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Coordination induced monolayer formation and fabrication of a novel conductive Langmuir–Schaefer film of benzimidazole-containing Schiff bases without a substituted alkyl chain

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Two benzimidazole-containing Schiff bases: 2-[(2′-hydroxybenzylidene)amino]benzimidazole (HBA) and 2-[(2′-hydroxynaphthylmethylidene)amino]benzimidazole (HNA), which have no substituted long alkyl chain, have been found to form stable monolayers at the air–water interface when Ag(I) ions are present in the subphase. The monolayers can be further transferred onto solid substrates using the horizontal lifting method. The transferred films were characterized by UV-Vis absorption, X-ray photoelectron spectra (XPS) and X-ray diffraction. It has been found that monolayers were formed through the coordination between the benzimidazole moiety and Ag(I) ions. The transferred Langmuir–Schaefer (LS) films thus formed showed a relatively large conductivity in the order of 10^{-1} S cm^{-1}. In addition, photoirradiation upon the film can cause a change in the conductivity.

1. Introduction

Investigations on the chemical reactions in organized media are attracting much interest.[1,2] A monolayer at the air–water interface provides a good limiting environment for the control of molecular orientations and packing[3] and various chemical reactions such as polymerization,[1] polycondensation[4,5] and photochemical reactions[6–9] have been widely investigated. Complex formation in the monolayer at the air–water interface is another important type of reaction. Different from those reactions between the monolayer-forming molecules, complex formation reactions are related to the interaction between the monolayer and the ions in the subphase. So far, a lot of long-chain amphiphiles modified with organic ligands such as crown ethers and analogues,[10–13] calixarenes,[14] imidazole,[15,16] pyridine,[17] and other groups,[18,19] have been synthesized and their complex formations with the metal ions in the subphase have been investigated. We have previously synthesized a series of amphiphile containing functional ligands such as thiazoresorcinol (TAR),[20] pyridylazoresorcinol (PAR)[21] and benzimidazole[22] and studied their complex formation with many transition metal ions at the air–water interface using surface pressure–area isotherms, UV-vis spectra and X-ray photoelectron spectra. However, in all these investigations, the ligands themselves can form stable monolayers. In this paper, we will report a new type of complex monolayer and their properties. In this monolayer, the ligand benzimidazole derivatives themselves cannot form a monolayer; however, induced by the *in situ* coordination reaction, stable monolayers were found to form. While benzimidazoles were reported to form polymeric complexes with many transition metal ions, their properties, especially the expected conductivity, could not be investigated due to the insolubility of the complexes in solvents. Induced by the coordination at the air–water interface, a monolayer of the polymeric compounds was successfully formed. Subsequent fabrication of the LB films led us to investigate the conductivity of the polymeric complexes of benzimidazoles and Ag(I) for the first time, which is in the order of 10^{-1} S cm^{-1}, a relatively large value for LB films.

2. Experimental

2.1 Materials

2-[(2′-Hydroxybenzylidene)amino]benzimidazole (HBA) and 2-[(2′-hydroxynaphthylmethylidene)amino]benzimidazole (HNA) were synthesized by the condensation of 2-aminobenzimidazole with corresponding aromatic aldehyde in ethanol solution. Equimolar mixtures of the two compounds were refluxed in ethanol solution for 4 hours. Cooling to room temperature caused a yellow or orange precipitate to form. After filtration and washing with ethanol, the solids were collected and recrystallized from ethanol–chloroform (1 : 1) twice to give crystals.

2-[(2′-Hydroxybenzylidene)amino]benzimidazole (HBA), mp: 235.0 °C (decomp.), ^{1}H-NMR (300 MHz, DMSO-d$_6$) δ (ppm) 7.03 (m, 2H), 7.20 (m, 2H), 7.49 (m, 2H), 7.60 (d, 1H), 7.88 (d, 2H), 9.65 (s, 1H), 12.09 (s, 1H). Anal. Calcd. For $C_{14}H_{11}N_3O$, C, 70.87; H, 4.67; N, 17.71. Found C, 70.78; H, 4.65; N, 17.60.

