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Langmuir−Blodgett Films of a Clay Mineral and Ruthenium(II) Complexes with a Noncentrosymmetric Structure

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Abstract: Mono- and multilayers of amphiphilic $[Ru(phen)_2(dcC12bpy)]^{2+}$ (phen = 1,10-phenanthroline, dcC12bpy = 4,4′-caboxyl-2,2′-bipyridyl didodecyl ester) hybridized with a clay mineral have been prepared by a modified Langmuir−Blodgett method, and their structures and properties have been investigated. Formation of a hybrid monolayer of the Ru(II) complex cations and the clay platelets at an air−clay suspension interface was confirmed by surface pressure−molecular area ($\pi - A$) isotherm measurement and atomic force microscopic (AFM) observation. Multilayers were fabricated by depositing the hybrid monolayers onto glass substrates. The absorbance at 492 nm due to the Ru(II) complex cation in the multilayer increased linearly with the increase in the layer number, indicating layer-by-layer deposition of the hybrid monolayers. Because no increase in the second-harmonic generation (SHG) signal from the multilayers against the layer number was observed, the orientation of the Ru(II) complex cations in the layer would be disturbed. The hydrophilic surface of the transferred hybrid monolayer can be converted to a hydrophobic surface by dipping it in an aqueous solution of octadecylammonium chloride ($ODAH^+Cl^-$). The multilayers modified with $ODAH^+$ showed a quadratic relation between the SHG intensity and the layer number. This means that the Ru(II) complex cations in the multilayer are successfully oriented in a noncentrosymmetric way by the conversion of the surface property. Both a racemic mixture and an enantiomer of the Ru(II) complex cations were employed to examine the chiral effect on the film properties. The chiral contribution to the SHG signal was enhanced in the multilayer modified with $ODAH^+$.

Introduction

Smectite clays have been of scientific and technological interest because of their use as ion-exchange materials, catalysts, modified electrodes, and inorganic/organic composite materials.[1−6] One of the outstanding properties of the clays is the simultaneous incorporation of polar or ionic molecules into the interlamellar spaces (intercalation).[1,7−11] The property of intercalation makes it easy to prepare the composite materials. If the orientation of the incorporated molecules can be controlled, the clay composite materials would be applicable to devices for current rectifying, nonlinear optics, and one-way energy transfer. However, the intercalated molecules in the interlamellar spaces of the smectite clay naturally tend to cancel any orientational anisotropy since both sides of a layer in a smectite clay are identical. Polar molecules, for example, orient in opposite ways at adjacent sites to cancel out their individual dipole moments.[7,8]

The Langmuir−Blodgett (LB) method is one of the most useful techniques to prepare a multilayered film.[12−17] Floating monolayers at an air−water interface are deposited in a layer-

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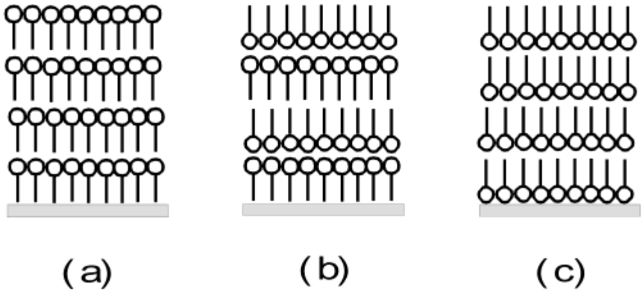


Figure 1. Deposition types of LB multilayers: (a) X-type, (b) Y-type, and (c) Z-type.

by-layer way to make a multilayer. It is easy to control a sequence of the layers in the multilayer at the molecular level, but it is difficult to orient the molecules in one direction in the film. Most LB films possess a Y-type structure (Figure 1b).[15−17] Even though a floating monolayer is deposited by horizontal dipping, it is likely that some molecules in the layer overturn to cancel out their dipole moments.[16,17]

