Crystallization of the oxalate-linked copper(II) coordination polymer by Langmuir-Blodgett technique

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Abstract: An oxalate-linked copper(II) coordination polymer, which was dissolved in water, was deposited at the air/water interface, in the presence of the monolayer spreading n-alkylamine ($C_{19}H_{39}NH_2$ or $C_{22}H_{45}NH_2$) out on the aqueous solution. Both monolayers of copper(II) coordination polymer/$C_{19}H_{39}NH_2$ and /$C_{22}H_{45}NH_2$ were easily formed at the interface. The $C_{22}H_{45}NH_2$ monolayer was stable on the aqueous solution to transfer onto a silica glass substrate compared with the $C_{19}H_{39}NH_2$ monolayer. Consequently, The $C_{22}H_{45}NH_2$ monolayer was accumulated on the substrate at pH 6.80 as the copper(II) coordination polymer crystallized on it. The fabricated LB film was characterized by x-ray diffractometry and UV-Vis spectroscopy. The LB film had Y-type deposition, and its d_{001} spacing was estimated to be above 57Å. The arrangements of the coordination polymer and $C_{22}H_{45}NH_2$ in the film have further discussed in this paper.

Key words: crystallization, coordination polymer, n-alkylamine, Langmuir-Blodgett, composite film

1. INTORDUCTION

By bridging between copper ions with oxalate ions, a wide variety of polynuclear compounds have been synthesized in recent years. All of them have opened a new perspective in the field of low-dimensional electronic and magnetic systems [1]. However, their crystals were not easily formed because of their high solubility. It is expected that Langmuir-Blodgett (LB) technique is a more effective method to build up [Cu(ox)] chain assemblies under mild condition. Using the LB technique, we have also studied on fabrication of multilayer films composed of inorganic/organic molecules, such as (clay unit layers)/alkylamines [2], (metal oxaletes)/alkylamines, (poloxoxmatalate anions)/alkylamines [3] and so on.

The oxalate-linked copper(II) coordination polymer as shown in Fig.1 was selected in this report. Here we discussed optimum conditions for fabrications of two LB films consisting of [Cu(ox)]/$C_{19}H_{39}NH_2$ and /$C_{22}H_{45}NH_2$.

2. EXPERIMENTAL PROCEDURES

$C_{22}H_{45}NH_2$ was prepared from $C_{22}H_{45}Br$ using NaN_3 [4]. All commercial compounds, such as $Cu(BF_4)_2 \cdot nH_2O$, $(COOK)_2 \cdot H_2O$, $C_{19}H_{39}NH_2$ and so on, were used without further purification.
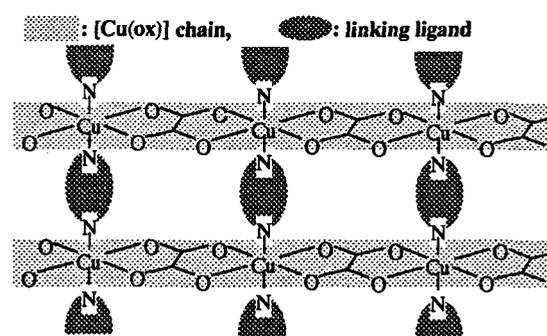
Fig.1 The infinite chain structure of the oxalate-linked copper(II) coordination polymer

The composite films were obtained at room temperature by a vertical lifting method. 0.0158g of 45wt% $Cu(BF_4)_2 \cdot nH_2O$ aqueous solution was added to the solution of 6.0×10^{-5}mol $(COOK)_2 \cdot H_2O$ dissolved in 1l of distilled water. After 0.0158g of 45wt% $Cu(BF_4)_2 \cdot nH_2O$ aqueous solution was further added to the solution, its total volume was adjusted to 2l with distilled water. This solution was used as a subphase and

pH-values were also adjusted with 1N NaOH. Each n-alkylamines dissolved in benzen (concentration ca. $2.0×10^{-3}$ M) was also used as a spreading solution. Maintaining temperature of the subphase (1000 cm²) in a Kyowa Interface Science trough at 16~18°C, 200ml of the spreading solution was dropped by a microsyringe on the subphase. After evaporation of benzen for 20 min, a monolayer composing of [Cu(ox)]/n-alkylamine was compressed by a barrier at a rate of 20 cm²/min to a surface pressure (25~30 dyne/cm). The monolayer was transferred onto hydrophilic silica or glass substrate, keeping the surface pressure. Dipping speed was generally set to 1.0 cm/min.

