

# Hybrid Films of a Clay Mineral and an Iron(II) Complex Cation Prepared by a Combined Method of the Langmuir–Blodgett and Self-Assembly Techniques

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Hybrid multilayers of an amphiphilic alkylammonium cation, a clay mineral, and an iron(II) complex cation have been prepared by a combined method of the Langmuir–Blodgett and self-assembly techniques. A monolayer of the amphiphilic alkylammonium cation floating on a clay suspension is hybridized with the clay platelets at an air–suspension interface. The outer surface of the film of the ammonium cation and the clay platelets transferred from the air–suspension interface onto a substrate has cation-exchange capacity, so the Fe(II) complex cations are adsorbed onto the surface of the film by the cation-exchange reaction. By repeating these procedures, hybrid multilayers of the amphiphilic ammonium cation, the clay platelets, and the Fe(II) complex cation were successfully fabricated in a layer-by-layer way. The electronic spectra of the hybrid multilayers indicated that the density of the Fe(II) complex cation in the film could be controlled by changing the clay concentration in the suspension. The results of the X-ray diffraction measurement for the hybrid films showed that the film possessed a stable layered structure. The intensities of the second-harmonic generation from the hybrid multilayers increased with the increase in the layer number, which suggested that the hybrid multilayer should have a noncentrosymmetric geometry.

## Introduction

Ultrathin films have been attractive to many researchers because of their applications to optical devices, microelectronic devices, and sensors.<sup>1–15</sup> The Langmuir–Blodgett (LB) method is one of the most useful techniques to prepare a multilayered film, in which the layer number and the layer sequence can be controlled at the molecular level.<sup>1,4,16,17</sup> When amphiphilic cations are spread onto the surface of an aqueous suspension of a smectite clay at a low concentration, a floating monolayer of the amphiphilic cations is hybridized with the negatively charged clay platelets at an air–suspension interface.<sup>15,18–23</sup> The hybrid floating films can be transferred onto a solid surface by horizontal dipping to form a multilayer.<sup>24</sup> Recently, this type of multilayer of clay platelets and amphiphilic Ru(II) complex cations with long alkyl chains has been fabricated.<sup>25</sup> This multilayer had a stable layered structure, but the orientation of the Ru(II) complex cations was disturbed. When the clay surfaces of the transferred hybrid films were modified with alkylammonium cations, the amphiphilic Ru(II) complex cations were successfully oriented in one direction in the multilayer. Although this preparation method of the hybrid films is promising, one of its shortcomings is that an organic material spread onto the suspension should be amphiphilic.<sup>1,4,16,17</sup> This is inevitable for the LB method.

In this paper, a novel type of clay hybrid films is reported. The LB method and the self-assembly method are combined (Scheme 1).<sup>26</sup> The hybrid floating film of amphiphilic cations and clay platelets formed at the air–clay suspension interface is transferred onto the surface of a substrate by horizontal dipping. The outer surface of the transferred film is covered with a clay layer, and some exchangeable cations such as Na<sup>+</sup> remain on the outer surface of the clay layer unless the negative charge of the clay layer is neutralized completely by the positive

