

Metal Ion Modulated Organization and Function of the Langmuir–Blodgett Films of Amphiphilic Diacetylene: Photopolymerization, Thermochromism, and Supramolecular Chirality

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Some novel properties of organized molecular films of 10,12-tricosadiynoic acid (TDA), which were modulated by transition metal ions, were investigated. It was found that metal ions such as Cu^{2+} , Zn^{2+} , Ni^{2+} , Cd^{2+} , and Ag^+ in the subphase can greatly affect the monolayer formation of TDA and the properties of the subsequently deposited Langmuir–Blodgett (LB) films, particularly in the case of Ag^+ , Zn^{2+} , and Cu^{2+} ions. TDA LB film from the subphase containing Ag^+ ion could not be photopolymerized. It was suggested that both the strong chelating property to the carboxylate and the easy reduction of Ag^+ in the film disrupted the topochemical sequence of TDA and resulted in no polymerization in the film. Zinc ion coordinated TDA film could be photopolymerized into a blue polydiacetylene (PDA) film, which showed a reversible thermochromism between blue and purple color upon thermal stimulation. Fourier transform infrared spectra revealed the difference of the Zn^{2+} -PDA film from those of the other ions, and the mechanism of the thermochromism was discussed. Copper ion coordinated TDA film could only be photopolymerized to a red PDA film, which showed supramolecular chirality although TDA itself was achiral. Atomic force microscopic measurements revealed the nanofiber structure in the Cu^{2+} -PDA film. The supramolecular chirality of the Cu^{2+} -PDA film was suggested to be due to the arrangement of the polymer backbone in a helical sense. Furthermore, it was found that the chiral assemblies from the achiral TDA molecules were very stable and the chirality could be kept even upon heating or treating with alkaline solution. While many synthetic efforts have been devoted to the functionalization of PDA films, we provided a simple method of modulating the organization and function of PDA films through metal ions.

Introduction

Metal ions play an important role in the organization of biological and supramolecular systems.^{1,2} One of the typical examples is the effect of metal ions on the properties of Langmuir and Langmuir–Blodgett (LB) films.³ Such an effect can be dated to the pioneer work of Katherine Blodgett from 1935, where metal ions were found to be effective in fabricating well-defined LB films.⁴ Currently, metal ions are widely used to modulate the surface properties of interfacial films. Generally, two kinds of effects of metal ions can be considered. One is to utilize metal ions to stabilize the monolayers and fabricate well-defined LB films. The other is to utilize metal ions to functionalize interfacial films. For the latter case, a series of functional organic ligands were designed and their metal ion regulated properties were investigated.^{5–10}

Diacetylene derivatives have been widely investigated due to their topochemical polymerization and subsequent elegant properties.¹¹ When the monomer of diacetylene was orderly arranged, it could be polymerized under UV irradiation and form blue or red polydiacetylene (PDA) film. The blue film is very sensitive to external stimuli such as temperature (thermochromism),^{12a} pH,^{12b} solvent (solvatochromism),^{12c} external stress (mechanochromism),^{12d} and interaction with biomolecules.^{12e} Such properties could be utilized to design biosensors, pathogenic agents, and functional materials.¹³ Many efforts have been

devoted to the design of the diacetylene derivative to realize the reversible color change of PDA. For example, Ahn and Kim et al. have synthesized a series of new diacetylene derivatives and found that PCDA-mBzA (3-(pentacosyl-10,12-diyneamido)-benzoic acid) showed reversible color change upon thermal and pH stimulus.¹⁴ Leblanc et al. reported that the polymer solid of 2-amino-4,6-bis[(10,12-pentacosadiynamido)ethylamino]-1,3,5-triazine and its assembly with barbituric acid were thermochromic.¹⁵ However, most of these properties have been realized through molecular design, and syntheses of new diacetylene derivatives were sometimes tedious and expensive work. Others have also reported reversible chromism in the Langmuir film induced by surface pressure or pH change of the subphase.¹⁶ The condition of reversible cycle could not be controlled easily, nor could the cycle be repeated many times. In this paper, we report the metal ion regulated novel properties of an organized molecular film of PDA by using a simple well-studied TDA amphiphile. Although the Langmuir film, the LB film, and the interaction of TDA with some metal ions have been reported,^{17,18} the effect of metal ions on the film properties was not sufficiently recognized. In our study, we have found that zinc ion coordinated PDA film showed a thermochromism between the blue and purple forms. Copper ion coordinated PDA film showed a supramolecular chirality, although the amphiphile was achiral.¹⁹ Silver ion coordinated TDA film could not be photopolymerized. The polymerization, thermochromism, and supramolecular chirality of the metal ion containing TDA LB