Infrared spectroscopy (IR) was used to monitor as to whether [Cu(ox)] and n-alkylamine were contained in the monolayer. IR spectra were all recorded on IR-460 Shimadzu spectrometer. X-ray diffraction was also used to study the structure of the film of [Cu(ox)]/$C_{19}H_{39}NH_2$ (or $C_{22}H_{45}NH_2$). All X-ray diffraction experiments were performed with XD-610 Shimadzu X-ray powder diffractometer.

The color of the films with the coordination polymer was observed by UV-265 Shimadzu u. v.–visible recording spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 LB film of [Cu(ox)] /$C_{19}H_{39}NH_2$

Π-A curves for monolayers of $C_{19}H_{39}NH_2$ spread on a subphases of (a) $2.5×10^{-5}$M Cu(BF$_4$)$_2$ solution (pH 6.93) and (b) $2.5×10^{-5}$M Cu(BF$_4$)$_2$ solution (pH 7.00) containing (COO⁻)$_2$, are shown in Fig.2. As shown in Fig.2, the surface pressures were both increased by ordering molecules of $C_{19}H_{39}NH_2$ at the air/water interface. The area per molecule of the monolayer (b) was larger than that of monolayer (a). It was revealed that the [Cu(ox)] chains were formed by linked between Cu²⁺/$C_{19}H_{39}NH_2$ with (COO⁻)$_2$ at the interface. However, the floating layer of [Cu(ox)]/$C_{19}H_{39}NH_2$ was not stable to transfer onto a substrate because of dissolving [Cu(ox)]/$C_{19}H_{39}NH_2$ monolayer in the subphase (Fig.2 (b)).

3. 2 LB film of [Cu(ox)]/$C_{22}H_{45}NH_2$

It is shown in Fig. 3 that Π-A curves for monolayers of $C_{22}H_{45}NH_2$ spread on various concentration subphases. In the Π-A curves for monolayers of $C_{22}H_{45}NH_2$ spread on $1.5×10^{-5}$M and $7.5×10^{-4}$M Cu(BF$_4$)$_2$ solutions, both

pressures gradually increased by collapsing their monolayers. On the other hand, the pressure increased steeply in the isotherm of $C_{22}H_{45}NH_2$ spread on $3.0×10^{-4}$M Cu(BF$_4$)$_2$ solution. It was revealed that $C_{22}H_{45}NH_2$ molecules were oriented in the monolayer.
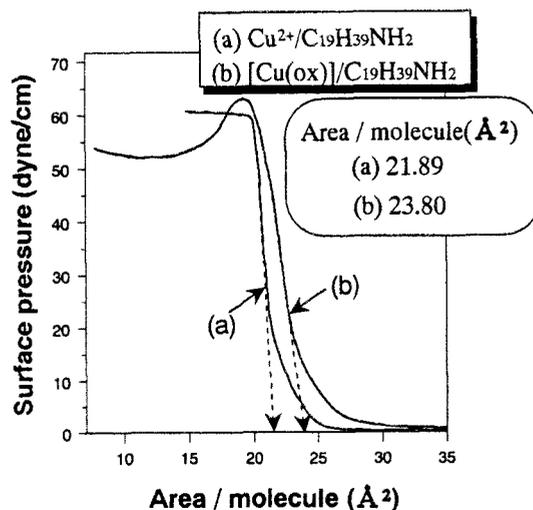
Fig.2 Pressure versus area per molecule isotherms for: (a) Cu²⁺/$C_{19}H_{39}NH_2$ and (b) [Cu(ox)]/$C_{19}H_{39}NH_2$.
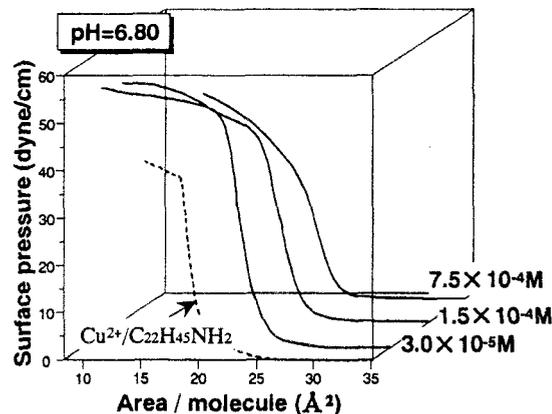
Fig.3 Pressure-area isotherms of the monlayers spreading $C_{22}H_{45}NH_2$ on various subphases for: $3.0×10^{-5}$, $1.5×10^{-4}$ and $7.5×10^{-4}$M Cu(BF$_4$)$_2$ solutions.