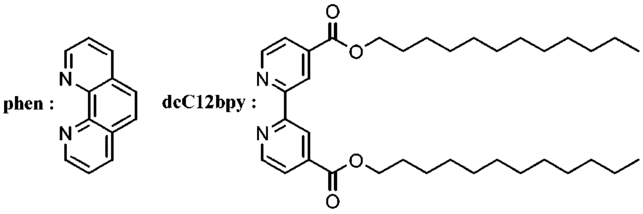
When amphiphilic cations are spread onto an aqueous suspension of a clay mineral in a LB trough, negatively charged clay platelets[1,7,8] in the suspension are adsorbed electrostatically onto a bottom of a floating monolayer of the cations at an air−suspension interface.[18−24] The hybrid monolayers of the clay platelets and the amphiphilic cations thus formed can be deposited on a solid surface by horizontal dipping.[22−24]

In this work, hybrid multilayers of natural saponite and amphiphilic ruthenium(II) complex cations have been prepared by two methods. In one method (Method A, Figure 2a), the hybrid monolayers of the clay platelets and the Ru(II) complex cations are deposited by horizontal dipping one after another. In the other method (Method B, Figure 2b), a hydrophilic surface of the hybrid monolayer transferred from the air−suspension interface is dipped in an aqueous solution of an alkylammonium salt to modify the surface with the alkylammonium cations to be hydrophobic. Metal cations such as Na^+ are left on the surface of the transferred monolayer, and those cations are replaced with the ammonium cations by a cation-exchange reaction when the surface of the film is dipped in the solution of the ammonium salt. Thereafter another hybrid monolayer is deposited on the hydrophobic surface of the film. It was expected that, in the multilayered film prepared by Method B, one side of the amphiphilic complex cation layer should be in contact with a hydrophilic surface of a clay layer and the other side should be in contact with a hydrophobic surface of an alkylammonium cation layer and that this asymmetric structure would keep the orientation of the complex cations in the film. Properties of these films have been characterized by surface pressure−molecular area ($\pi - A$) isotherm measurement, atomic force microscopy (AFM), electronic spectroscopy, X-ray diffraction (XRD) measurement, and second-harmonic generation (SHG) measurement.

Both a racemic mixture and an enantiomer of the ruthenium(II) complex cations were employed in this work. The difference in the film properties caused by the chirality was also examined.

Experimental Section

Materials. An amphiphilic ruthenium(II) complex salt with two long alkyl chains, $[Ru(phen)_2(dcC12bpy)](ClO_4)_2$ (phen = 1,10-phenanthroline, dcC12bpy = 4,4′-caboxyl-2,2′-bipyridyl didodecyl ester), was synthesized and optically resolved according to previous reports.[18,20,25] The Ru(II) complex salt was dissolved in chloroform to prepare a solution at 1.9×10^{-4} mol dm^{-3}.



Saponite from the Source Clay Minerals Repository of the Clay Minerals Society was used as a clay mineral. The size fraction of the clay platelets is <0.05 μm. The clay mineral has a cation exchange capacity (CEC) of 738 μequiv g^{-1}.[26,27] The thickness of a clay platelet estimated from its crystal structure is 0.96 nm.[1,26] A stock suspension of the clay was prepared by dispersing 1 g of the clay in 1 dm^3 of pure water. It was diluted to a given concentration with pure water just before use as a subphase.

A straight-chain fatty ammonium salt of octadecylammonium chloride ($C_{18}H_{37}NH_3^+Cl^-$, $ODAH^+Cl^-$) was prepared by a reaction of the corresponding amine and hydrochloric acid. The ammonium salt was recrystallized in ethanol twice. The concentration of an aqueous $ODAH^+Cl^-$ solution was 1.0×10^{-5} mol dm^{-3}.