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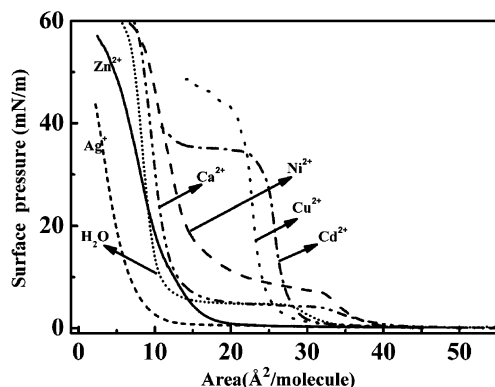


Figure 1. Surface pressure–area (π – A) isotherms of TDA monolayers on pure water and 1 mM aqueous solutions of metal salts (AgNO_3 , $\text{Zn}(\text{NO}_3)_2$, CaCl_2 , $\text{Ni}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, and $\text{Cd}(\text{NO}_3)_2$).

films were investigated through ultraviolet–visible (UV–vis), Fourier transform infrared (FT–IR), and circular dichroism (CD) spectra.

Experimental Section

1. Materials. 10,12-Tricosadiynoic acid ($\text{CH}_3-(\text{CH}_2)_9-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-(\text{CH}_2)_8-\text{COOH}$) (abbreviated as TDA) was purchased from Dojindo Laboratory and used as received. AgNO_3 , $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, and CaCl_2 were all analytical reagents and used without further purification. Milli-Q water (18 M Ω cm) was used in all cases.

2. Procedure. Monolayers of TDA were formed by spreading a chloroform solution (ca. 1×10^{-3} M) onto a water surface or aqueous subphase containing different metal salts (1×10^{-3} M). The pH values of the water and the subphases containing different metal ions were pure water (pH 6.5), AgNO_3 (pH 5.4), $\text{Cu}(\text{NO}_3)_2$ (pH 4.9), $\text{Zn}(\text{NO}_3)_2$ (pH 5.4), CaCl_2 (pH 5.6), $\text{Cd}(\text{NO}_3)_2$ (pH 4.9), and $\text{Ni}(\text{NO}_3)_2$ (pH 5.5). After the evaporation of chloroform for 30 min, the surface pressure–area (π – A) isotherms were recorded at a compression speed of 5 mm min $^{-1}$. The air–water interface was kept at a constant temperature of 15 °C by circulating thermostated water around the trough. The measurements of the monolayer properties and Langmuir–Blodgett film transfer were carried out using a KSV 1100 Teflon-coated LB trough (KSV Instruments, Helsinki, Finland). Polymerization was performed by UV irradiation using a lower pressure mercury lamp (25 W, 254 nm) either on solid substrates or in situ at the air/water interface. All the experiments were carried out in the dark except for those polymerized samples. The TDA monolayer was compressed to 20 mN/m, and multilayer films were deposited onto quartz and CaF_2 plates by a horizontal lifting method. One hundred layers of multilayer films was used for FT–IR measurements. UV–vis, CD, and FT–IR spectra were measured with a JASCO UV-530, JASCO J-810, and FT–IR 660 spectrophotometer, respectively. One layer of PDA monolayer which had been in situ polymerized at 20 mN/m on the surface of the $\text{Cu}(\text{NO}_3)_2$ subphase was deposited onto a freshly cleaved mica surface by the vertical lifting method. The atomic force microscopy (AFM) images of the transferred films were measured by the Digital Instruments Nanoscope IIIa Multimode System (Santa Barbara, CA) with a silicon cantilever using the tapping mode.