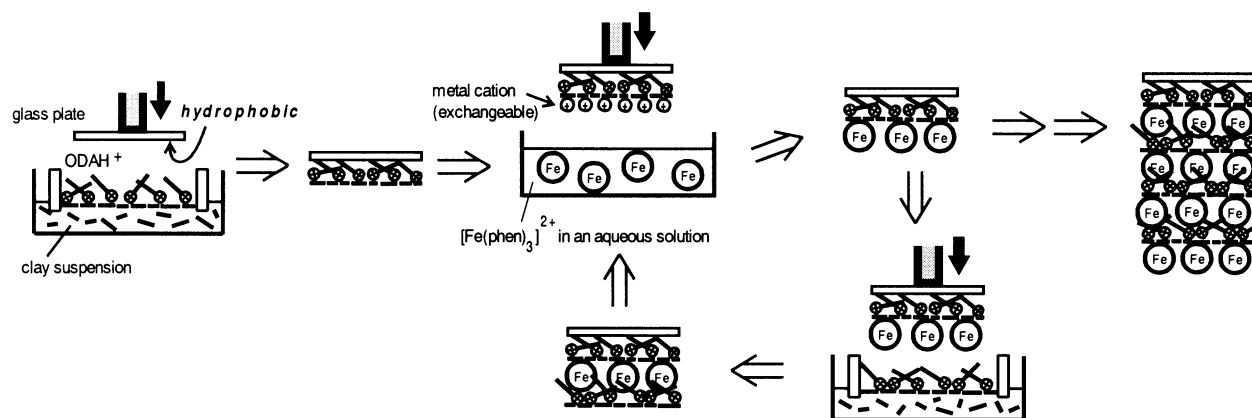
charge of the amphiphilic cation.<sup>25</sup> The metal cations remaining on the outer surface are ion-exchangeable. When the outer surface of the film is dipped in a solution of a cationic compound, the cationic compound is adsorbed on the surface by an ion-exchange reaction to form a layer. By repeating these procedures, one can prepare a hybrid multilayer of the amphiphilic cations, the clay platelets, and the adsorbed cations. The hybrid multilayer thus prepared is expected to possess some remarkable features: (1) The layered structure of the film is quite stable because of the rigid clay layers in the film. (2) One can introduce thin layers of any cationic compound into the film as the adsorbed layers. (3) It is easy to control the density of the adsorbed cations by changing the clay concentration in the suspension because the cation-exchange capacity of the outer surface of the transferred film depends on the concentration of clay in the suspension. (4) The cations in the adsorbed layer are sandwiched noncentrosymmetrically between the clay layer and the amphiphilic cation layer. To demonstrate these features of the films, hybrid multilayers of an Fe(II) complex cation have been prepared and characterized in this work.

## Experimental Section

**Materials.** The hybrid multilayers were composed of the octadecylammonium cation (C<sub>18</sub>H<sub>37</sub>NH<sub>3</sub><sup>+</sup>/ODAH<sup>+</sup>) as the amphiphilic cation, montmorillonite as the clay mineral, and the tris(1,10-phenanthroline)iron(II) cation, [Fe(phen)<sub>3</sub>]<sup>2+</sup>, as the adsorbed cation. Octadecylammonium chloride (ODAH<sup>+</sup>Cl<sup>−</sup>) was prepared by a reaction of the corresponding amine and hydrochloric acid. The ammonium salt was recrystallized in ethanol twice. The smectite clay mineral of montmorillonite was Kunipia P from Kunimine Co., Japan. The cation-exchange capacity (CEC) of the clay was 1.074 mequiv g<sup>−1</sup>. The iron(II) complex salt of [Fe(phen)<sub>3</sub>]Cl<sub>2</sub> was synthesized according to literature methods.<sup>27–29</sup>

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## SCHEME 1: Preparation of a Hybrid Multilayer



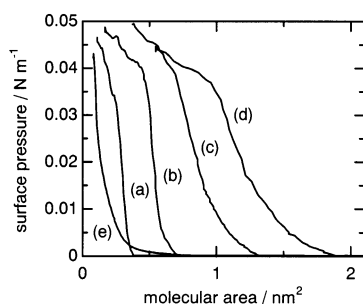
**Film Preparation.** Amphiphilic  $\text{ODAH}^+\text{Cl}^-$  dissolved in chloroform ( $2 \times 10^{-4} \text{ mol dm}^{-3}$ ) was spread onto the surface of the clay suspension at a given concentration (2–50 ppm). A floating film of  $\text{ODAH}^+$  was hybridized with the clay platelets at the air–suspension interface. Fifteen minutes later, the floating hybrid film was compressed up to the surface pressure of  $10 \text{ mN m}^{-1}$ . At this pressure, the whole surface of the floating film was mostly covered with the clay platelets.<sup>23,24</sup> The hybrid floating film of  $\text{ODAH}^+$  and the clay platelets was transferred onto the hydrophobic surface of a glass substrate by horizontal dipping. (The surface of the glass plate was modified with phenyltrimethoxysilane.) After rinsing the surface of the transferred film with pure water several times, the surface was dipped in an aqueous solution of  $[\text{Fe}(\text{phen})_3]\text{Cl}_2$  ( $1 \times 10^{-3} \text{ mol dm}^{-3}$ ) for 10 s. The surface was again rinsed with pure water several times and then dried. These procedures were repeated to fabricate the hybrid multilayer.

