Hybrid Films of Metal Complexes and a Clay Mineral Prepared by the Langmuir-Blodgett Method: Effect of the Alkyl-Chain Length of Amphiphilic Ruthenium (II) Complex

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Organized organic-inorganic ultrathin films have been fabricated with a clay nanolayer and amphiphilic ruthenium(II) complex monolayers using the conventional Langmuir-Blodgett (LB) technique. The following three types of Ru (II) complex were synthesized: 1 $[Ru(bpy)_2(4,4'dC11bpy)](ClO_4)_2$ (4,4'dC11bpy = 4,4'-diundecyl-2,2' -bipyridine); 2 $[Ru(bpy)_2(5,5'dC11bpy)](ClO_4)_2$ (5,5'dC11bpy = 5,5'-diundecyl-2,2' -bipyridine); 3 $[Ru(bpy)_2(4,4'dC18bpy)]$ (4.4'dC18bpy $(ClO_4)_2$ 4,4'-dioctadecyl-2,2'-bipyridine). These complexes possess two alkyl chains at 4,4'- or 5,5'- positions of the 2,2'-bipyridine ligand. A chloroform solution of a Ru(II) complex was spread onto a subphase containing ether exfoliated clay suspension in a LB trough at 20 °C. Brewster angle microscopic (BAM) observation showed that the Ru(II) complex molecules formed a self-assembled monolayer on the water surface and that clay particles were adsorbed by the monolayer from the aqueous subphase. The composite film that the Ru(II) complex and clay particles thus formed was transferred onto a hydrophilic substrate by the vertical dipping method. The surface structure of the deposited film was studied using UV-visible spectroscopy, and atomic force microscopy (AFM). Key words: Langmuir-Blodgett films, Clay, ruthenium complex, Brewster angle microscope

1. INTRODUCTION

The fabrication of organic/inorganic nanostructured materials is an important target of modern materials research. The research objective is to develop functional materials such as sensors, electrode-modifiers, nonlinear optical pyroelectric materials.^{1,2} devices and Of particular interest is the preparation of highly ordered organic/inorganic ultrathin films, in which a small organic molecule or macromolecule is sandwiched between inorganic sheets. An inorganic layer is incorporated to reinforce the lamella structure of the film.

One method of preparing such a hybrid film is to chemically bond an inorganic sheet to an organic anchor, which is self-assembled on a solid surface.³ Multilayer formation is accomplished by bridging neighboring layers with a bifunctional agent. Another method is to deposit a polyelectrolyte and an inorganic layer alternatively onto a solid substrate by immersing the substrate into these respective solutions.⁴ A layer-by-layer structure is maintained by electrostatic intercalation between the oppositely charged layers.

Although the classical Langmuir-Blodgett

(LB) technique is an effective approach for the fabrication of multilayer molecular assemblies, the method unfortunately suffers from critical drawbacks, such as mechanical weakness and sensitivity to contamination. Recently the LB method was applied to the preparation of ultra thin films of a clay mineral and an amphiphilic metal complex.⁵ According to the method, a monolayer of an amphiphilic Ru(II) complex was formed on an aqueous dispersion of clay. The monolayer was used as the template for adsorption of the clay particles.

In the traditional concept, the polar or charged hydrophilic head of an amphiphilic molecule interacts attractively with water, while the hydrophobic aliphatic chains prevent the molecules from being dissolved into the water, thereby efficiently reducing the interfacial free energy. In this study, three types of amphiphilic tris-bipyridyl ruthenium(II) complexes were synthesized, as shown in Figure 1. Among these complexes, compound 2 is a nontraditional amphiphile, with branch di-alkyl chains horizontally on the side of the head group.⁶

The purpose of this study is to evaluate the efficacy of this method by varying the length and

orientation of alkyl chains attached to a ligand on the hybrid film structures. Ruthenium(II) polypyridyl complexes are known to be efficient converters of photon energy. Such a new hybrid film could be an important step towards the creation of organized layered compounds for controlling the deposition sequence and orientation of intercalated molecules.



Figure 1 Structures of the Ru(II) complexes investigated.

2. EXPERIMENTAL

The procedure for the synthesis of the amphiphilic Ru(II) complexes 1, 2 and 3 has been previously reported.⁶ Perchlorate salts of Ru(II) complexes were obtained by adding excess NaClO₄. The crystals were finally purified using a HPLC column (Capcel Pack, Shiseido Co.,Ltd.), with a water-methanol solution as an eluent.

The clay mineral used was saponite, from the Source Clay Minerals Repository of the Clay Minerals Society. The size fraction was < 0.05 μ m. It has a cation exchange capacity (CEC) of 73.8 meq/100g. The expected layer thickness was calculated as 0.96 nm from the crystal structure. A stock suspension of the clay was prepared by dispersing 1 g of saponite clay in 1 L of pure water. This was then diluted further with pure water to a given concentration just prior to use. Surface pressure - area (π -A) curves were measured with a Langmuir trough (Minitrough, KSV Instruments Ltd). A solution of a Ru(II) complex salt was spread onto an aqueous subphase in the Langmuir trough. After 30 minutes, the floating film was compressed at a rate of 10 cm² min⁻¹.

