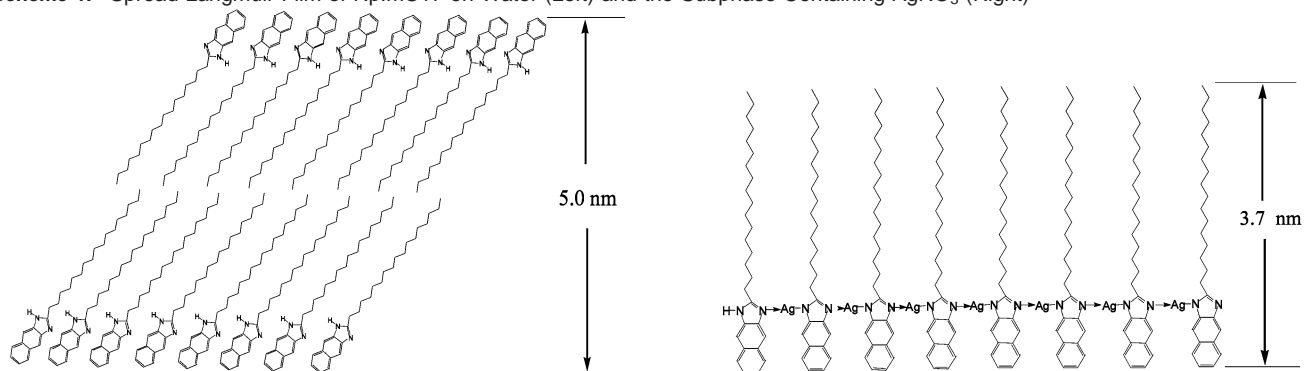
Chirality plays an important role in life and material sciences. Recently, besides the persistent interests in the asymmetric synthesis to create chiral molecules, increasing attention has been drawn to the chiral supramolecular assemblies.<sup>1–12</sup> Generally, the chirality of supramolecular systems can be generated through the assembly of chiral molecules<sup>1,2</sup> or the combination of chiral and achiral molecules.<sup>3–5</sup> On the supramolecular level, the spontaneous formation of chiral aggregate from achiral molecules is also important and currently has received much attention.<sup>6–12</sup> Monolayer and Langmuir–Blodgett (LB) films are sophisticated supramolecular systems in which molecules can be orderly arranged.<sup>13,14</sup> So far, research on the chiral LB

films is greatly concerned with the chiral amphiphiles;<sup>15–18</sup> in this paper, we report the formation of a chiral monolayer and LB film from an achiral amphiphile through the interfacial coordination.

Previously, in a series of study on the interfacial coordination in Langmuir monolayer and LB films, we have found that 2-substituted benzimidazoles can easily coordinate with Ag(I) ions to form a coordination polymer film at the air/water interface.<sup>19</sup> Under the coordination inducement, those benzimidazole derivatives with a very short alkyl chain or even no alkyl substitute can form a stable monolayer through the coordination with Ag(I) ions.<sup>19a,b</sup> In this work, we have extended the benzimidazole ring to the naphthaimidazole and designed a 2-(heptadecyl) naphtha[2,3]imidazole (Scheme 1, abbreviated as NpImC17) for investigating the interfacial coordination. We have found that this amphiphilic compound can coordinate with Ag(I) ions either at the air/water interface or in the LB film. It is interesting to find that, in both cases, the Ag(I)-coordinated films show chirality although the ligand itself is achiral. To the best of our knowledge, this is the first report on the formation of chiral monolayer and LB films from an achiral molecule through interfacial coordination. The interfacial coordination and

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**Scheme 1.** Spread Langmuir Film of NpImC17 on Water (Left) and the Subphase Containing AgNO<sub>3</sub> (Right)

the chirality of the LB films were investigated through a series of characterization methods such as the surface pressure–area ( $\pi$ - $A$ ) isotherms, UV spectra, circular dichroism (CD) spectra, and atomic force microscopy (AFM) measurements.

### Experimental Section

**Materials.** 2-(Heptadecyl) naphtha[2,3]imidazole (NpImC17) was synthesized by the condensation of 2,3-naphthylenediamine (Tokyo Kasei) with stearic acid (Tokyo Kasei) according to the literature method.<sup>20</sup> Equimolar mixtures of the two compounds were heated at 140 °C for 8 h under the N<sub>2</sub> atmosphere. The resultants were dissolved in methanol and recrystallized by adding carbon black. After filtration, the clear solution was cooled gradually, and a colorless crystal was obtained. NpImC17: mp 115–116 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.88 (t, 3H), 1.26 (m, 28H), 1.91 (m, 2H), 2.98 (t, 2H), 7.39 (m, 2H), 7.94 (m, 4H). Anal. Calcd for C<sub>28</sub>H<sub>42</sub>N<sub>2</sub>: C, 82.70; H, 10.41; N, 6.89. Found: C, 82.58; H, 10.43; N, 6.76.