Results and Discussion

1. Surface Pressure–Area Isotherms (π – A) of TDA.

Figure 1 shows the π – A isotherms of TDA on the surfaces of pure water and the solutions containing various metal ions (1

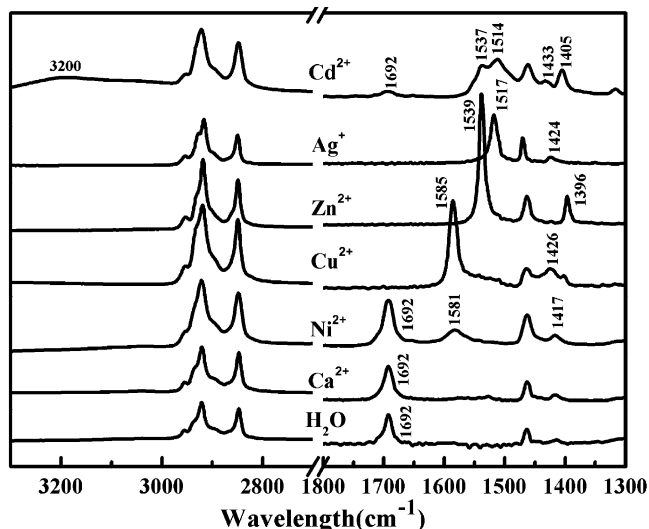


Figure 2. FT–IR spectra of LB films of TDA deposited from water surface or 1 mM solution of metal salts onto CaF_2 plate using a horizontal lifting method at 20 mN/m.

mM) at 15 °C. The isotherm on pure water shows a plateau region from a low surface pressure of about 5 mN/m. This is in agreement with the previous report that a trilayer film is formed on the water surface.²⁰ When metal ions existed in the subphase, significant changes were observed. The π – A isotherms of TDA on surfaces of the solutions of CaCl_2 and $\text{Ni}(\text{NO}_3)_2$ retained the plateau regions, and the shapes of the curves were similar to that of the one on the water surface. This suggests that most of the TDA had not formed a complex with either of these two metal ions. As for the other metal ions, condensed or expanded type monolayers without any LE/LC phase transition were obtained. This indicates that the carboxylate groups and the metal ions might form different coordination complexes in the monolayer. On the subphase containing Ag^+ or Zn^{2+} ions, the molecular areas for the isotherms were too small to be regarded as monolayers and a multilayer film might be formed. On the subphase containing Cu^{2+} or Cd^{2+} ions, the π – A isotherms were much expanded. These differences clearly indicate that the metal ions in the subphase can greatly affect the surface behavior of TDA monolayers.^{17,18}

2. FT–IR Spectra of the Transferred LB Films. FT–IR spectroscopy is a powerful method to study the interaction between the carboxylate and metal ions. We have deposited the films from the subphases containing various metal ions and measured FT–IR spectra of the multilayer LB films, as shown in Figure 2. A strong band appeared at 1692 cm $^{-1}$ for the film deposited from pure water. This band can be ascribed to the hydrogen-bonded carbonyl stretching band $\nu(\text{C}=\text{O})$. For the film transferred from the subphases containing metal ions, some new bands appeared around 1585–1510 and 1433–1397 cm $^{-1}$, which could be ascribed to the antisymmetric $\nu_{\text{as}}(\text{COO})$ and symmetric $\nu_{\text{s}}(\text{COO})$ stretching vibrations of carboxylate anion, respectively.^{18,20} The hydrogen-bonded carbonyl stretching band remained at 1692 cm $^{-1}$ in the cases of Ca^{2+} and Ni^{2+} , and a weak band was still at 1692 cm $^{-1}$ for Cd^{2+} . This indicated that in our experimental conditions coordination between carboxylic acid and the metal ions was incomplete when TDA was spread on the subphase containing Ca^{2+} , Ni^{2+} , and Cd^{2+} . In the FT–IR spectra of the films deposited from the other metal ions of Ag^+ , Zn^{2+} , and Cu^{2+} , however, no 1692 cm $^{-1}$ band was detected, indicating the complete reaction of the carboxylic acid with these three metal ions. It is well-known that in FT–IR spectrum the separation (Δ) between the antisymmetric and symmetric

TABLE 1: Wavenumbers of Antisymmetric and Symmetric Vibrations of Carboxylate Anion and Assignment of Corresponding Coordination Type in Multilayer Films