**Instruments.** A KSV minitrough was used for the preparation of the floating hybrid films and for measurements of their surface pressure–molecular area ( $\pi$ – $A$ ) isotherms. Electronic spectra of the films were measured in transmission with a Hitachi U-4100 spectrophotometer. X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert MRD high-resolution X-ray diffractometer using Ni-filtered  $\text{Cu K}\alpha$  radiation. Second-harmonic-generation (SHG) measurements were carried out using a Q-switched Nd/YAG laser (8 ns, 20 Hz, 1064 nm). The SHG signals from the films were detected in transmission.

## Results and Discussion

 $\pi$ – $A$  Isotherms of Floating Films on Clay Suspensions.

Figure 1 shows  $\pi$ – $A$  isotherm curves of the floating films when a solution of  $\text{ODAH}^+\text{Cl}^-$  was spread onto the surface of the clay suspensions at 5, 10, 25, and 50 ppm and onto pure water. The  $\pi$ – $A$  isotherm of the floating film on the suspension at 50

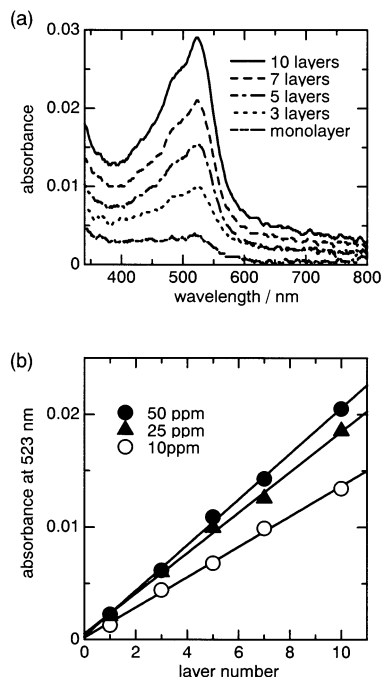


**Figure 1.**  $\pi$ – $A$  isotherm curves for floating monolayers of  $\text{ODAH}^+$  on clay suspensions at (a) 5, (b) 10, (c) 25, and (d) 50 ppm and on (e) pure water

ppm (Figure 1d) lifts off around  $1.9 \text{ nm}^2 \text{ molecule}^{-1}$  from the surface pressure of  $0 \text{ mN m}^{-1}$ , and as the film is compressed, the surface pressure increases up to  $37 \text{ mN m}^{-1}$ . At this point ( $1.0 \text{ nm}^2 \text{ molecule}^{-1}$ ), the slope of the isotherm curve changes, indicating a collapse of the floating film. As the clay concentration in the suspension decreases (Figure 1a–d), the  $\pi$ – $A$  isotherms of the floating films on the suspensions shift to the smaller molecular area side and approach that on pure water (Figure 1e).<sup>23–25</sup> The hybridization of  $\text{ODAH}^+$  and the clay platelets at the air–suspension interface gives rise to this dependence of the isotherm on the clay concentration in the suspension. These isotherm data indicate that the density of  $\text{ODAH}^+$  in the film can be controlled by changing the concentration of clay in the suspension.<sup>24</sup>

The formation mechanism of the floating hybrid film was proposed in the previous paper.<sup>24</sup> When the solution of  $\text{ODAH}^+\text{Cl}^-$  is spread onto the surface of the clay suspension, the clay platelets in the suspension are adsorbed onto the bottom of the floating  $\text{ODAH}^+$  monolayer. If the clay concentration is high, the adsorption rate of the clay platelets is high. In such a case,  $\text{ODAH}^+$  cations are captured immediately by the clay platelets at the air–suspension interface before  $\text{ODAH}^+$  cations aggregate to form monolayer domains. As a result, the density of  $\text{ODAH}^+$  adsorbed on clay platelets is low.