Film Preparation. The solution of the Ru(II) complex salt was spread on a subphase of the clay suspension in a LB trough (KSV minitrough) at room temperature. After 30 min, the floating film was compressed at a rate of 0.02 nm^2 molecule^{-1} min^{-1}. The film was transferred by horizontal dipping onto a hydrophobic surface of a glass plate modified with phenyltrimethoxysilane. A surface of the transferred film was hydrophilic. It was rinsed with pure water several times and dried. A multilayer was fabricated by depositing the floating films at a surface pressure of 20 mN m^{-1} repeatedly in Method A. After every deposition, in Method B, the surface of the film was dipped in the aqueous solution of $ODAH^+Cl^-$ to change the surface property from being hydrophilic to being hydrophobic. During this procedure, metal cations (Na^+) on the clay surface were exchanged for the alkylammonium cations. The surface was rinsed well with pure water and dried, and then another floating film was deposited onto the surface.

Instruments. Atomic force microscopic (AFM) images of the films were obtained with a Topometrix Discoverer System TMX 2010 by using a commercially available Si_3N_4 cantilever with a force constant of 0.04 N m^{-1}. Electronic spectra of the films were recorded on a Perkin-Elmer Lambda 12 UV/VIS spectrometer. X-ray diffraction

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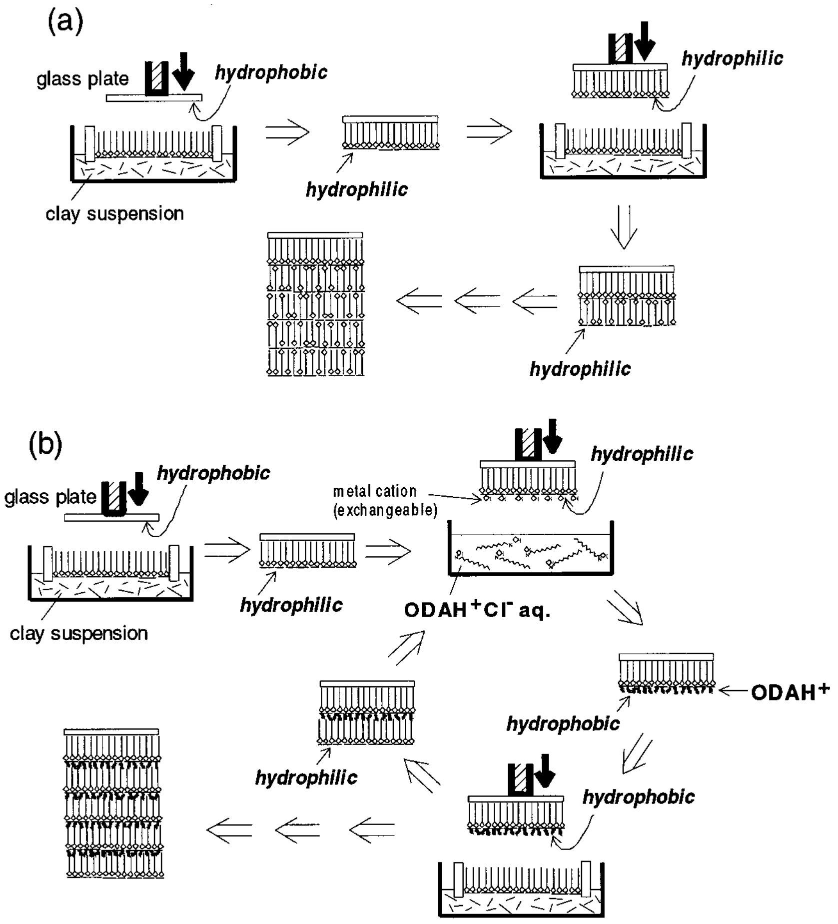

Figure 2. Preparation methods of hybrid LB multilayers of amphiphilic ruthenium(II) complex cations and clay platelets: (a) Method A and (b) Method B.