Brewster angle microscopy (BAM) measurements were performed with a BAM instrument (BM-1000, U.S.I,System Co.,Ltd). The monolayer was then transferred to hydrophilic plates made of quartz (for UV-visible measurements), and silicon wafer (for AFM images) at a surface pressure of 15 mN m^{-1} at 20 °C.

3. RESULTS and DISCUSSION

Figure 2 summarizes the results of the π -A isotherms, for a chloroform solution of a racemic mixture spread on a 0.01 M NaClO₄ aqueous solution, and on the clay suspensions at 10, 50, and 100 mg L⁻¹ at 20 °C.

The π -A isotherms for the films of 1 $[Ru(bpy)_2(4,4'dC11bpy)](ClO_4)_2$ spread on a 0.01 M NaClO₄ aqueous solution and on the clay suspensions at 10, 50, and 100 mg L⁻¹, are shown in Figure 2(A). The isotherm for a 0.01 M NaClO₄ aqueous solution indicates a lift-off area



Figure 2 π -A isotherms for floating monolayers of Ru(II) complexes spread on a NaClO₄ aqueous solution and on clay suspensions at 10, 50, and 100 mg L⁻¹, at 20 °C: (**A**) [Ru(bpy)₂(4,4'dC11bpy)](ClO₄)₂, (**B**) [Ru(bpy)₂(5,5'dC11bpy)](ClO₄)₂, and (**C**) [Ru(bpy)₂(4,4'dC18bpy)](ClO₄)₂.

at 130 Å² molecule⁻¹, and then a gradual surface pressure rise up to 38 mN m⁻¹. At this point, the floating monolayer of the Ru(II) complex cation collapsed. The lift-off areas for floating films on the clay suspensions at 10, 50, and 100 mg L⁻¹ were 80, 170, and 270 Å² molecule⁻¹, respectively. The π -A isotherm curve of the monolayer on the suspension at 100 mg L⁻¹ lifts off at approximately 270 Å² molecule⁻¹. Although the curve rises gradually with the decrease in the molecular area, the data are scattered and show no clear collapse point. It is probable that the clay mineral, natural saponite, used in this work would not be exfoliated into single clay platelets at this concentration and this may be the main reason for the lack of the reproducibility of the π -A isotherm.

Figure 2(B) shows the isotherms for 2 [Ru(bpy)₂(5,5'dC11bpy)](ClO₄)₂, which possesses two undecyl groups at 5,5'-positions in a bpy ligand. When the subphase is pure water (dotted line 4) or clay-pure water suspension (not shown), the Langmuir monolayer formed spontaneously dissolved into the subphase. On the other hand, substantial surface pressure appears on the clay suspension that includes the NaClO₄ solution. For the 1.0×10⁻³ M NaClO₄ aqueous solution, a lift-off area at 165 Å² molecule⁻¹ was observed. The isotherm increased steeply until a plateau above 20 mN m⁻¹ was reached, at equilibrium with the spreading pressure. The plateau continued through to the molecular area as low as 50 Å² molecule⁻¹. The lift-off areas for the floating films on the clay suspensions at 10 and 50mg L^{-1} were 175 and 195 Å² molecule⁻¹, respectively. Figure 2(C) also shows the isotherms for $[Ru(bpy)_2(4,4'dC18bpy)]$ (ClO₄)₂, which possesses two octadecyl groups at 4,4'-positions in a bpy ligand. The lift-off areas for the floating films on the clay suspensions at 0, 10, 50, and 100 mg L⁻¹ were 80, 90, 130 and 170 Å² molecule⁻¹, respectively.

The isotherms of the films on the clay suspensions approach that on the NaClO₄ solution with a decrease in the clay concentration, except for the isotherm of compound 1 on the 10 mg L⁻¹saponite suspension. All of the complexes display essentially similar clay concentration-dependent behavior. This dependence of the isotherm on the clay concentration suggests the formation of a hybrid monolayer of the Ru(II) complex and the clay at the air-suspension interface. The lift-off area for compound 1 on the 10 mg L^{-1} (80 Å² molecule⁻¹) suspension is smaller than that on the 0.01 M NaClO₄ aqueous solution (130 Å² molecule⁻¹). The positive charge of the Ru(II) complex should be neutralized by the negative charge of the clay platelets, when a hybrid monolayer is formed. A neutralization of the positive charge would result in a contraction of the film area.