2-[(2′-Hydroxynaphthylmethylidene)amino]benzimidazole (HNA), mp: 288.0 °C (decomp.), ^{1}H-NMR (300 MHz, DMSO-d$_6$) δ (ppm) 7.21 (m, 4H), 7.48 (m, 2H), 7.55 (m, 1H), 7.65 (m, 2H), 7.93 (d, 1H), 8.11 (d, 1H), 8.57 (d, 1H), 10.29 (s, 1H). Anal. Calcd. For $C_{18}H_{13}N_3O$, C, 75.25; H, 4.56; N, 14.63. Found C, 75.30; H, 4.65; N, 14.54.

2.2 Procedures

Monolayers were formed by spreading 20 µl 2×10^{-3} M chloroform solution onto the subphase containing various concentrations of $AgNO_3$. The subphase was made by dissolving $AgNO_3$ in Milli-pore Q water (18 MΩ cm) without further adjusting of the pH value. $AgNO_3$ was recrystallized before use. After 10 min waiting for the evaporation of the solvent, the surface pressure–area (π–A) isotherms were recorded using a KSV 1100 mini-trough at 20 °C. The Langmuir–Schaefer (LS) films were fabricated by a Langmuir–Schaefer method or a horizontal lifting method[23] onto quartz, indium–tin oxide (ITO) coated glass and glass plates for UV-Vis (JASCO UV-530), X-ray photoelectron spectra (XPS, VG

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Scientific ESCALAB220I-XL system) and X-ray diffraction (XRD, Rigaku D/Max-RB) measurements, respectively. Conductivity was measured in a similar way to that reported previously.[24] Twenty-layer LS films from the monolayer on the aqueous subphase containing 10 mM $AgNO_3$ were fabricated on a glass slide (1 × 4 cm^2). Aluminium electrodes (3 × 13 mm^2) were coated on the surface of the LS film by a vacuum deposition technique. The distance between electrodes was 2 or 3 mm. A Precision Voltmeter was used to measure the resistance between the parallel electrodes and the conductivity was obtained using the following equation $\sigma = d/RA$, where d is the distance between the two electrodes and A is the area through which the electric current passes. The total thicknesses of the LS films were determined by the above mentioned X-ray diffraction. A UV lamp (254 nm, 10 W) was used to perform the photoirradiation. The distance between the LS films and the light source was 20 cm.

3. Results and discussion

3.1 Monolayer formation at the air–water interface

When the two compounds were spread on a water surface, no surface pressure was detected even when the surface was compressed to very lower molecular areas. When $AgNO_3$ was added to the subphase, however, surface pressures were observed. Fig. 2 illustrates the surface–pressure area isotherms of HBA and HNA under various conditions. Two distinct features are found for the isotherms. Firstly, the isotherms are dependent on the $AgNO_3$ concentration in the subphase. The more concentrated the subphase, the larger the molecular area. When the concentration of the subphase was more than 10 mM, the curves did not change significantly. Secondly, from the isotherms, the collapse pressures are found to be more than 30 mN m^{-1} for HBA and 20 mN m^{-1} for HNA. These phenomena are essentially the same as those reported for the 2-alkyl substituted benzimidazoles,[25] suggesting the complex formation was at the air–water interface. By extrapolating the linear part of the isotherms of the 10 mM $AgNO_3$ surface to zero surface pressure, limiting areas of 0.31 and 0.36 nm^2 $molecule^{-1}$ can be obtained for HBA and HNA, respectively. Based on the CPK model as shown in Fig. 1, the dimensions of the two compounds can be estimated to be 0.74 × 1.54 × 0.34 and 0.79 × 1.74 × 0.34 nm for HBA and HNA, respectively. It can be considered that the molecules are oriented vertically to the water surface.

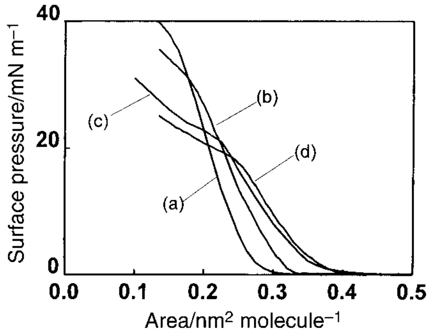

Fig. 2 Surface pressure–area isotherms of HBA and HNA on an aqueous subphase containing various concentrations of $AgNO_3$: (a) 1×10^{-3} M (HBA), (b) 1×10^{-2} M (HBA), (c) 1×10^{-3} M (HNA) and (d) 1×10^{-2} M (HNA).