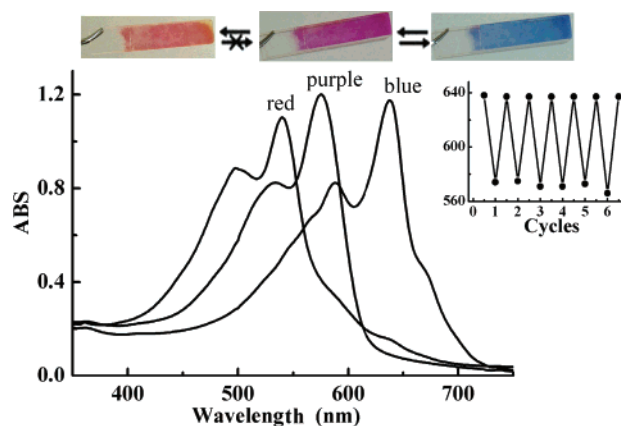
metal ion	$\nu_{\text{as}}(\text{COO})$ (cm^{-1})	$\nu_{\text{s}}(\text{COO})$ (cm^{-1})	$\Delta = \nu_{\text{as}} - \nu_{\text{s}}$ (cm^{-1})	coordination type
Ni(II)	1581	1417	164	ionic
Cd(II)	1537	1405	132	H-bonded monodentate
Cd(II)	1514	1433	81	chelating bidentate
Ag(I)	1517	1424	93	chelating bidentate
Cu(II)	1585	1426	159	bridging bidentate
Zn(II)	1539	1396	143	bridging bidentate

stretching vibrations of carboxylate ($\Delta = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$) could be used as a diagnosis to determine the coordination type (ionic, monodentate, bridging bidentate, chelating bidentate) between the carboxylate and metal ions.^{18,21–24} Although there are slight differences among various studies in the literature, the relationship between the separation values and the coordination types can be generalized as follows: ionic (164 cm^{-1}), monodentate (200–300 cm^{-1}), bridging bidentate (140–170 cm^{-1}), and chelating bidentate (40–110 cm^{-1}).^{18,21–24} Table 1 lists the wavenumbers of antisymmetric $\nu_{\text{as}}(\text{COO})$ and symmetric $\nu_{\text{s}}(\text{COO})$ vibrations of the carboxylate anion and their assignments of the coordination type for various metal ion incorporated films.

From the similarity of the FT-IR spectrum of the TDA film on Ca^{2+} subphases to that of water surface, it can be suggested that there is almost no interaction between TDA and Ca^{2+} . An ionic complex is suggested for the film spread on the subphases containing Ni^{2+} . When Cd^{2+} was added in the subphase, a broad band appeared at 3200 cm^{-1} , which could be assigned to the $\nu(\text{O}-\text{H})$ band. This coordination type was H-bonded monodentate.^{25–27} Therefore, two kinds of coordinated complexes were formed in the case of Cd^{2+} , which were chelating bidentate and the H-bonded monodentate complex. A different coordination type was observed for Cu^{2+} , Ag^{+} , and Zn^{2+} ions. There is no doubt that a chelating bidentate complex was obtained in the case of Ag^{+} based on the separation value. In the cases of Cu^{2+} and Zn^{2+} , both separation values followed in the region of bridging bidentate. However, the difference of the separation values was as large as 16 cm^{-1} for the two metal ions. Such a difference could be due to different coordination geometries of Zn^{2+} and Cu^{2+} . Another reason may be because in the case of Zn^{2+} partial chelating bidentate and unsymmetric chelating bidentate modes may be present.²⁸ These FT-IR results clearly indicate that the TDA exhibited different coordination types with metal ions in the subphases. The difference of the interaction type could cause distinct properties of the TDA films, which will be discussed in the following.

3. Photopolymerization of TDA LB Films with Different Metal Ions. Photopolymerization could be performed in both the Langmuir film on water surface and the Langmuir-Blodgett films on solid substrates. Blue film was obtained, and it could change to red by external stimuli. For the film deposited from the subphases containing metal ions (Ni^{2+} , Cd^{2+} , Ca^{2+}), the color changes were the same as those reported. However, for metal ions such as Ag^{+} , Cu^{2+} , and Zn^{2+} , TDA showed unique properties. The LB film of Ag^{+} -TDA showed a pale yellow color under photoirradiation. It is better to suggest that no polymerization took place in the film. The Cu^{2+} -TDA film could form a chiral red film after UV irradiation. Zn^{2+} -TDA film showed thermochromism between purple and blue, which were observed for the first time.