**Procedures.** The monolayers were formed by spreading a chloroform solution ( $1 \times 10^{-3}$  mol/L) onto the surface of pure water and the aqueous subphases containing various concentrations of AgNO<sub>3</sub> (purified by recrystallization from ethanol/water). Surface pressure–area ( $\pi$ - $A$ ) isotherms were recorded on a KSV (KSV 1100, Finland) instrument with a compressing speed of 7.5 cm<sup>2</sup>/min after waiting 20 min for the evaporation of the solvent or for the completion of the reaction with the metal ions in the subphase. For UV and CD spectral measurements, the monolayers were transferred at a pressure of 20 mN/m onto quartz plates by a vertical dipping method with a down- and upstroke rate of 3 mm/min. For the FT-IR measurement, CaF<sub>2</sub> plates were used instead. The ex situ coordination of the ligand LB film with AgNO<sub>3</sub> was performed by immersing the transferred NpImC17 LB film fabricated from the pure water surface into an aqueous AgNO<sub>3</sub> solution ( $1 \times 10^{-2}$  mol L<sup>-1</sup>). The UV and FT-IR spectra were recorded after the films were immersed for a desired time and rinsed thoroughly with the pure water. Millipore-Q water (18 M $\Omega$  cm) was used in all of the cases.

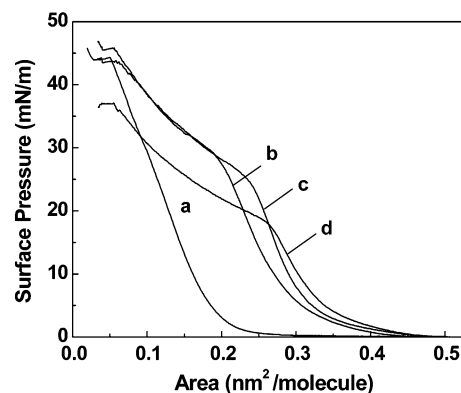
The monolayer formation and LB film deposition were performed using a KSV 1100 LB apparatus. UV and CD spectra of the transferred LB films were recorded by a JASCO UV-530 and a JASCO J-810 CD spectrophotometer, respectively. FT-IR spectra were recorded with a Bio-Rad FT-IR spectrometer. In the process of measuring CD spectra, the LB film was placed perpendicular to the light path and rotated within the film plane to avoid the polarization-dependent reflections and eliminate the possible angle dependence of the CD signals.<sup>11a</sup>

**Atomic Force Microscopy.** The freshly cleaved mica plate was first immersed into the pure water or aqueous AgNO<sub>3</sub> subphase. The amphiphile in chloroform solution was then spread on the subphase. In the case of Ag(I) ions containing subphase, the concentration of  $1 \times 10^{-3}$  M was used because higher concentration will conduce to the

physical adsorption of Ag(I) ions on the substrate. After the spread film was compressed to a constant surface pressure (10 mN/m) and waiting for 5 min for the equilibrium of the monolayer, the mica substrates were vertically lifted through the monolayer at a speed of 1 mm/min. Only one layer was transferred onto the mica surface, and the prepared LB film was measured by AFM immediately. AFM images of the monolayers were recorded on a Seiko Instrument SPA 400 Multimode system (Japan) with a SI-DF20 silicon cantilever (resonance frequency 138 kHz, spring constant 16 N/m) using the tapping mode. AFM images are shown in the height mode without any image processing except flattening.