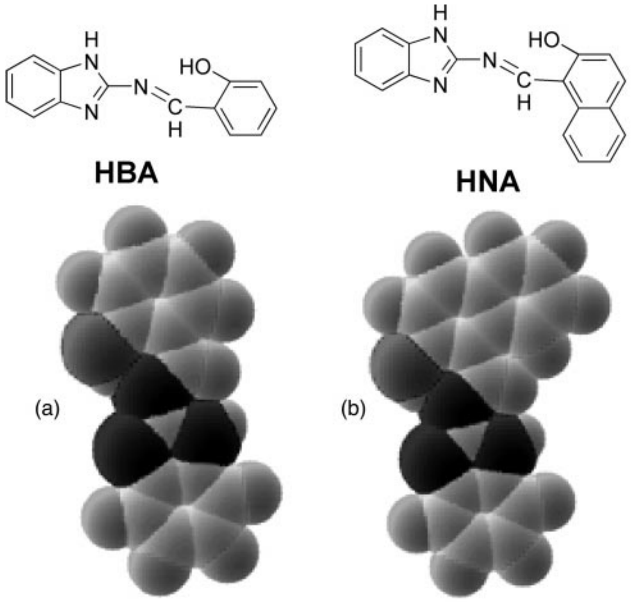

Fig. 1 Structures and abbreviations of the benzimidazole derivatives used in this work. CPK models of HBA (a) and HNA (b).

3.2 Characterization of the transferred LB films

3.2.1 XPS study. In order to clarify the above monolayer formation on the subphase containing Ag(I) ion, 40-layer films were transferred onto ITO glass for HBA and HNA at 20 and 13 mN m^{-1}, respectively, and their XPS spectra were measured, as shown in Fig. 3. In the case of HBA (Fig. 3A), binding energies for C1s, N1s, O1s and Ag $3d_{5/2}$ are observed at 284.6, 400.4, 532.8 and 368.8 eV, respectively. It is well known that N1s in a nitrate anion is found at around 407 eV; the fact that this peak was not found in our LB films indicates that no nitrate anion was incorporated into the films. In addition, the atomic concentrations of C, N, Ag and O derived from a careful investigation on each band were determined to be 74.02, 13.69, 6.61 and 5.67%, respectively. This is in very close agreement with the composition of HBA: Ag(I) = 1 : 1 ($C_{14}H_{11}N_3OAg$). These results indicate that the monolayer of HBA is formed in a similar manner as in the case of 2-alkyl substituted benzimidazoles.[25] In the case of compound HNA (Fig. 3B) a similar XPS spectrum is obtained. However, the atomic concentrations of C, N, Ag and O were found to be 77.46, 12.05, 2.87, 7.61%, respectively. It was obvious that although the ratio of C, N and O is consistent with compound HNA, Ag(I) concentration was much smaller for a 1 : 1

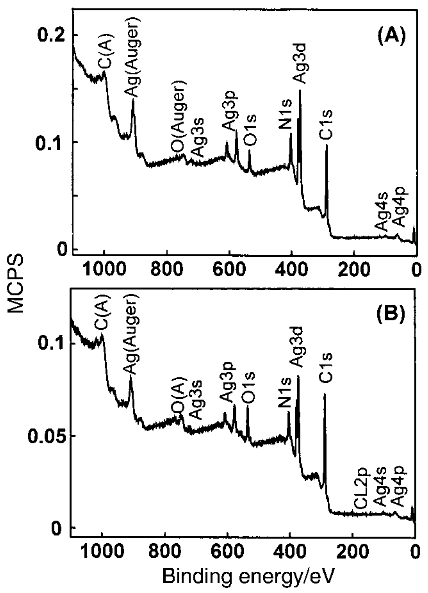

Fig. 3 XPS spectrum of a 40-layer LB film of HBA (A) and HNA (B) on ITO glass.