The reason for the unpolymerization of Ag^{+} -TDA film can be explained as follows. It was known that the polymerization of diacetylene is a topochemical photoreaction and that it

**Figure 3.** UV-vis spectral changes of LB film of Zn^{2+} -PDA film upon thermal stimulus. Above: photos of blue, purple, and red plates. Insert: cycle between blue and purple films.

requires a repeating distance of ≤ 5 Å between diacetylene groups.²⁹ Silver ion can be reduced easily by UV irradiation. Due to the reduction and aggregation of the Ag particles inserted in the TDA monolayers, the diacetylene groups deviated from the topochemical requirement of the photopolymerization and no polymerization was observed in the case of Ag^{+} -TDA. The TDA films containing Cu^{2+} and Zn^{2+} ions were interesting, and a detailed discussion will be given in the next section.

4. Thermochromism of Zn^{2+} -TDA Film. The Langmuir and Langmuir-Blodgett films of Zn^{2+} -TDA can be polymerized to blue. It is interesting to note that the LB films show a reversible color change between blue and purple forms upon thermal stimulus. Figure 3 shows the UV-vis spectral changes of Zn^{2+} -PDA multilayer film deposited at 20 mN/m upon heating at different temperatures. The blue film showed maximum absorption at 638 nm. When the blue film was heated to 90 °C, it turned purple, which showed a peak maximum around 575 nm. It is found that the purple film returned to blue in about 5 min when it spontaneously cooled to room temperature. When the cooled film was heated again, the film would turn purple again. Such cycles could be repeated many times, as shown in the insert of Figure 3. In addition, the purple film showed a slight difference in the maximum absorption positions depending on the temperature. If the film was heated to 160 °C, the absorption of purple film could shift to 565 nm. It was further found that the blue Zn^{2+} -PDA could be heated to the purple form at 90–160 °C and return to its original blue color upon cooling. With further heating of the purple film above 180 °C, the film became red and the maximum absorption was at 540 nm. The red film would no longer return to blue. The photos of the blue, purple, and red films on the plates are shown at the top of Figure 3.

To elucidate this particular thermochromism, we measured the FT-IR spectra of the Zn^{2+} -PDA films at different states. Figure 4 shows the FT-IR spectra of Zn^{2+} -PDA films at different vibration regions. In the region from 3000 to 2800 cm^{-1} , the Zn^{2+} -PDA film showed $\nu_{\text{s}}(\text{CH}_2)$, $\nu_{\text{as}}(\text{CH}_2)$, and $\nu_{\text{as}}(\text{CH}_3)$ at 2848, 2918, and 2954 cm^{-1} , respectively (Figure 4a), before UV irradiation. In addition, a band at 2933 cm^{-1} was also observed, which was assigned to a band arising from Fermi resonance between $\nu_{\text{as}}(\text{CH}_3)$ and an overtone of a CH_3 deformation.²⁹ Upon photopolymerization, $\nu_{\text{as}}(\text{CH}_2)$ shifted from 2918 cm^{-1} to a lower wavenumber of 2915 cm^{-1} and the Fermi bands disappeared. Upon further heating of the blue film (Figure 4b) to purple and red, the $\nu_{\text{as}}(\text{CH}_2)$ band did not change (Figure 4c,d). It has been known that if $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$ shift to a higher wavenumber, this indicates the appearance of gauche conformation.^{30,31} In our case, a shift to the lower wavenumber