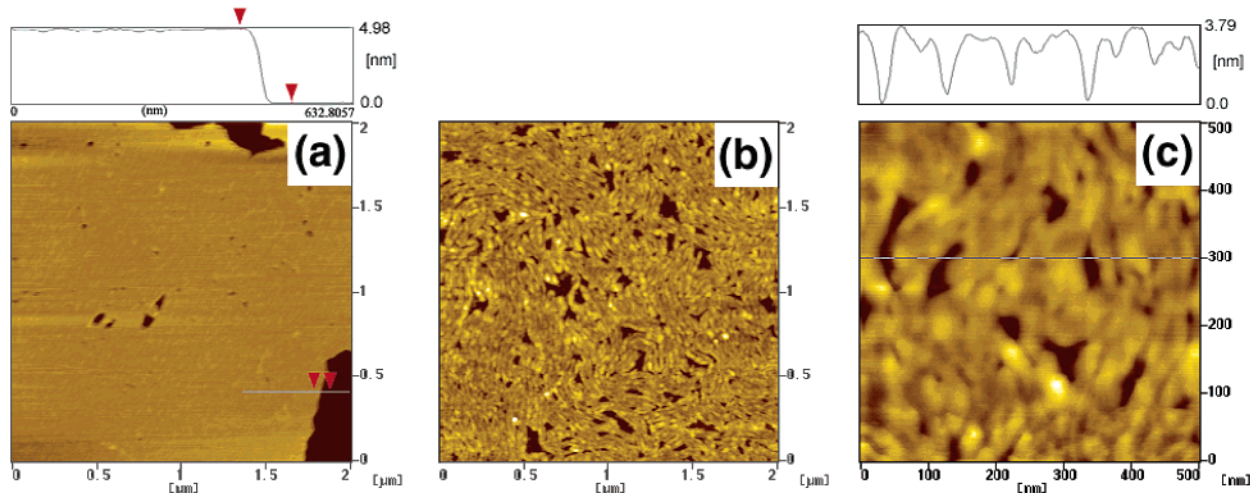
### Results and Discussion

**In Situ Coordination in Spreading Langmuir Film at the Air/Water Interface. Surface Pressure–Area Isotherms.** Figure 1 shows the surface pressure–area ( $\pi$ - $A$ ) isotherms of NpImC17 Langmuir film spread on pure water and the aqueous subphase containing various concentrations of AgNO<sub>3</sub>. On the pure water surface, the isotherm was typical for the condensed Langmuir film. The extrapolating area from the linear part of the isotherm was 0.19 nm<sup>2</sup>/molecule, which was too small to be regarded as a true monolayer. Addition of AgNO<sub>3</sub> to the subphase led to an enlargement of the molecular area. On a subphase containing  $1 \times 10^{-2}$  M AgNO<sub>3</sub>, a monolayer with a limiting area of 0.35 nm<sup>2</sup>/molecule was obtained. Further addition of AgNO<sub>3</sub> to the subphase did not affect the isotherm significantly. Previously, we have found that a series of 2-alkyl benzimidazole compounds formed stable monolayers on the subphase containing AgNO<sub>3</sub> through an in situ coordination between the benzimidazole moiety and the Ag(I) ion in the subphase.<sup>19a</sup> Taking into account the structural similarity



**Figure 1.** Surface pressure–area isotherms of NpImC17 on the pure water (a) and the subphases containing various concentrations of AgNO<sub>3</sub>: (b) 0.1 mM; (c) 1 mM; (d) 10 mM.

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**Figure 2.** AFM images of one-layer NpImC17 LB films from pure water (a) and  $10^{-3}$  M aqueous  $\text{AgNO}_3$  solution (b, c) at a surface pressure of 10 mN/m.

between NpImC17 and the benzimidazole derivatives, we found that the enlargement of the  $\pi$ - $A$  isotherms of NpImC17 on aqueous  $\text{AgNO}_3$  subphase was also attributed to the in situ coordination between NpImC17 and  $\text{Ag(I)}$  ions at the interface. In addition, from the dimension of the naphthaimidazole<sup>21</sup> and assuming a radius of  $\text{Ag(I)}$  ions as 0.116 nm,<sup>22</sup> the limiting area of 0.35 nm<sup>2</sup>/molecule is very close to a vertical arrangement of the NpImC17 with one naphtha[2,3]imidazole moiety connected with  $\text{Ag(I)}$  ions. This indicates that, through the in situ coordination, NpImC17 can form a monolayer with  $\text{Ag(I)}$  ions at the air/water interface.

**AFM Investigation.** From the  $\pi$ - $A$  isotherms, it is clear that different Langmuir films were obtained when NpImC17 was spread on water and aqueous  $\text{AgNO}_3$  subphase. To clarify this difference, an atomic force microscopy (AFM) measurement was performed for one-layer LB on mica, as shown in Figure 2.