**Electronic Spectra of Hybrid Films.** A hybrid floating film was transferred onto a glass surface, and the surface of the transferred film was dipped in an aqueous solution of  $[\text{Fe}(\text{phen})_3]\text{Cl}_2$ . Complex cations were adsorbed onto the film's surface by a cation-exchange reaction. Multilayered films of  $\text{ODAH}^+$ , the clay platelets, and  $[\text{Fe}(\text{phen})_3]^{2+}$  were built up by repeating the deposition of the hybrid floating film and the dip in the solution of  $[\text{Fe}(\text{phen})_3]\text{Cl}_2$ . One unit layer composed of  $\text{ODAH}^+$  cations, the clay platelets, and the complex cations is designated as one hybrid layer hereafter. The electronic spectra of the hybrid films (1–10 hybrid layers) prepared by using the clay suspension at 50 ppm are shown in Figure 2a. Each spectrum gives an absorption maximum at 523 nm and a shoulder around 485 nm that are assigned to metal-to-ligand charge-transfer bands<sup>30–32</sup> of  $[\text{Fe}(\text{phen})_3]^{2+}$  in the film. The absorption intensity increases with the increase in the hybrid layer number. The absorbance at 523 nm is plotted as a function of the hybrid layer number in Figure 2b, together with the absorbance of the hybrid films prepared from the clay suspensions at 10 and 25 ppm. As can be seen in the Figure, the absorbance increases linearly as the hybrid layer number increases for each series of the hybrid films. It should be pointed out that the slopes of the lines are steeper as the clay concentrations of the suspensions are higher. This indicates that the density of the  $[\text{Fe}(\text{phen})_3]^{2+}$  cation in one layer



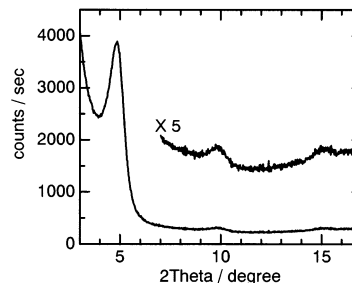
**Figure 2.** (a) Electronic spectra for hybrid films of ODAH<sup>+</sup>, clay platelets, and [Fe(phen)<sub>3</sub>]<sup>2+</sup> prepared from a clay suspension at 50 ppm. (b) Relation between absorbance at 523 nm and the hybrid layer number for hybrid films prepared from clay suspensions at 10, 25, and 50 ppm.

in the hybrid film can be controlled by changing the clay concentration in the suspension.

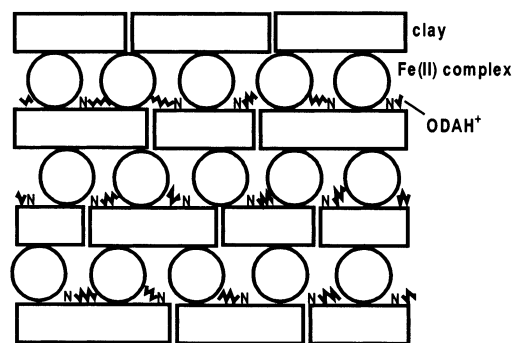
When the floating hybrid film of ODAH<sup>+</sup> and clay platelets is formed on the surface of the clay suspension at high concentration, the density of ODAH<sup>+</sup> is low, and a large amount of the exchangeable cation remains on the clay surface. Therefore, the cation-exchange capacity of the film is high, and a large amount of [Fe(phen)<sub>3</sub>]<sup>2+</sup> is adsorbed on the film surface.