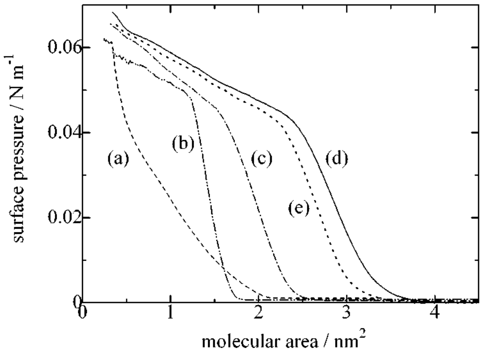

Figure 3. $\pi-A$ isotherm curves for floating monolayers of Λ-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ on (a) pure water and on clay suspensions at (b) 10, (c) 50, and (d) 100 ppm, and (e) a $\pi-A$ isotherm curve for a floating monolayer of rac-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ on a clay suspension at 100 ppm.

(XRD) patterns were measured with a Rigaku RAD-1A diffractometer using Ni-filtered Cu Kα radiation. Second-harmonic generation (SHG) measurement was carried out using a Q-switched Nd:YAG laser (10 ns, 50 Hz, 1064 nm). The fundamental beam was incident on the film at 90°. The SHG signals from the samples were detected in transmission.

Results and Discussion

$\pi-A$ Isotherms of Floating Films on Clay Suspensions. The $\pi-A$ isotherms for the films of Λ-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ spread on pure water and on the clay suspensions at 10, 50, and 100 ppm are shown in Figure 3a−d. The isotherm on pure water gives a lift-off area at 2.1 nm^2 molecule^{-1}, and then the surface pressure rises gradually up to 62 mN m^{-1}. At this point, the floating monolayer of the Ru(II) complex cation collapsed. The lift-off areas for the floating films on the clay suspensions at 10, 50, and 100 ppm are 1.7, 2.5, and 3.7 nm^2 molecule^{-1}, respectively. The isotherms of the films on the suspensions approach that on pure water with the decrease in the clay concentration.[24,28,30] This dependence of the isotherm on the clay concentration suggests formation of a hybrid monolayer of Λ-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ and the clay at the air−suspension interface. The lift-off area for the film on the suspension at 10 ppm (1.7 nm^2 molecule^{-1}) is smaller than that on pure water (2.1 nm^2 molecule^{-1}). The positive charge of the Ru(II) complex cations should be neutralized by the negative charge of the clay platelets when the hybrid monolayer is formed. The neutralization of the positive charge would bring about the contraction of the film area.[15]

The $\pi-A$ isotherm of rac-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ on the clay suspension at 100 ppm (Figure 3e) shows a little shift to the smaller area side from that of Λ-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ on the suspension at 100 ppm (Figure 3d). However, no significant difference was observed between the isotherm for the film of Λ-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ and that of rac-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ on the clay suspension at a lower

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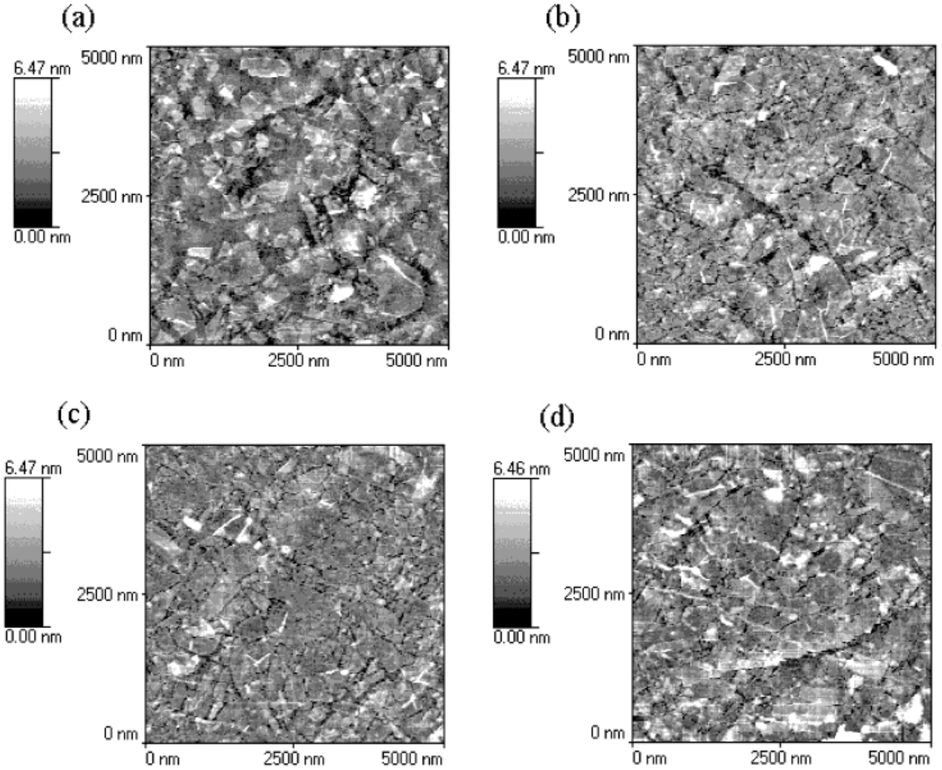