The LB film deposited from the water surface is very flat (Figure 2a). As compared to the molecular length of NpImC17 calculated from the space-filling molecular (CPK) model (ca. 3.2 nm),<sup>23</sup> the observed height of 5.0 nm indicates that a bilayer NpImC17 film was formed on a pure water surface, in which the alkyl chain was rather inclined, as shown in Scheme 1. This explains why we obtained such small extrapolated molecular areas for the Langmuir film of NpImC17 spread on water surface. While the bilayer or multilayer formation on water surface is a rare case, this was indeed observed for some other systems.<sup>24</sup> In our case, the bilayer formation might be attributed to the less hydrophilicity of the headgroup of NpImC17.

For the film transferred from aqueous  $\text{AgNO}_3$ , a fiberlike superstructure with a width of approximately 20 nm was observed as shown in Figure 2b. The height of the fiber ( $3.6 \pm 0.6$  nm) was very close to the molecular length of NpImC17. This indicated that upon coordination with  $\text{Ag(I)}$  ions, NpImC17 formed a monolayer, as shown in Scheme 1 (right), which is in

accordance with the result of the above  $\pi$ - $A$  measurements. The difference between the Langmuir films of the ligand NpImC17 and the coordinated one can be regarded as due to the different hydrophilicity. Upon coordination, the hydrophilicity of the headgroup was increased, and a monolayer was formed. On the other hand, it is well known that imidazole can form a linear polymeric coordination compound with  $\text{Ag(I)}$  ions.<sup>19,25</sup> The fiberlike AFM images suggested that a linear coordination polymeric film might be formed when NpImC17 coordinated with  $\text{Ag(I)}$  ions in the monolayer. The fibers are aligned and can be considered as aggregates formed from an adjacent linear coordination polymer through the hydrophobic interaction of the alkyl chain and the  $\pi$ - $\pi$  stacking of the naphtha[2,3]imidazole moieties.

**Ex Situ Coordination in the LB films.** In our present system, it was found that when the ligand NpImC17 LB film was put into an aqueous  $\text{AgNO}_3$  solution, the  $\text{Ag(I)}$  ion can penetrate into the LB film, and the coordination between NpImC17 and  $\text{Ag(I)}$  can also occur. This provided another way to fabricate the coordination LB film. The coordination process could be monitored by the UV and FT-IR spectra.

**UV Spectroscopy.** Figure 3 shows the UV spectral changes of the NpImC17 LB film fabricated from the pure water surface after immersion in an aqueous solution of  $1 \times 10^{-2}$  M  $\text{AgNO}_3$ . The significant changes in the spectra are the disappearance of the two peaks at 332 and 350 nm with new peaks appearing at 340 and 357 nm. Simultaneously, the absorption peak at 245 nm disappeared, and the peak at 219 nm changed to 230 nm. In addition, three isosbestic points can be seen at 336, 343, and 353 nm. The final UV spectrum is very similar to that of the LB film deposited from the subphase containing  $\text{AgNO}_3$ . These spectral changes indicate that the coordination can progress between the NpImC17 LB film and  $\text{Ag(I)}$  ions by immersing it into the aqueous solution of  $\text{AgNO}_3$ . Using this technique, we could control the incorporation of  $\text{Ag(I)}$  ions into the LB film.

**FT-IR Spectra.** The progress of ex situ coordination in the LB film can be further verified by the FT-IR spectral measurement. Figure 4 shows the FT-IR spectra in the regions of 3430–