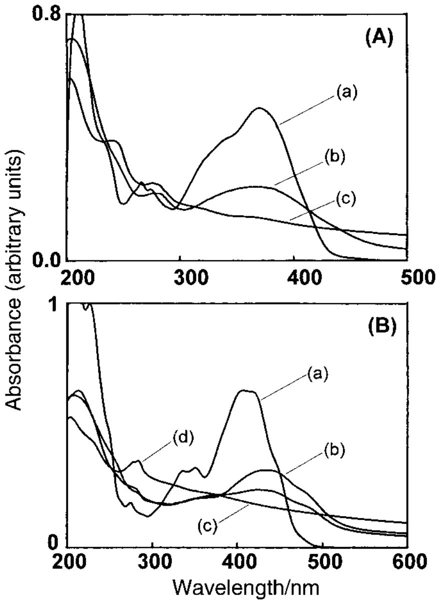

Fig. 4 UV-Vis spectra of HBA (A) and HNA (B) at various conditions: (a) in methanol, (b) film transferred from the monolayers on the subphase containing 10 mM $AgNO_3$; (c) the film after exposure to HCl gas for 1 min; (d) the film after exposure to HCl gas for 50 min.

complex. This suggests that the formation of the complex in the monolayer is incomplete. This could be understood by the larger size of the naphthyl ring compared to the phenol group, which hindered the complex formation.

3.2.2 UV-Vis absorption. Fig. 4 shows the UV-Vis spectra of LB films of HBA and HNA at various conditions. In comparison with the spectrum in solution, where peaks and shoulders are found at 369, 338, 274, 266 and 233 nm, only a broad peak at 369 nm and a shoulder at 338 nm are observed for the transferred film of HBA from aqueous $AgNO_3$ (Fig. 4A). The shoulder at 233 nm is related to deprotonation of imidazole[26,27] and its disappearance in the film from $AgNO_3$ confirms the complex formation. Such complex formation can be further verified by exposing the film to HCl gas. After only one minute's exposure (Fig. 4A (c)), a peak at 245 nm was observed, indicating the breaking of the N(imidazole)–Ag bond. Another interesting feature is also observed for the film, *i.e.* the peak at 369 nm disappeared upon exposure to HCl gas. Since the peak at 369 nm is related to the charge transfer band through the imine group of the Schiff base, the disappearance of the peak indicates the breaking of the imine group upon exposure to HCl gas. Similar spectral changes are found for the LB film of HNA (Fig. 4B). However, it takes a long time for HNA film to break the imine group upon exposing it to HCl. It should be further noted that a peak around 240 nm appeared after the film was exposed to HCl gas for 50 minutes.

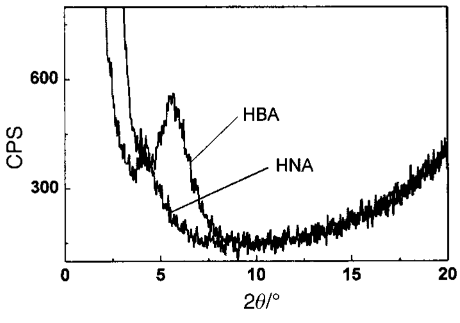

Fig. 5 X-Ray diffraction pattern of 40 layers LB films of HBA ($20\ \mathrm{mN\ m^{-1}}$) and HNA ($13\ \mathrm{mN\ m^{-1}}$).

3.2.3 X-Ray diffraction of the LB films. From the above discussions, we have shown that both HBA and HNA can form stable monolayers on an aqueous $AgNO_3$ subphase under coordination inducement. On the other hand, the regular layered structure is typical of LB films. For those LB films fabricated from typical long-chain amphiphiles, a larger amount of papers have verified this. However, how about the films in the case of HBA and HNA without any substituted alkyl chain? In order to make this problem clear, we have measured the X-ray diffraction (XRD) pattern of the transferred LB films. Fig. 5 shows the XRD pattern of the 40 layer LB films of HBA and HNA. In the scan range of 1.2 to 20 degrees, the diffraction peaks are found at 2θ equal to 5.59 and 4.25 for HBA and HNA, respectively. These diffraction peaks are broad and only one peak is observed in each of the films. This indicates that although the films are much less ordered as in the case of the LB films of cadmium arachidate, a regular layered structure exists in the LB films of both HBA and HNA. In addition, the long spacings of the LB films can be estimated using Bragg's equation:

$$2d\sin\theta = n\lambda \qquad (1)$$

The long spacings for the two films can be obtained as 1.58 and 2.10 nm for HBA and HNA, respectively. As shown in the above CPK model, the lengths of HBA and HNA are 1.54 and 1.74 nm, respectively. It is obvious that HBA takes an X-type film structure with the molecules vertical to the film surface. This is in accordance with the results from the π–A measurement. The difference between HBA and HNA can be understood by the incomplete formation of HNA. In the case of HBA, due to complete polymeric complex formation, overturn cannot occur. In the case of HNA, however, an incomplete monolayer was formed due to the steric hindrance, as verified from XPS measurement. This makes it possible for the monolayer to overturn in the transfer process.

In addition, other metal ions such as Cu(II), Ni(II) and Zn(II) are reported to form metal complexes with benzimidazole. We have measured the monolayer formation of HBA and HNA on the subphases containing metal ions such as $CuCl_2$, $NiCl_2$, $ZnCl_2$ and CuCl, it is interesting to note that monolayers cannot be formed on these subphases. This may be due to the hardness of the complex formation of benzimidazole with ions other than Ag(I). Moreover, some short and long-chain derivatives of *N*-alkylbenzimidazole did not show similar properties. This indicates that complex formation is indeed through deprotonation in the imidazole group.

3.3 Conductivity of the LB films

Benzimidazoles form metal complexes with many transition metal ions. These complexes are essentially polymeric in nature and insoluble in most organic solvents.[28,29] The complexes are expected to be conductive due to the conjugation of the metal ions with the benzimidazoles. Especially, in the case of the Ag(I)-coordinated compound, it is expected that there exists a conductivity along the polymer main chain. However, due to the insolubility, the conductivity was hard to investigate. The above *in situ* coordination formation of the monolayers of the benzimidazole with Ag(I) made it possible to investigate the conductivity of the LB film.

Table 1 lists the in-plane conductivity of the LB films of the

Table 1 Conductivity of the LB films

Compound	HBA	HNA
Conductivity ($\mathrm{S\ cm^{-1}}$)	0.33 ± 0.01	0.15 ± 0.01
Conductivity (after photo, $\mathrm{S\ cm^{-1}}$)[a]	0.64 ± 0.01	0.28 ± 0.01

[a] The photo-irradiation was performed using UV light (254 nm, 10 minutes).

compounds. The conductivities of the LB films of HBA and HNA are 0.33 and 0.15 S cm^{-1}, respectively. These values are relatively large for LB films.[30] In addition, the conductivity of HNA is smaller than that of HBA. This may be due to the incomplete formation of the coordination monolayer in the case of HNA. On the other hand, the LS films of the compounds are unstable. Upon photoirradiation, the film changes, such changes cause the change in conductivity, it is noted that upon photoirradiation with UV light, the conductivities of the LB films are increased.

It should be further noted that when HBA or HNA was mixed with $AgNO_3$ in methanol solution, a yellow-colored metal complex could be obtained. However, the complexes could not be fabricated into ultrathin films due to the insolubility in organic solvent. By taking advantage of the coordination induced monolayer formation at the air–water interface, it becomes possible to fabricate the ultrathin films and makes it possible to measure the conductivity. Our results presented a new way to investigate the functional ultrathin films of some water-insoluble polymers.

Conclusion

Two benzimidazole-containing Schiff bases, which have no substituted alkyl chain, can form monolayers at the air–water interface induced by coordination with the Ag(I) ions. Such a kind of monolayer formation is regarded as being due to an *in situ* formation of a polymeric complex between the benzimidazole moiety of the compound and Ag(I) ions. The LB films, fabricated by a horizontal lifting method, showed a conductivity in the order of 10^{-1} S cm^{-1}, a first reported value for the compound. The conductivity of the LB film can be enhanced by photoirradiation.

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