Each area per molecule is represented in Table 1. The area per molecule above $3.0×10^{-5}$M Cu(BF$_4$)$_2$ solution were about 3~6 Å² larger than it of Cu²⁺/$C_{22}H_{45}NH_2$. This difference corresponded to the size of (COO⁻)$_2$ anion.

Pressure-area isotherms of $C_{22}H_{45}NH_2$ spread on subphases at various pH are shown in Fig.4. As shown in Π-A curves in pH ranging from 4.5 to 5.5, the monolayers were not stable for fabricating the LB film. On the other hand, Π-A curves at pH 6.0 and 6.8 were both stable, however, the monolayer at pH 6.0 was slightly unstable. Therefore the pH-value transferring

onto a substrate was at around 6.8. It was concluded that optimum subphase for fabricating the LB films containing [Cu(ox)] was 3.0×10^{-5}M Cu(BF$_4$)$_2$ solution with (COO$^-$)$_2$ at pH 6.80.

Table I Area per molecule of C$_{22}$H$_{45}$NH$_2$ monolayers on the subphases having different concentrations.

C/M×10^{-5}	75	15	3.0	2.0	(Cu^{2+})^a
A/Å^2	26.25	23.88	23.26	21.18	19.93

a) C$_{22}$H$_{45}$NH$_2$ monolayer on 5.0×10^{-5}M CuCl$_2$ solution.
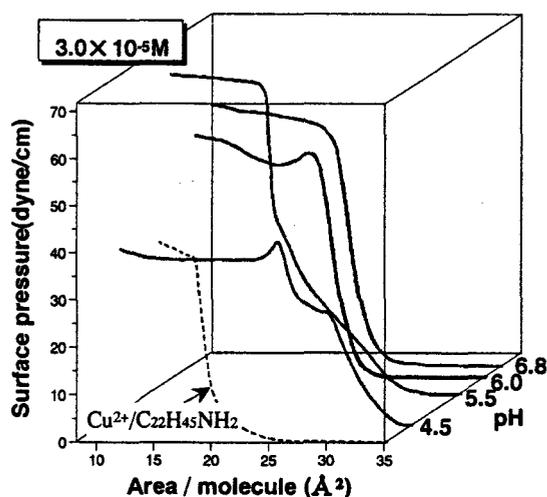
Fig.4 Pressure versus area per molecule isotherms, at different pH values, for monlayers of C$_{22}$H$_{45}$NH$_2$ spread on 3.0×10^{-5}M Cu(BF$_4$)$_2$ solution.
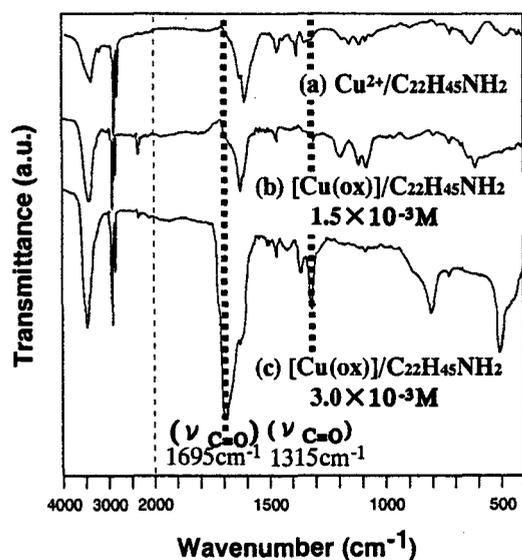
Fig.5 IR spectra of the monolayers spread C$_{22}$H$_{45}$NH$_2$ on the subphases of (a) 5.0×10^{-5}M CuCl$_2$ solution, (b) 1.5×10^{-5}M and (c) 3.0×10^{-3}M Cu(BF$_4$)$_2$ solutions containing (COO$^-$)$_2$ anions.