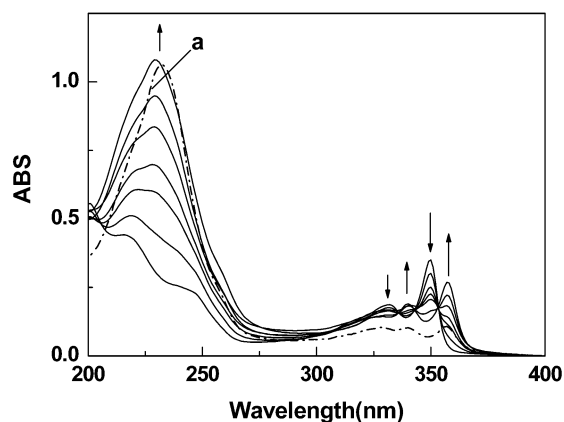
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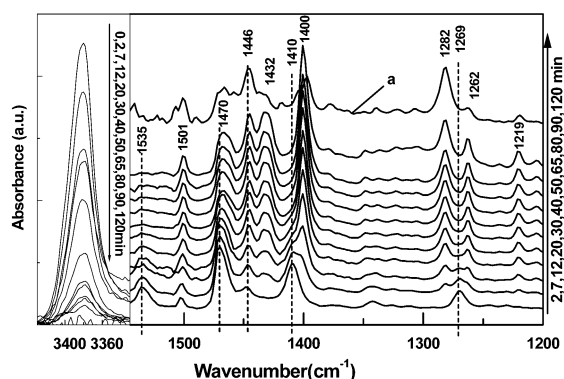
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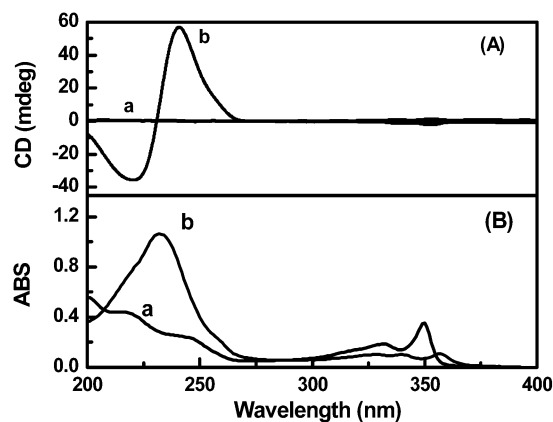
**Figure 3.** UV-vis spectra of a 10-layer NpImC17 LB film before and after immersion in  $1 \times 10^{-2}$  M  $\text{AgNO}_3$  solution at different time intervals. The dotted line (a) represents the spectrum of a 20-layer Ag(I)-NpImC17 LB film fabricated from  $1 \times 10^{-2}$  M aqueous  $\text{AgNO}_3$  subphase.



**Figure 4.** FT-IR spectra of a 40-layer NpImC17 LB film on a  $\text{CaF}_2$  substrate before and after immersion in  $1 \times 10^{-2}$  M  $\text{AgNO}_3$  solution in different time intervals. The dotted line (a) represents the Ag(I)-NpImC17 LB film fabricated from  $1 \times 10^{-2}$  M aqueous  $\text{AgNO}_3$  subphase.

$3340$  and  $1550$ – $1200$   $\text{cm}^{-1}$  of a 40-layer NpImC17 LB film before and after immersion in aqueous solutions of  $1 \times 10^{-2}$  M  $\text{AgNO}_3$ .

The spectrum prior to immersion shows characteristic vibration bands at  $1269$  and  $1410$  (ring breathing),  $1470$  ( $\text{CH}_2$  scissoring), and  $1501$  and  $1535$  (imidazolyl ring stretching)  $\text{cm}^{-1}$  in the region of  $1200$ – $1600$   $\text{cm}^{-1}$ . After immersing the film into the  $\text{AgNO}_3$  solution, the band at  $1535$   $\text{cm}^{-1}$  disappeared. The band at  $1269$   $\text{cm}^{-1}$  split into two absorption bands at  $1262$  and  $1282$   $\text{cm}^{-1}$ , and the latter band increased its intensity with immersion time. The bands at  $1410$   $\text{cm}^{-1}$  shifted to  $1400$   $\text{cm}^{-1}$  after the film was immersed in the solution. Further, a new vibrational band appeared at  $1432$   $\text{cm}^{-1}$  and the band at  $1446$   $\text{cm}^{-1}$  increased its intensity with increasing immersion time. These vibrational band changes indicated coordination of Ag(I) ions with NpImC17. In addition, we have not seen any change or appearance of a band around  $1345$   $\text{cm}^{-1}$ , which can be assigned to the  $\text{NO}_3^-$  anion. This indicates that only Ag(I) ions were incorporated into the LB film. Another important feature is the disappearance of the vibration band at  $3376$   $\text{cm}^{-1}$ , which can be assigned to the N–H stretching vibration. After the film was immersed into the  $\text{AgNO}_3$  solution, the band kept on decreasing, and after 120 min, the band disappeared completely. This further indicated that the coordination occurred through the deprotonation of the N–H in the imidazole ring. In addition, we have measured the FT-IR spectra of the LB



**Figure 5.** Circular dichroism (CD) (A) and UV (B) spectra of a 10-layer NpImC17 LB film transferred from the pure water surface (a) and a 20-layer Ag(I)-NpImC17 LB film (b). The CD spectra were the averages of 36 CD spectra measured by rotating the film around the incident light in a  $10^\circ$  step.

film deposited from the NpImC17 monolayer on aqueous subphases containing  $\text{AgNO}_3$ . The final spectrum is the same as the spectrum of the in situ coordinated NpImC17–Ag(I) LB films, indicating that a similar reaction occurred in the LB films and in the monolayers.