On the assumption that the extinction coefficient ( $\epsilon$ ) of [Fe(phen)<sub>3</sub>]<sup>2+</sup> in the film is the same as that in the aqueous solution ( $\log \epsilon = 4.05$ ),<sup>30</sup> the areas per [Fe(phen)<sub>3</sub>]<sup>2+</sup> cation in the films prepared from the clay suspensions at 10, 25, and 50 ppm can be calculated from their slopes in Figure 2b to be 1.38, 1.04, and 0.92 nm<sup>2</sup> cation<sup>-1</sup>, respectively. Considering a cross-sectional area of an analogous complex of the tris-(2,2'-bipyridine)ruthenium(II) complex cation (0.92 nm<sup>2</sup>),<sup>33</sup> [Fe(phen)<sub>3</sub>]<sup>2+</sup> cations would be packed closely in the hybrid film prepared from the 50-ppm suspension. From the CEC of the clay, the area per negative charge on the clay platelet is estimated to be about 0.5 nm<sup>2</sup> charge<sup>-1</sup>. Unfortunately, an equilibrium constant between ODAH<sup>+</sup> and the corresponding amine in the film is unknown, so a precise determination of the charge balance in the film is impossible. Nevertheless, it seems that almost all of the ODAH<sup>+</sup> cations in the film might exist as the neutral amine because the calculated areas per [Fe(phen)<sub>3</sub>]<sup>2+</sup> in the hybrid films are around 1 nm<sup>2</sup> cation<sup>-1</sup>, which is twice the area per negative charge on the clay platelet.

**XRD Patterns of Hybrid Films.** The XRD pattern for the 10-layered hybrid film prepared from the suspension at 50 ppm (Figure 3) gives three diffraction peaks at  $2\theta = 4.83$ , 9.8, and 15°, though the second and third peaks are very weak. This XRD pattern indicates that the hybrid film possesses the layered structure. The XRD patterns for the hybrid films prepared from the suspensions at 25 and 10 ppm were almost the same as that for the film prepared from the suspension at 50 ppm (Figure 3). The layered structure of the hybrid film was independent of the clay concentration in the suspension.



**Figure 3.** XRD pattern for a 10-layered hybrid film of ODAH<sup>+</sup>, clay platelets, and [Fe(phen)<sub>3</sub>]<sup>2+</sup> prepared from a clay suspension at 50 ppm.

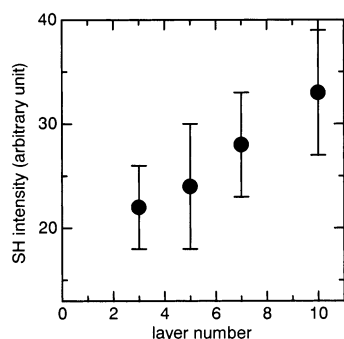


**Figure 4.** Schematic view of a layered structure in a hybrid film of ODAH<sup>+</sup>, clay platelets, and [Fe(phen)<sub>3</sub>]<sup>2+</sup>.

The thickness of the hybrid layer calculated from the first peak in Figure 3 is 1.83 nm. Because the thickness of the clay platelet is 0.96 nm,<sup>34–36</sup> the thickness of the [Fe(phen)<sub>3</sub>]<sup>2+</sup> and ODAH<sup>+</sup> layers is 0.87 nm in the hybrid film, which is too small for the cation layers. The thickness of the hybrid layer (1.83 nm) is in good agreement with the basal spacing of a clay–[Fe(phen)<sub>3</sub>]<sup>2+</sup> intercalation compound (1.78 nm).<sup>37</sup> The complex cations in the hybrid film might be in contact with the clay layers on both sides as the complex cations in the intercalation compound (Figure 4). This structural model is supported by the fact that the XRD pattern of the hybrid film is independent of the clay concentration in the suspension.

