A Clay-Metal Complex Ultrathin Film as Prepared by the Langmuir-Blodgett Technique

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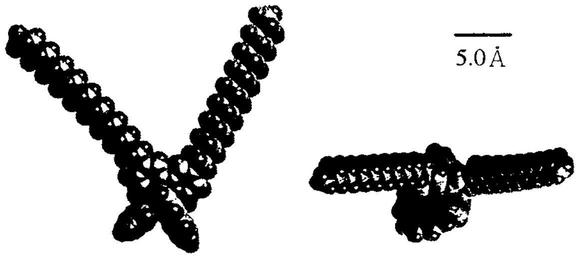
A clay-metal complex hybrid film with the thickness of 5.0 ± 1.0 nm was prepared by the Langmuir-Blodgett technique. According to the method, a hectorite clay dispersed in an aqueous subphase was adsorbed by a cationic monolayer of amphiphilic Ru(II) complex. The surface structure of a film deposited onto a hydrophilic glass plate was studied with an atomic force microscope (AFM).

Preparation of an organic/inorganic nanostructured film has been currently studied with a purpose of developing functional materials such as sensors, nonlinear optical devices and pyroelectric materials.[1-4] A film is prepared either by attaching an inorganic layer onto a self-assembled organic anchor or by immersing alternatively a solid substrate into a polyelectrolyte solution and a suspension of inorganic layer compound.[5,6]

In this communication, we report an attempt to form a clay monolayer at an air-water interface by the Langmuir-Blodgett (LB) method. The method is an extension of our previous works on the LB films of inorganic layer compounds and amphiphilic metal complexes.[7-9] In the previous method, a clay was ion-exchanged with alkyl ammonium and spread onto a water surface as a chloroform suspension. Here we show that a hybrid film can be built by fixing a single clay layer in a subhase on a metal complex monolayer.

An amphiphilic Ru(II) complex, $[Ru(phen)_2(dC18bpy)]^{2+}$ (phen = 1,10-phenanthroline, dC18bpy = 4,4'-dioctadecyl-2,2'-bipyridyl) (Figure.1), was synthesized by reacting $[Ru(phen)_2Cl_2]$ with dC18bpy in ethanol. It was resolved with sodium antimonyl tartrate. A surface pressure-molecular area (π-A) isotherm was obtained by spreading a chloroform solution of racemic or enantiomeric $[Ru(phen)_2(dC18bpy)] (ClO_4)_2$ on an aqueous 0.1 M $NaClO_4$ solution at 25 °C (Figure 2). Comparing



(a) Side view (b) Top view

Figure 1. A molecular model of $[Ru(phen)_2(dC18bpy)]^{2+}$

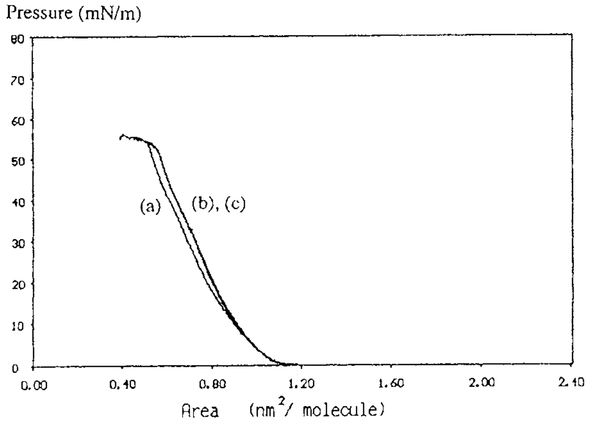


Figure 2. Surface pressure-molecular area (π-A) curves at 25 °C when chloroform solutions of (a) racemic, (b) Δ– , and (c) Λ– $[Ru(phen)_2(dc18bpy)] (ClO_4)_2$ were spread onto an aqueous $NaClO_4$ solution.

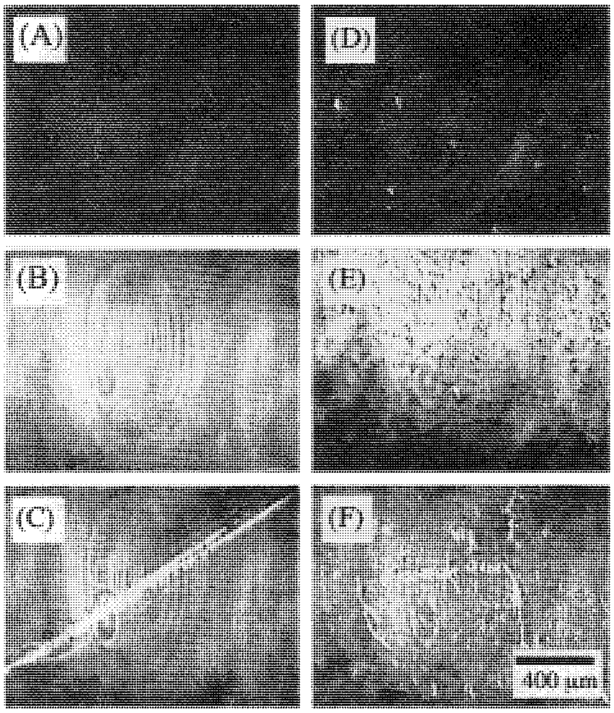


Figure 3. Brewster angle microscope images of a trough surface: (A) a surface of an aqueous $NaClO_4$ solution; (B) the same surface compressed to 20 mN/m after a chloroform solution of $[Ru(phen)_2(dC18bpy)](ClO_4)_2$ was spread; (C) the same surface compressed to 50 mN/m; (D) a surface when a chloroform solution of $[Ru(phen)_2(dC18bpy)](ClO_4)_2$ was spread onto an aqueous dispersion of Li-HT (0.010 g/L); (E) the same surface compressed to 20 mN/m; (F) the same surface compressed to 40 mN/m.