Figure 4. AFM images for hybrid monolayers of Λ-$[Ru(phen)_2(dcC12bpy)]^{2+}$ and clay particles transferred onto glass plates at the surface pressure of (a) 0 (before compression), (b) 5, (c) 20, and (d) 55 mN m^{-1}. The clay concentration in the suspension was 10 ppm.

concentration (50 or 10 ppm) or on pure water.[19,25] The difference would probably be within the experimental error.

AFM Observation of Hybrid Monolayers on Glass Plates. The floating hybrid monolayers of the Λ-Ru(II) complex cations and the clay platelets formed on the surface of the 10 ppm suspension were transferred onto glass plates at 0 (before compression), 5, 20, and 55 mN m^{-1}, and their surface structures were observed by AFM (Figure 4). The clay platelets are observed in the images, which indicates the formation of the hybrid monolayer at the air−suspension interface. Before the compression (0 mN m^{-1}, Figure 4a), there can be seen the isolated clay platelets and the empty space between them. Just after the onset of the surface pressure (5 mN m^{-1}, Figure 4b), the clay platelets are in contact with each other with small vacant spaces between them. These images reveal that the hybridization of the Ru(II) complex cations and the clay platelets occurred before the compression and that the floating platelets were gathered as the film was compressed until they contacted each other at the onset of the surface pressure. On further compression (20 mN m^{-1}, Figure 4c), the platelets are packed closely, and there is little vacant space between them. After the collapse of the film (55 mN m^{-1}, Figure 4d), the surface of the hybrid monolayer is disturbed, and some clay platelets are overlapped.[23,24]

Similar results were obtained for the hybrid monolayers transferred from the surface of the clay suspensions at 50 and 100 ppm, and no remarkable difference could be detected between the films of the Λ-complex cation and those of the racemic one.

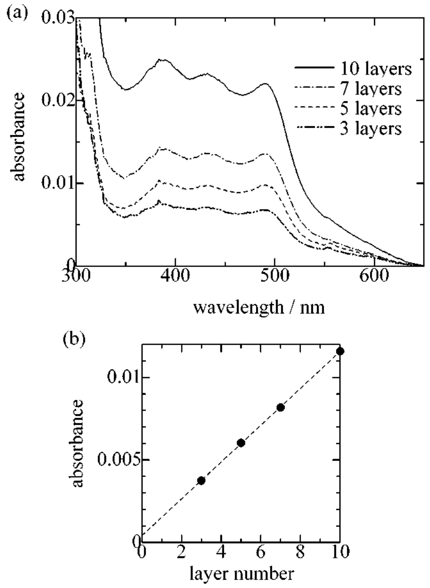

Figure 5. (a) Electronic spectra of hybrid multilayers of Λ-$[Ru(phen)_2(dcC12bpy)]^{2+}$ and a clay prepared by Method B. (b) Relation between absorbance at 492 nm and layer number.