The existence of ODAH<sup>+</sup> in the hybrid films was confirmed by the infrared spectra of the films.<sup>38</sup> According to this structural model, ODAH<sup>+</sup> cations should occupy the empty spaces between the complex cations in the film. The alkyl chain of ODAH<sup>+</sup> in the film lies on the surface of the clay layer. As shown in the  $\pi$ -A isotherms for the floating films of ODAH<sup>+</sup> and clay platelets (Figure 1b–d), the densities of ODAH<sup>+</sup> are lower than that in the closely packed monolayer of ODAH<sup>+</sup> on pure water (Figure 1e). The density of ODAH<sup>+</sup> in the floating film on the clay suspension at 10 ppm (0.56 nm<sup>2</sup> cation<sup>-1</sup> at 10 mN m<sup>-1</sup>) is the highest among the hybrid films prepared in this work. The density of [Fe(phen)<sub>3</sub>]<sup>2+</sup> in the hybrid film prepared from the 10-ppm suspension is estimated to be 1.38 nm<sup>2</sup> cation<sup>-1</sup>, indicating that the complex cations are not closely packed. Therefore, there would be enough space between the complex cations to accommodate ODAH<sup>+</sup> cations. On the contrary, the density of [Fe(phen)<sub>3</sub>]<sup>2+</sup> in the hybrid film prepared from the suspension at 50 ppm is 0.92 nm<sup>2</sup> cation<sup>-1</sup>. The complex cations in this film would be closely packed. However, the density of ODAH<sup>+</sup> in this film is so low (1.4 nm<sup>2</sup> cation<sup>-1</sup> at 10 mN m<sup>-1</sup>) that all of the ODAH<sup>+</sup> cations could be in the small empty spaces between the Fe(II) complex cations. Interestingly, the layered structure of the hybrid film was stable because the XRD patterns of the films showed no change for at least 1 year.





**Figure 5.** Relative SH intensities for hybrid films of ODAH<sup>+</sup>, clay platelets, and [Fe(phen)<sub>3</sub>]<sup>2+</sup> prepared from a clay suspension at 50 ppm as a function of the hybrid layer number.

**SHG Measurement of Hybrid Films.** The SHG measurement was carried out for hybrid films prepared from the clay suspension at 50 ppm. The films were SHG-active because Maker fringe patterns were observed. The structure of the Fe(II) complex cation is centrosymmetric. Hence, the noncentrosymmetric structure of the hybrid film would bring about this nonlinear optical property. The relative SH intensities of the films is plotted against the hybrid layer number in Figure 5. The relative SH intensities increase with the increase in the hybrid layer number, although the quadratic relation between the relative SH intensities and the hybrid layer number<sup>1,4</sup> is not clear. The absolute SH intensities for the films were so weak ( $<10^{-5}$  of that of a quartz crystal) that the data contain large experimental errors. A quantitative discussion about the SHG result is difficult. However, the result suggests that the hybrid multilayer should have been fabricated in a noncentrosymmetric fashion.

## Conclusions

A hybrid film of a clay mineral and cationic compounds prepared by a combined method of the Langmuir–Blodgett and self-assembly techniques is expected to possess the following features: (1) its layered structure is stable; (2) any cationic compound can be introduced into the film; (3) the density of the cationic compound in the film is easily controlled; and (4) the structure of the film is noncentrosymmetric.

In this work, hybrid films of ODAH<sup>+</sup>, clay platelets, and [Fe(phen)<sub>3</sub>]<sup>2+</sup> were prepared and were characterized by  $\pi$ -A isotherm, XRD, and SHG measurements and electronic spectroscopy. On the basis of these experimental data, it has been demonstrated that the hybrid films have all of the expected features except for feature 2.

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- (38) A rough estimation of the densities of ODAH<sup>+</sup> in the hybrid films was made by measuring the absorption intensities at the peak of 1920 cm<sup>-1</sup>, which was assigned to the antisymmetric stretching vibration of the CH<sub>2</sub> group in the ODAH<sup>+</sup> cation (see ref 24). The densities of ODAH<sup>+</sup> in the films prepared from the clay suspensions at 10, 25, and 50 ppm were estimated to be 0.66, 0.85, and 1.5 nm<sup>2</sup> cation<sup>-1</sup>, respectively. These estimated values are in agreement with the densities of ODAH<sup>+</sup> in the floating films of the ammonium cation and the clay platelets obtained from their  $\pi$ -A isotherms. This suggests that ODAH<sup>+</sup> in the films would not have been replaced with [Fe(phen)<sub>3</sub>]<sup>2+</sup> when the film surfaces were dipped in the Fe(II) complex salt solution.