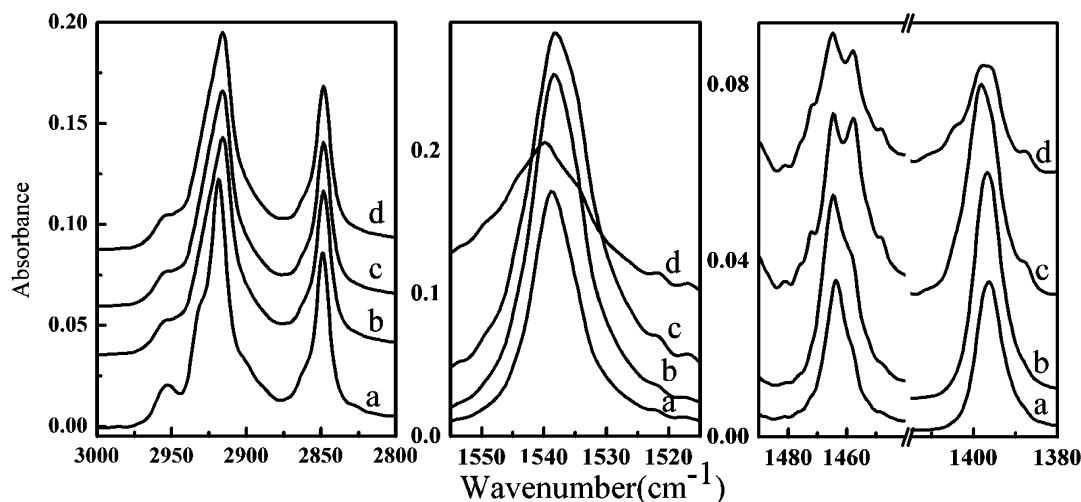


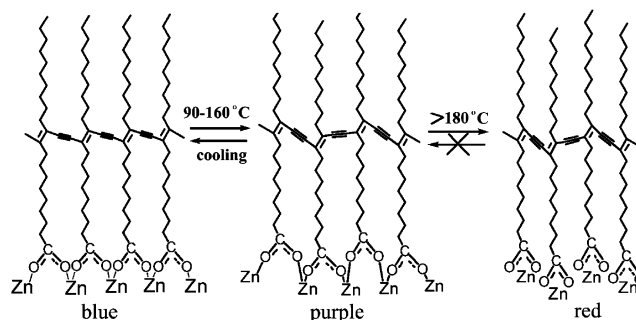
Figure 4. FT-IR spectra of Zn-PDA LB film on the CaF₂ plates: (a) before UV irradiation; (b) blue film; (c) purple film; (d) red film.

was observed, which suggested that all the blue, purple, and red Zn²⁺-PDA films were in an ordered structure and the alkyl chains kept all-trans conformation. Several reports suggested that the alkyl groups of the PDA undergo a change from order to disorder as PDA changes from blue to red.³² However, Charych demonstrated by AFM and FT-IR that the red film became more ordered and the side chains assumed the all-trans conformation when the mixed PDA and sugar-modified PDA LB film changed from blue to red.³³ Leblanc's group has also reported that a more ordered phase was observed and assumed a nearly perfect hexagonal packing in the red film of a diacetylene derivative.³⁴ Our results suggested a similar change to these two cases in the Zn²⁺-PDA film.

During the color changes, a clear change in the methylene scissoring band $\delta(\text{CH}_2)$ was also observed. Before UV irradiation, the $\delta(\text{CH}_2)$ band was at 1465 cm⁻¹ (Figure 4a), which indicated a triclinic subcell structure.^{25,33} After photopolymerization, a shoulder band emerged at 1458 cm⁻¹ (Figure 4b). After subsequent heating to the purple form, the band was split into 1465 and 1458 cm⁻¹ (Figure 4c), suggesting that an orthorhombic subcell was adopted.^{30,31,33} The changes of $\delta(\text{CH}_2)$ were also reversible upon heating and cooling. On the other hand, $\nu_s(\text{COO})$ at 1396 cm⁻¹ (Figure 4a,b) shifted to 1398 cm⁻¹ (Figure 4c) upon heating. It was also reversible between blue and purple films. When the film was heated to the red form (Figure 4d), $\nu_s(\text{COO})$ became broad at 1398 cm⁻¹. $\nu_{as}(\text{COO})$ was at 1539 cm⁻¹ in Figure 4a–c, while for the red film the strength was greatly decreased and the band shifted to 1540 cm⁻¹ (Figure 4d). These bands of the red film (Figure 4d) could not recover again upon cooling, suggesting that coordinated headgroups were partially disrupted. These results indicated that the Zn²⁺ bridging bidentate coordinated carboxylate groups were important for the Zn²⁺-coordinated PDA film to recover its color.