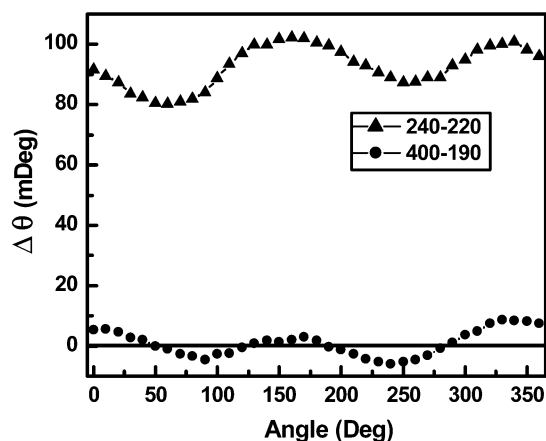
**Chirality of the Coordination-Induced Organized Molecular Films. Chirality of the in Situ Coordinated Films.** It is interesting to discover that the in situ coordinated Ag(I)-NpImC17 LB film showed a strong split circular dichroism (CD), while no CD signal was found for the LB film deposited from the water surface, as shown in Figure 5. The CD spectrum for the film deposited from the  $\text{AgNO}_3$  subphase consisted of an intense exciton couplet (maximum at  $240$  nm and minimum at  $220$  nm) with a crossover at  $231$  nm. This crossover was very close to the absorption maximum of the Ag(I)-NpImC17 LB film. Therefore, the exciton couplet could be assigned to the coupling of the  $^1\text{B}_b$  transition of the naphthaimidazole moieties.

For the solid state samples, because the observed CD spectra are usually accompanied by artifacts which originate from the interaction between the macroscopic anisotropies of a sample such as birefringence and linear dichroism (LD), it could not be exclusively determined whether the film was chiral or not just from conventional CD measurement.<sup>26,27</sup> A useful method for the CD measurement of films has been proposed by Spitz et al. to distinguish the intrinsic chirality from the possible parasitic artifacts, and the method was applied to our LB films.<sup>11a</sup>

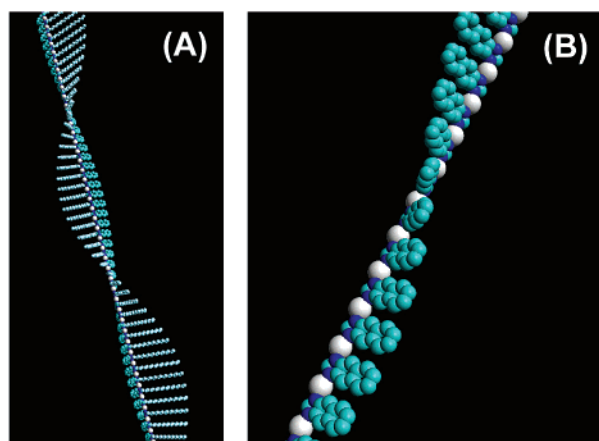
First, in all of our CD measurements, the birefringence contribution was avoided by carefully placing the LB film perpendicular to the light path. The angle dependence behavior of all 36 CD spectra which were measured in a step of  $10^\circ$  about the optical axis has been checked. The angle dependence of the amplitude was determined by the difference between the maximum value at  $240$  nm and minimum value at  $220$  nm, and the angle dependence of the background was determined by the difference between the values at the upper wavelength edge at  $400$  nm and lower edge at  $190$  nm, which were shown as filled triangles and filled circles, respectively, in Figure 6. Both

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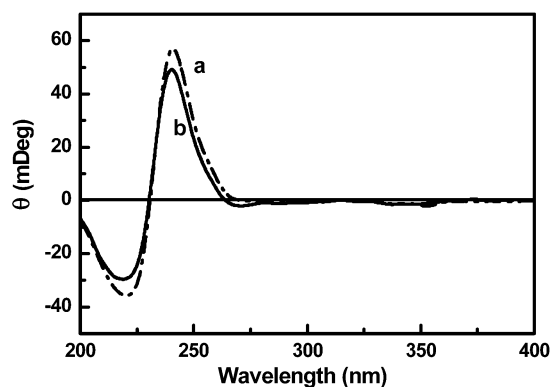
**Figure 6.** Angle dependence of the CD amplitude ( $\blacktriangle$ ) and the background ( $\bullet$ ) of the CD spectra measured while the NpImC17-Ag(I) LB film was turned about the optical axis in a step of  $10^\circ$  within the sample plane.