Electronic Spectra of Hybrid Multilayers. The multilayers of the Ru(II) complex cations and the clay platelets were prepared by depositing the hybrid monolayers floating on the surface of a 100 ppm suspension at the surface pressure of 20 mN m^{-1} (Figure 2). According to the AFM results, the whole of the surface of the hybrid monolayer was mostly covered with the clay platelets at 20 mN m^{-1}.

Electronic spectra of the hybrid multilayers of Λ-$[Ru(phen)_2(dcC12bpy)]^{2+}$ and the clay prepared by Method B are shown in Figure 5a. Three absorption maxima at 387, 432, and 492 nm are observed in each spectrum. These absorption bands are assigned to metal-to-ligand charge transfer bands of the Ru(II) complex cations[25,31] in the film. The absorption by these bands increases with the increase in the layer number. The absorbance

Table 1. Values of Area per Cation in a Layer, Peak Positions of 2θ in XRD Patterns, and Layer Distances for Hybrid Multilayers of Ruthenium(II) Complex Cations and Clay Platelets

	method	area per cation[a] / nm²	XRD peak position (2θ)/deg	XRD layer distance /nm
Λ-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$	A	3.8	2.5	3.5
	B	2.5	2.2	4.0
rac-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$	A	2.3	2.6	3.4
	B	2.0	2.3	3.8

[a] Estimated from electronic spectral data.

at 492 nm (the background in the spectrum is subtracted) is plotted as a function of the layer number in Figure 5b. The absorbance increases linearly against the layer number, indicating that the hybrid monolayers were deposited in a layer-by-layer way in the multilayers.

Similar spectral profiles were observed for the films of Λ- and rac-complex cations prepared by both Methods A and B, and linear relations between the absorbance and the layer number were given. The layer-by-layer deposition of the hybrid monolayers was confirmed for these multilayers.

On the assumption that an extinction coefficient (ϵ) of [Ru(phen)$_2$(dcC12bpy)]$^{2+}$ in the multilayer is the same as that in the aqueous solution ($\epsilon = 16\,500$),[25] area per complex cation in the layer is estimated from the slope of the line in Figure 5b. The calculated value of area per complex cation is 2.5 nm^2 cation^{-1} for the film of Λ-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ prepared by Method B. The calculated values of area per complex cation for the films prepared in this work are listed in Table 1. Comparing the values between the film of the Λ-complex cation and that of the rac-complex cation, the former value is larger than the latter one in each case of Methods A and B. This is consistent with the previous study on racemic adsorption of [Ru(phen)$_3$]$^{2+}$ by a clay mineral.[32−34] The value of area per cation for the multilayer prepared by Method A is larger than that by Method B for either case of Λ- or rac-complex cation. It is difficult to explain the difference, because the floating hybrid monolayers of the Ru(II) complex cation and the clay were identical in both preparation methods. One possibility is that the extinction coefficients of [Ru(phen)$_2$(dcC12bpy)]$^{2+}$ in the films prepared by Methods A and B might be different because of the different orientation of the Ru(II) complex cations in the films.

XRD Patterns of Hybrid Multilayers. XRD measurement was carried out for the 10-layered hybrid films of the Λ- and rac-Ru(II) complex cations prepared by Methods A and B. The XRD patterns of the multilayers of Λ-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ by both methods are exhibited in Figure 6, together with a XRD pattern of a 10-layered LB film of Λ-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ prepared by depositing monolayers of the Ru(II) complex cation floating on pure water (without the clay). The multilayer without the clay shows no diffraction peak in its XRD pattern (Figure 6a). This means that the layered structure of the film is disturbed. The pattern for the hybrid film by Method A (Figure 6b) gives one peak at $2\theta = 2.5°$. In the XRD pattern for the hybrid film by Method B, there are two peaks at $2\theta = 2.2°$ and 5.2°. Since the second diffraction peak is observable, the structure of the multilayer by Method B would be more definite than that by Method A.