On the basis of the above results a possible model could be proposed to explain the thermochromism of the Zn²⁺-PDA film, as shown in Scheme 1. Zn²⁺-coordinated PDA film was formed through UV irradiation, in which Zn²⁺ ion was coordinated with carboxylate in a bridging bidentate. Based on the scissor vibration of CH₂, the polymerized film was in a triclinic subcell and the alkyl chains adopted an all-trans conformation. Upon heating, the subcell of the film changed from triclinic to orthorhombic which caused the small reorganization of the polymer backbone, and the blue film changed to purple. During this process, the bridging bidentate headgroup of the Zn²⁺-PDA film was not changed significantly, as shown in the $\nu_{as}(\text{COO})$

SCHEME 1: Mechanism for the Thermochromism of Zn²⁺-PDA LB Film



vibrations in Figure 4. The color change between purple and blue was reversible. This is because, in the confined temperature regions, the carboxylate headgroups were fixed by the coordinated zinc ions, which make the polymer backbone to not change to the more distorted structure when heated and to recover its blue form upon cooling. The role of bridging coordinated Zn²⁺ resembles the role of the double hydrogen bonding among headgroups of PCDA-mBzA, which can recover its initial molecular organization and color upon heating and cooling.¹⁴ When the Zn²⁺-PDA film was heated above 180 °C, the film became red where bridging Zn²⁺-COO was partially disrupted, as verified by the FT-IR spectra. Such a change was irreversible and the red film could not return to the original color.

5. Supramolecular Chirality of PDA LB Films. Previously, we have reported that chiral PDA films could be obtained through the organization at the air–water interface from achiral TDA.¹⁹ It was suggested the supramolecular chirality of the PDA film resulted from a helical stacking of both the long alkyl chains and the polymer backbone. We briefly reported that only the Cu²⁺ ion coordinated PDA film could show chirality while the other metal ions could not. Here we further investigated the nature of the chirality of Cu²⁺-coordinated PDA film through AFM and FT-IR spectra. In addition, we investigated the stability of the chiral assemblies.

5.1. AFM Investigation. Figure 5 shows an AFM picture of the film deposited from the subphase containing Cu²⁺ ions. Nanofibers were observed for the one-layer in situ polymerized Cu²⁺-PDA film. Only flat block or irregular domains were observed in the case of other metal ion coordinated films. Previously, we have observed that the PDA film from the water surface showed helical nanofibers and attributed the supra-

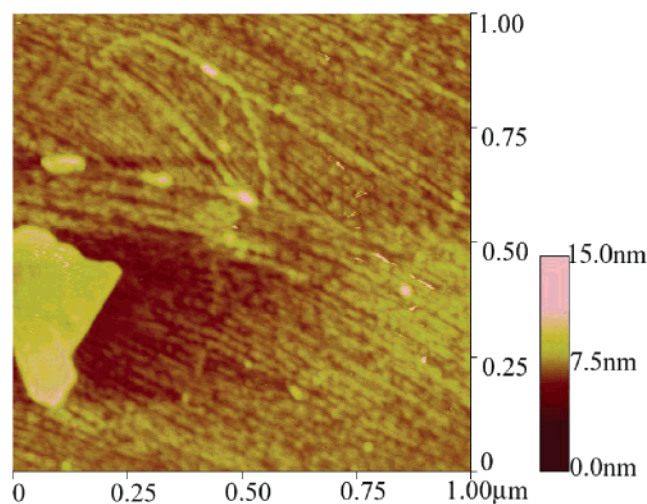


Figure 5. AFM image of in situ polymerized PDA film from subphase containing copper ion at 20 mN/m by vertical lifting method.

molecular chirality of the PDA film to the helical stacking of the repeat unit along the polymer backbone. The difference of the morphology of the Cu^{2+} -PDA film from the other metal ions indicated that the nanofiber structure played an important role in forming the supramolecular chirality of the Cu^{2+} -PDA film. Although the helix was not observed in the case of Cu^{2+} -PDA film, the repeat units in the backbone were suggested to arrange along the nanofiber in a helical sense and thus formed the supramolecular chirality. It is further suggested that the formation of such a fiber structure is related to the subtle difference in the coordination mode between TDA and different metal ions, as can be seen in the above FT-IR spectra.