**Figure 7.** The possible model for the formation of the chiral NpImC17-Ag(I) coordination films. The planform view (A) and the exploded view omitted the long alkyl chain (B).

of them can be approximated to a  $\cos(2\beta)$  function as it was expected. The slight deviation from the symmetry could be explained by a small inhomogeneity in the film. Moreover, while the cosine function of the background (filled circle) situated around zero, that of the amplitude (filled triangle) was positively shifted about 90 millideg. This clearly verified that besides LD there should be another angle-independent effect contributing to the observed ellipticity, which could only be the intrinsic circular dichroism. Thus, these data unambiguously indicated that the in situ coordinated Ag(I)-NpImC17 film was indeed chiral.

In the discussion of the  $\pi$ -A isotherm above, it was suggested that linear polymer might be formed when the NpImC17 molecule coordinated with Ag(I) ions at the air/water interface. During the coordination, the adjacent naphtha[2,3]imidazole groups were connected by Ag(I) ions in the monolayer. Because the naphtha[2,3]imidazole group is very large, the aromatic rings are sterically overcrowded to align in the same plane during the coordination. Therefore, the aromatic groups have to twist to some extent along the polymer backbone, as can be comprehensibly seen in Figure 7. Once an aromatic ring started to distort in a certain direction, the other aromatic rings would follow to form a semihelical structure at the air/water interface. This caused the chirality of the coordinated LB film.



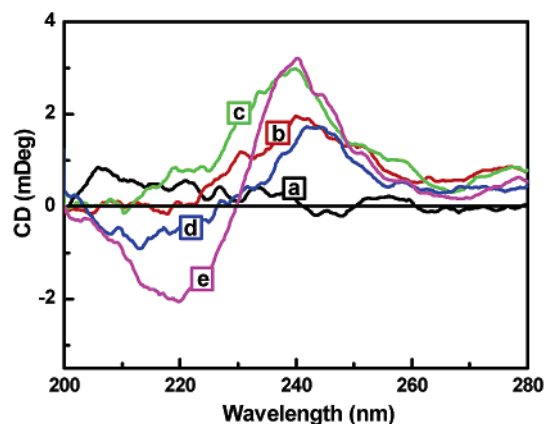
**Figure 8.** The CD spectra of the same NpImC17-Ag(I) coordinated LB film measured by the average method (a) and a continue rotation method (b).

Such a deduction can be further supported from the following results. We have found that although we can always get a strong split CD signal in the LB films deposited from the aqueous  $\text{AgNO}_3$  subphase, the sign of the chirality was rather undetermined for LB films fabricated in different batches. This indicated that the chirality for the LB film was indeed not from any chiral purity but from the helical structures formed in the film. In principle, the chance of the backbone forming the right- or left-handed helical structure is equal. However, the experimental results revealed that a chiral LB film was indeed formed. This indicated that during the film formation, the symmetry was broken through an interfacial coordination. In the formation of the film, every aromatic ring acted cooperatively, and a small distortion in the starting unit to a helical sense yields a considerable larger excess of helical sense, thus causing a macroscopic chirality. In forming such a chiral structure, the sterical hindrance of the naphtha[2,3]imidazole ring also played an important role. We have investigated the LB films of long chain benzimidazole derivatives. Although these compounds showed interfacial behavior similar to that of NpImC17,<sup>19a</sup> no chirality of the deposited LB film was detected in the CD spectra. This gave further support that the chirality of the Ag(I)-coordinated NpImC17 LB film was due to the distorted arrangement of sterically overcrowded naphtha[2,3]imidazole.

**Development of CD Signal in the ex Situ Coordinated LB Films.** In the previous discussion, we have revealed that the Ag(I)-coordinated NpImC17 LB film can be obtained through both in situ and ex situ coordination. Because chiral LB films could be obtained through the in situ coordination, can it also be formed through the ex situ coordination of an achiral NpImC17 LB film with Ag(I) ions? Our experiment revealed that the answer is yes. Moreover, the results gave further support of the development of the chirality.

In the above CD measurement, we have averaged 36 CD spectra to get a correct CD spectrum for the LB films.<sup>11a,28</sup> While the averaging of the 36 CD spectra with a rotation step of  $10^\circ$  was a good method to obtain a correct CD spectra, a continued rotation of the film during the measurement was also effective, as shown in Figure 8. The slight differences in the intensity of the CD spectra might come from the inhomogeneity of the film. Therefore, in monitoring the coordination process of the NpImC17 LB film with  $\text{AgNO}_3$ , we have measured the CD spectra using a rotation method.