As shown in Fig.5 (b) and (c), both band at 1695 and 1315cm^{-1} were assigned to C=O stretching ($\nu_{C=O}$) of (COO$^-$)$_2$. It was confirmed that (COO$^-$)$_2$ anions existed in the monolayers.

Fig.6 shows UV-Vis spectra of the LB films fabricated from the monolayers of C$_{22}$H$_{45}$NH$_2$ and [Cu(ox)]/C$_{22}$H$_{45}$NH$_2$. As shown in Fig.6, there were no absorptions at the wavelengths ranging from 200 to 900nm in the spectrum of the LB film consisting of C$_{22}$H$_{45}$NH$_2$ alone. On the other hand, shoulder absorption peaks were observed at around 250nm in both spectra of (b) and (c). The shoulder peaks were assigned to transition from n to π^* for (COO$^-$)$_2$. Increasing the number of accumulating layer, the broad peak was also observed at the wavelengths ranging from 300~500nm. The absorption corresponded to d-d transition of Cu^{2+} ion. This result suggested that Cu^{2+} ions were formed [Cu(ox)] chain structure by (COO$^-$)$_2$ anions as ligand.
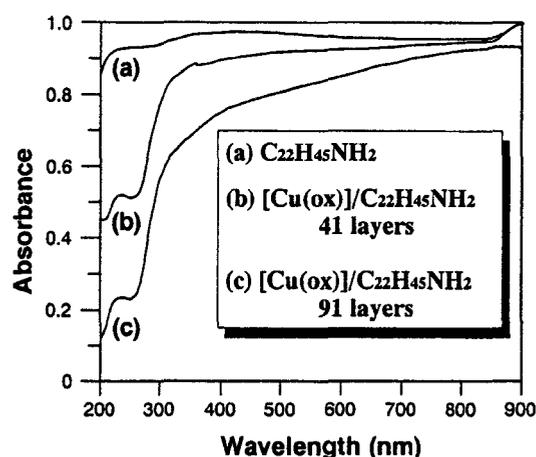
Fig.6 UV-Vis spectra of three LB films of (a) C$_{22}$H$_{45}$NH$_2$, (b) 41-layer [Cu(ox)]/C$_{22}$H$_{45}$NH$_2$ and (c) 91-layer [Cu(ox)]/C$_{22}$H$_{45}$NH$_2$.

Fig.7 (a) shows X-ray diffraction patterns of the alternate-LB films of the monolayer spreading C$_{22}$H$_{45}$NH$_2$ only on the 6.0×10^{-5}M Cu(BF$_4$)$_2$ solution. The X-ray diffraction data from the LB films accumulating the monlayer of [Cu(ox)]/C$_{22}$H$_{45}$NH$_2$ at two kinds of surface pressures of (b) are also shown in Fig.7 (b) and (c). All films were Y-type LB films. Both peak intensities indexed (002) in Fig.7 (b) and (c), were larger than it in Fig.7 (a). This is due to formation of [Cu(ox)] chain with (COO$^-$)$_2$ parallel to the substrate. The d$_{001}$ values of LB films were estimated to be (a) 63.6Å, (b)

57.9Å and 58.9Å, respectively. The d_{001}-values in Fig.7 (b) and (c) were shorter than it in Fig.7 (a). It is considered that molecules of $C_{22}H_{45}NH_2$ inclined at an angle of 24.44° in the film.