In the FT-IR spectra of the M^{2+} -TDA films, it was observed that vibration bands were observed at 1692 cm^{-1} for the cases of Ca^{2+} , Ni^{2+} , and Cd^{2+} and not Ag^{+} , Zn^{2+} , and Cu^{2+} . This indicated that the reaction was complete in three metal ions (Ag^{+} , Zn^{2+} , and Cu^{2+}) due to their strong affinity to the carboxylic acid. Unique properties are only found in the cases of Cu^{2+} and Zn^{2+} , in which the carboxylate formed the bridging bidentate coordination type. Usually Zn^{2+} can form a typical tetrahedron structure and Cu^{2+} uses a square planar tetracoordinated structure³⁵ due to the Jahn–Teller effect. The square planar tetracoordinated structure of Cu^{2+} -PDA is similar to the arrangement of red PDA on the pure water surface and shows chirality. It seems that the square planar tetracoordinated Cu^{2+} -PDA ensures the backbone of the PDA film in a helical sense, which is important for the chirality of the film, while a tetrahedral tetracoordinated Zn^{2+} -PDA is in favor of thermochromism.

5.2. Stability of the Chiral Supramolecular Assemblies. From the discussion above, it is clear that the chirality of the PDA supramolecular assemblies was due to a stereoregular arrangement of both the polymer side chain and backbone. This is different from molecular chirality, where the chiral center or axis exists within a molecule. Usually, supramolecular chirality is not as stable as molecular intrinsic chirality. To check the stability of the supramolecular chirality in our PDA films, we measured the CD spectral changes of the films upon external stimulation. Figure 6 shows the CD spectral changes of the PDA and Cu^{2+} -PDA film before and after immersion in NaOH aqueous solution. The blue film of PDA changed into red film immediately upon treatment with alkaline solution. Interestingly, when the film turned red, the CD signal shifted accordingly. This indicated that although the backbone structure changed when the film turned from blue to red, the chiral sense of the backbone did not change. On the other hand, the red Cu^{2+} -PDA film was very stable when treated with alkaline solution. Both the UV–vis and the CD spectra of the Cu^{2+} -PDA film did not change upon heating or immersion in strong alkaline solution. We could obtain the same results by heating the film while treating with alkaline solution. These results indicated that our present chiral supramolecular assemblies from achiral amphiphile are very stable.

Conclusion

In conclusion, it is suggested that metal ions in the subphase could modify the function of the TDA films. The different coordination modes of the metal ions to the carboxylate anion greatly affect the polymerization and subsequent properties of the metal ion incorporated TDA films. Ag^{+} -TDA film cannot be polymerized because the molecular packing of the TDA deviated from the topochemical requirement for the photopolymerization. The Zn^{2+} -PDA film showed a thermochromism between blue and purple. The Zn^{2+} -coordinated headgroups and the reversible change of the alkyl chains packing were supposed to be responsible for the reversible color change. The Cu^{2+} -coordinated PDA film showed supramolecular chirality due to the arrangement of the polymer backbone in a helical sense, and the chirality of this film was very stable to pH change and heating. These results suggest that, without synthesizing new derivatives, some unique properties of PDA films can be realized simply by adding metal ions in the subphase, which opens a new way of regulating film properties through metal ions.

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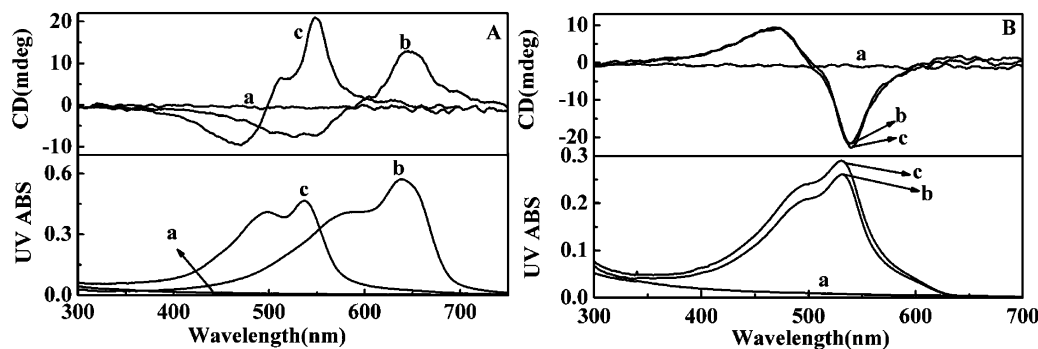


Figure 6. UV–vis and CD spectra of TDA (A) and Cu^{2+} -TDA LB films (B). (a) Before UV irradiation; (b) after UV irradiation; (c) subsequent treating of the film in NaOH aqueous solution.

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