Interaction of clay with a floating molecule was studied in situ using a Brewster angle microscope (BAM). When compound 2 [Ru(bpy)₂(5,5'dC11bpy)](ClO₄) was spread on an aqueous 0.01 M NaClO₄ solution, a bright region, with a size of a few thousand micrometers, was observed floating on the water surface. This implied that the complex had formed a monolayer island even at zero surface pressure. The whole surface was uniformly bright at 15 mN m⁻ indicating that the surface was completely covered with the monolayer (Figure 3B). When the surface pressure exceeded 20 mN m⁻¹, a straight line with bright intensity appeared that extended over a few thousand micrometers (Figure 3C). This phenomenon indicated the collapse of the resulting in monolayer a multilayer or microcrystalline formation. When the same metal complex was spread on a NaClO₄-clay suspension (10 mg L^{-1} saponite in a 1.0×10⁻³ M NaClO₄ solution), bright spots with radii of 10 - 100 µm were observed at zero surface pressure (Figure 3D). These spots were undoubtedly due to clay particles adsorbed to the monolayer islands of the metal The density of these spots increased complex. upon compression of the surface, until the whole surface was covered with spots at 15 mN m⁻¹ (Figure 3E). When the surface pressure exceeded 23 mN m^{-1} , zigzagged bright lines appeared, indicating the collapse of the film (Figure 3F).



Figure 3 (A) A surface of NaClO₄ solution, (B) a surface compressed to 15 mN m⁻¹ after a chloroform solution of **2** [Ru(bpy)₂(5,5'dC11bpy)](ClO₄)₂ was spread onto an aqueous NaClO₄ solution, (C) the same surface as (B) compressed to 20 mN m⁻¹, (D) a surface when a chloroform solution of **2** [Ru(bpy)₂(5,5'dC11bpy)](ClO₄)₂ was spread onto a saponite suspension (10mg L⁻¹ in a 0.001 M NaClO₄ solution), (E) the same surface as (D) compressed to 15 mN m⁻¹.

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Figure 4 Electronic spectra of hybrid multilayers of 2 $[Ru(bpy)_2(5,5'dC11bpy)]$ (ClO₄)₂ and clay prepared by the vertical lifting method. (inset) Relation between absorbance at 452 nm and the number of layers.

Monolayers could be efficiently deposited onto a solid substrate such as a hydrophilic quartz plate and silicon wafer. Deposition took place only in the upward direction (Z-type deposition). Multilayers of the Ru(II) complex and the clay platelets were prepared by depositing the hybrid monolayers, floating on the surface of a 10 mg L^{-1} suspension at the surface pressure of 15 mN m⁻¹. onto a quartz substrate. Typical UV-vis spectra for the hybrid multilayers of compound 2 and the clay are shown in Figure 4. Three absorption maxima at 256, 290, and 452 nm are observed in each spectrum. The 452 nm absorption band is assigned to the metal-to-ligand charge transfer bands of the Ru(II) complex. Absorption by these bands increases with an increase in the number of layers. Absorbance at 452 nm is plotted as a function of the number of layers in Figure 4(inset). The absorbance increases linearly against the layer number, indicating that the hybrid monolayers were deposited successively, layer by layer, to form the multilayer.

floating hybrid monolayers The of compound 2 and the clay platelets, formed on the surface of the 10 mg L^{-1} clay suspension, were transferred onto a silicon wafer at 15 mN m⁻¹, and their surface structures were observed by AFM (Figure 5A). The clay platelets were observed in the AFM images, indicating the formation of a hybrid monolayer at the air-suspension interface, similar to the traditional molecules (compound 1 and **3**). The substrate was covered with planar sheets with length and thickness estimated to be 0.5-1.0 µm and approximately 2.5nm. respectively (Figure 5B). The thickness of a sheet was close to that of 2-3 clay layers. Isolated clay platelets and the vacant spaces between them were observed. On further compression (25 mN m⁻¹), the platelets were packed closely, and there was minimal vacant space between the platelets (not shown).



Figure 5 (A) The 5.0 μ m × 5.0 μ m AFM image for a hybrid monolayer of 2 [Ru(bpy)₂ (5,5'dC11bpy)](ClO₄)₂ and clay particles transferred onto silicon wafer at a surface pressure of 10 mN m⁻¹. The clay concentration in the suspension was 10 mg L⁻¹. (B) The cross section profile was determined along the line in image.

4. CONCLUSION

The effects of the length and orientation of alkyl chains attached to a ligand on the hybrid film structures have been investigated. As a result, ultrathin films were fabricated by fixing a rigid clay sheet to all amphiphilic ruthenium monolayers. Non-traditional amphiphilic molecules, with horizontal side alkyl-chains to a hydrophilic head, of 2 [Ru(bpy)₂(5,5'dC11bpy)](ClO₄)₂ could also form a stable Langmuir monolayer on the clay suspension, if an excess of ClO₄ ions was present in the subphase. Layer hybridization is facilitated by the electrostatic anchoring of the cationic head group of a metal complex onto an anionic sheet of clay. The method described in this work can be extended to other types of amphiphilic molecules in order to produce new lamella organized materials. The appropriate design of amphiphilic molecules and clays may allow the construction of LB films particular with optical and electrochemical properties.

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