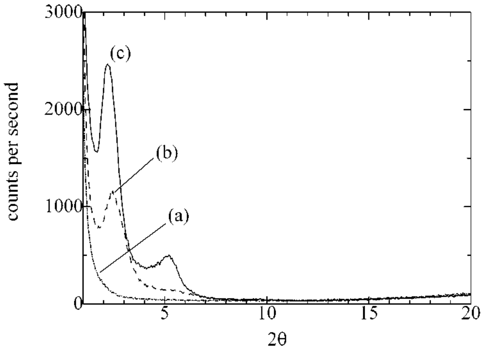

Figure 6. XRD patterns of 10-layered LB films: (a) a multilayer of Λ-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$, (b) a hybrid multilayer of Λ-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ and a clay prepared by Method A, and (c) a hybrid multilayer of Λ-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ and a clay prepared by Method B.

Similar results were obtained from XRD data for multilayers of rac-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ prepared by Methods A and B.

If the multilayers have the layered structure, their layer distances can be calculated from the positions of the first diffraction peaks, and those values are listed in Table 1 together with the first peak positions. The layer distances of the multilayers of Λ-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ prepared by Methods A and B are identical with those of rac-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ by the corresponding methods within the experimental error, respectively. Taking the thickness of a clay platelet (0.96 nm)[1,26] into consideration, the thickness of the [Ru(phen)$_2$(dcC12bpy)]$^{2+}$ layer in the multilayers by Method A is 2.4−2.5 nm. This thickness of the complex cation layer is in good agreement with the length of the Ru(II) complex cation (∼2.5 nm) estimated from its molecular model. This means that the alkyl chains of the complex cations are perpendicular to the clay layer. The multilayers by Method B are composed of the [Ru(phen)$_2$(dcC12bpy)]$^{2+}$ layer, the clay layer, and the ODAH$^+$ layer. If the alkyl chains of the complex cations are perpendicular to the layer, that is, the thickness of [Ru(phen)$_2$(dcC12bpy)]$^{2+}$ layer was ∼2.5 nm, the thickness of the ODAH$^+$ layer is estimated to be 0.3−0.5 nm. If it is true, the alkyl chains of ODAH$^+$ would lie down on the surface of the clay layer.

SHG Signals from Hybrid Multilayers. To get information on the orientation of [Ru(phen)$_2$(dcC12bpy)]$^{2+}$ in the hybrid multilayers, SHG measurement was performed.[16,17,35]

The SHG intensities for the hybrid multilayers of Λ- and rac-[Ru(phen)$_2$(dcC12bpy)]$^{2+}$ prepared by Method A are shown in Figure 7a and b, respectively. No increase in SHG signal is observed against the layer number for both series of the hybrid multilayers. This means that the Ru(II) complex cations are not oriented in a noncentrosymmetric fashion in these multilayers (Figure 2a). The orientation of the complex cations would be disturbed during the deposition when the hydrophobic part of the Ru(II) complex cation in the floating monolayer comes in contact with the hydrophilic surface of the multilayered film

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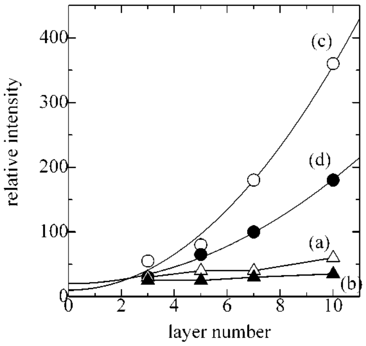

Figure 7. SHG intensities for hybrid multilayers of $[Ru(phen)_2(dcC12bpy)]^{2+}$ and a clay as a function of layer number: (a) multilayers of Λ-$[Ru(phen)_2(dcC12bpy)]^{2+}$ and a clay prepared by Method A, (b) multilayers of rac-$[Ru(phen)_2(dcC12bpy)]^{2+}$ and a clay prepared by Method A, (c) multilayers of Λ-$[Ru(phen)_2(dcC12bpy)]^{2+}$ and a clay prepared by Method B, and (d) multilayers of rac-$[Ru(phen)_2(dcC12bpy)]^{2+}$ and a clay prepared by Method B.