the isotherms between racemic and enantiomeric $[Ru(phen)_2dC18bpy]^{2+}$, it was concluded that packing density was higher in the heterochiral monolayer than in the homochiral one.[9]

Interaction of a clay with a monolayer was studied with a Brewster angle microscope (BAM). A floating bright region was observed on a trough surface when a chloroform solution of racemic $[Ru(phen)_2(dC18bpy)](ClO_4)_2$ was spread on an aqueous $NaClO_4$ solution. It implied that $[Ru(phen)_2(dC18bpy)]^{2+}$ molecules formed a monolayer domain already at zero surface pressure. On compressing a surface, the surface increased brightness until the whole surface became bright at the on-set of surface pressure (Figure 3B). At the surface pressure > 50 mN/m, the intensely bright straight region appeared, indicating that a monolayer was collapsed to form a multilayer film or micro-crystalline (Figure 3C). The same metal complex was spread on an aqueous suspension (0.010 g/l) of lithium hectorite $[Li_{0.6}(Mg_{2.5}Li_{0.6})Si_{3.9}O_{9.8}F_{2.2}]$ (denoted by Li-HT; Topy Ind. Ltd.). Intensely bright spots with the radii of 10 - 100 μm appeared in a bright region (Figure 3D). High brightness was undoubtedly due to the high refractive index of clay layers (1.53).[10] Thus adsorption of a clay to a cationic monolayer region took place already at zero surface pressure. On compressing a surface, the density of bright spots increased until it covered the whole surface (Figure 3E). For an aqueous Li-HT suspension, surface pressure rose from zero at 1.8 nm^2/molecule, which was 1.0 nm^2 larger than for an aqueous $NaClO_4$ (Figure 2) On the basis of the elemental compositions, a clay carries -2.2e per 1.8 nm^2. The value is nearly equal to the positive charge of the metal complex (+2). At the surface pressure > 45 mN/m, a bright linear region appeared, indicating the collapse of a film (Figure 3F).

A floating film was transferred onto a hydrophilic glass plate with a transfer ratio of 0.82 at 20 mN/m under the conditions of Figure 3E. The surface of a deposited film was studied with an atomic force microscope (AFM; a Nanoscope III (Digital Instruments)) in a tapping mode. As shown in Figure 4A, a surface was nearly covered with planar sheet-like particles (denoted by **a**). The size of a particle was several ten micrometers, corresponding to the size of bright spots in Figure 3D and 3E. There was a lower part (denoted by **b**) among the particles. The surface of **a** was estimated to be 1.5 ± 0.5 nm higher than that of **b**. The value was comparable to the thickness of a single clay layer (1.0 nm).[17] In the image of a different part, particles were partially overlapped to form a double layer as indicated by **c** (Figure 4B). The thickness of the upper layer was estimated to be 5.0 ± 1.0 nm. The value was nearly equal to the sum (4.5 nm) of the molecular height of $[Ru(phen)_2(dC18bpy)]^{2+}$ (3.5 nm) and the thickness of a single clay layer (1.0 nm).

The above AFM results were consistent with a view that parts **a, b** and **c** were a monolayer of $[Ru(phen)_2(dC18bpy)]^{2+}$/hectorite, a monolayer of $[Ru(phen)_2(dC18bpy)](ClO_4)_2$ and a double layer of $[Ru(phen)_2(dC18bpy)]^{2+}$/hectorite, respectively. Notably a double layer region **c** was connected smoothly with a single layer region **a**, implying that a clay layer was so flexible as to change its shape according to the up-and-down of an underneath surface.

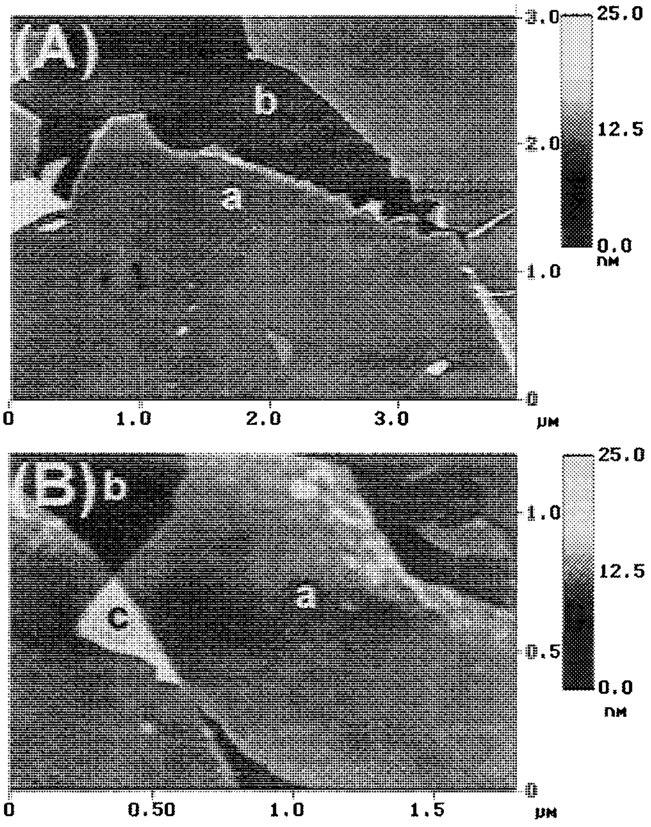


Figure 4. (**A**) A 3.9μm × 3.0μm AFM image of a film deposited onto a hydrophilic glass plate under the conditions of Figure 2(E); (**B**) A 1.8μm × 1.2μm AFM image of another part of the same smaple, showing the overlap of two layers.

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