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**Figure 9.** CD spectra of the NpImC17 LB film before and after immersion in  $1 \times 10^{-2}$  M  $\text{AgNO}_3$  solution. The soak time was (a) 0 min, (b) 12 min, (c) 22 min, (d) 32 min, and (e) 70 min.

Figure 9 shows the CD spectral changes for the NpImC17 LB film deposited from the water surface as a function of immersion time in aqueous  $\text{AgNO}_3$  solution. At the beginning, no CD signal was observed. After 12 min, a positive CD signal was observed at 240 nm (Figure 9b). With the time increased, the CD signal increased its intensity. After 32 min (Figure 9d), the CD signal shows a split; that is, a positive and negative Cotton effect was observed at 243 and 213 nm, respectively. After further reaction, the split become strong, and the shape of the spectrum became the same as that of the in situ coordinated  $\text{Ag(I)-NpImC17}$  LB film.

These spectral changes indicate that the CD signal in the LB film was caused by the coordination between NpImC17 and  $\text{Ag(I)}$  ions. In the initial coordination stage, the CD signal appeared as a positive peak at 240 nm, which could be assigned to the uncoupled chromophore because the CD band showed no shift in comparison to the UV spectra at this stage.<sup>29</sup> At last, a split was observed with a crossover at 232 nm. According to the exciton coupling theory, the split of the CD signal is related to the interaction between the adjacent chromophores.<sup>30</sup> In our case, the interaction between the adjacent naphtha[2,3]imidazole groups was responsible for such a split. The only positive Cotton effect observed in the initial stage of the reaction indicates that the interaction between the adjacent naphtha[2,3]imidazole groups was not strong enough to cause the split due to the incomplete reaction. When the reaction progressed, more naphtha[2,3]imidazole groups were connected, and their interaction became strong enough to cause the split. Finally, the same CD spectra as in the case of in situ coordinated LB film were obtained when the reaction was completed. In addition, although the absorption intensity of the ex situ coordinated LB film in the final case approached that of the in situ coordinated LB film, the intensity of the CD signal was

relatively weak. This indicates that the in situ coordination at the air/water interface is more efficient than the reaction in the LB films in obtaining a chiral LB film. This is reasonable because in the LB films, the functional groups are strictly confined, and the reaction cannot progress efficiently.

It should be noted that the sign of the CD spectra is rather undetermined for different samples in the in situ coordinated LB films although we can always get strong split CD signals. However, in the case of ex situ coordinated LB films, CD spectra with the same sign were always observed in 30 repeated ex situ coordination experiments. The epitaxial deposition of ligand on the quartz substrate might be the reason, although we cannot verify this at the present stage.<sup>31,32</sup>

It should be further noted that, although the coordination reaction could also occur in methanol solution, no CD signal was observed. It was reported that for the reaction of imidazole and  $\text{AgNO}_3$ , a silver salt was predominantly formed in solution, while a polymeric complex could be formed on a solid surface where a large amount of  $\text{Ag(I)}$  ions existed.<sup>25,33</sup> When we added a large excess of  $\text{AgNO}_3$  to the solution, the solution became turbid, and a polymeric compound was supposed to form. However, no CD signal was detected for either the solution or the case film. This indicated that the ordered arrangement of the NpImC17 molecule played an important role in forming the chiral molecular assemblies.

## Conclusions

A newly synthesized 2-(heptadecyl) naphtha[2,3]imidazole (NpImC17) was found to form a bilayer film on a water surface. NpImC17 can coordinate with  $\text{Ag(I)}$  ions in situ in the spreading Langmuir film when spread on an aqueous  $\text{AgNO}_3$  subphase. The in situ coordinated  $\text{Ag(I)-NpImC17}$  LB films showed chirality, although both ligand and metal ions are achiral. The chirality of the LB film was due to the formation of a helical coordination polymer where the naphtha[2,3]imidazole group distorted in a certain degree along the polymer backbone. Moreover, the chirality of the LB films could be also developed through the ex situ coordination between the achiral ligand NpImC17 LB film with  $\text{Ag(I)}$  ions. The coordination and the interaction between the naphtha[2,3]imidazole rings play an important role in forming the chiral LB films. The results give important clues to the design and fabrication of chiral molecular assemblies from achiral molecules.

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(29) It should be noted that during the progress of the reaction, the UV absorption maximum shifted from 245 to 240 and to a final 230 nm.

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