on the substrate. Since the molecular structure of the Λ- Ru(II) complex cation is noncentrosymmetric, the multilayer composed of the enantiomer is SHG active even if the molecular orientation is disturbed. However, it would be difficult to discuss the chiral contribution to the SHG property, because the difference in the intensity between the films of the enantiomer and those of the racemic mixture is as low as the experimental error.

However, the hybrid multilayers prepared by Method B exhibit SHG intensities as shown in Figure 7c and d. The SHG intensities of the multilayers increase in a quadratic way with the increase in the layer number for the multilayers of the Λ- (Figure 7c) and rac-$[Ru(phen)_2(dcC12bpy)]^{2+}$ (Figure 7d). These SHG data imply that the complex cations are arranged in a noncentrosymmetric way; that is, they are oriented in one direction.[16,17] As shown in Figure 2b, one side of the Ru(II) complex cation layer is in contact with the hydrophobic surface of the $ODAH^+$ layer and the other side is in contact with the hydrophilic surface of the clay layer. The orientation of the amphiphilic Ru(II) complex cations would be stabilized between the hydrophobic $ODAH^+$ layer and the hydrophilic clay layer. The hydrophobic alkyl chains of the Ru(II) complex cation would be directed to the $ODAH^+$ layer, and the hydrophilic headgroup of the complex cation (Ru^{2+} and phenanthroline ligands) would face the clay layer.

It should be pointed out that there is a clear difference in the SHG behavior between the multilayers of Λ-$[Ru(phen)_2(dcC12bpy)]^{2+}$ (Figure 7c) and rac-$[Ru(phen)_2(dcC12bpy)]^{2+}$ (Figure 7d). The SHG intensities of the former series increase more steeply than that for the latter series. The difference is caused by the chiral effect. The chiral effect is enhanced in the multilayers prepared by Method B in comparison with that in the multilayers prepared by Method A (Figure 7a and b). The chiral contribution to SHG comes not only from the noncentrosymmetric molecular structure but also from supramolecular organization in a system.[36] Distribution of Λ- or Δ-$[Ru(phen)_3]^{2+}$ adsorbed on a clay mineral is different from that of rac-$[Ru(phen)_3]^{2+}$.[32−34,37,38] The supramolecular distribution of Λ-$[Ru(phen)_2(dcC12bpy)]^{2+}$ on the clay layer in the hybrid film prepared by Method B might cause the enhancement.

Conclusion

The hybrid mono- and multilayers of $[Ru(phen)_2(dcC12bpy)]^{2+}$ and the clay platelets have been prepared by the modified LB technique and characterized by $\pi-A$ measurement, AFM observation, electronic spectroscopy, XRD measurement, and SHG measurement. The two methods, Methods A and B (Figure 2), were taken for the preparation of the hybrid multilayers. It is revealed that the multilayer by Method A is fabricated by layer-by-layer deposition of the hybrid monolayers. However, the orientation of the Ru(II) complex cations in the layer is disturbed.

The multilayer prepared by Method B is built up in a layer-by-layer way, and its structure is more definite than that prepared by Method A. One of the most important properties of the multilayer prepared by Method B is that the Ru(II) complex cations in the layer are oriented in one direction. Furthermore, the chiral contribution to the SHG intensity is enhanced in the multilayers prepared by Method B in comparison with that in the film prepared by Method A.

In this work, the noncentrosymmetric orientation of molecules in the LB films hybridized with the clay has been realized simply by the dipping of the film surface in the solution of the alkylammonium salt to convert the surface property to be hydrophobic. This technique has opened a novel way for preparing ultrathin films toward the development of devices requiring noncentrosymmetric properties.

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