By using $C_{22}H_{45}NH_2$, the LB film having high orientation for the oxalate-linked copper(II) coordination polymer was easily fabricated under the mild condition. It was also proposed that the alternate-layer film had the structure described in Fig.8.
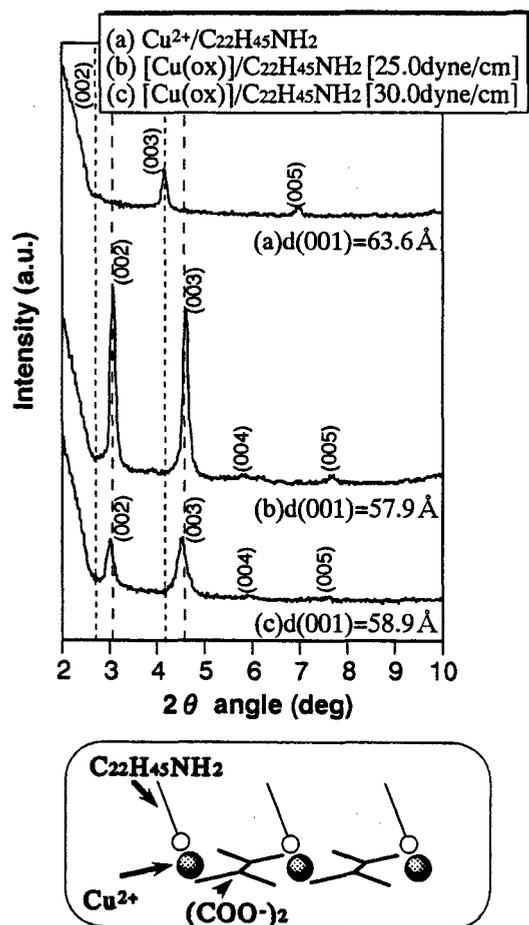
Fig.7 X-ray diffraction patterns of three LB films consisting of (a) $Cu^{2+}/C_{22}H_{45}NH_2$, and accumulating the monolayer of [Cu(ox)]/$C_{22}H_{45}NH_2$ at two kinds of surface pressures of (b) 25.0dyne/cm and (c) 30.0dyne/cm.

4. CONCLUSION

The LB film composed of the oxalate-linked copper(II) coordination polymer having [Cu(ox)] chain and $C_{22}H_{45}NH_2$ was prepared by depositing the coordination polymer at the air /water interface. On the other hand, the solubility of the monolayer of $C_{19}H_{39}NH_2$ in water increased by forming [Cu(ox)]/$C_{19}H_{39}NH_2$ at the interface.

Consequently, the alkyl chain must have at least 22 carbon atoms to obtain the insoluble monolayer.
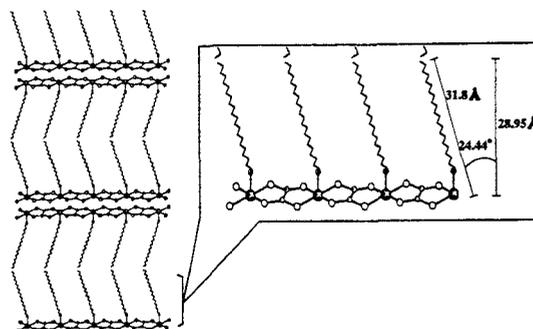
Fig.8 The configuration model of the alternate-layer Langmuir-Blodgett film built up from monolayers of [Cu(ox)]/$C_{22}H_{45}NH_2$.

LB technique is most useful to order the copper(II) coordination polymer with n-alkylamine, as the crystalline form. It is also expected that the LB films were applied to the detection of organic vapors, for example benzene, ethanol, acetonitrile [5] and so on.

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