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Molecular orientation of Ru(II) complexes introduced in hybrid Langmuir–Schaefer films of clay nanosheets and alkylammonium cations

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ABSTRACT

Ternary component hybrid films of amphiphilic alkylammonium cations, clay nanosheets, and ruthenium(II) complex cations were prepared by the modified Langmuir–Schaefer method. When a solution of the amphiphilic ammonium salt (octadecylammonium chloride, $ODAH^+Cl^-$) was spread at an air–clay dispersion interface, the clay nanosheets in the dispersion were adsorbed on the floating molecular film of $ODAH^+$ by the electrostatic interaction. Then the floating film of $ODAH^+$ and the clay was deposited on a glass plate and immersed in an aqueous solution of $[RuL_3]Cl_2$ (L = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 5,6-dimethyl-1,10-phenanthroline (dmphen), and 4,7-diphenyl-1,10-phenanthroline (dpp)) to form a ternary component hybrid monolayer. By repeating these procedures, a hybrid multilayer was fabricated. Characterization of the hybrid multilayers was carried out by electronic and IR spectral measurements and X-ray diffraction (XRD) method. Areas per $[RuL_3]^{2+}$ estimated from the analysis of the electronic spectra suggested that the Ru(II) complex cations interacted with each other through hydrophobic interaction. IR and XRD data indicated disordered alkylchains of $ODAH^+$ which would occupy spaces between the $[RuL_3]^{2+}$ cations in the film. The tilt angles of 3-fold axes of $[RuL_3]^{2+}$ were determined to be 32–35° by analyzing electronic spectra measured with p- and s-polarized beams. An orientation model of the $[RuL_3]^{2+}$ cations in the film was proposed, in which substitution groups at 4- or 5-positions of 1,10-phenanthroline ligand were in contact with the clay nanosheet layers. It was likely that the sizes of the ligands and the interaction between the ligands affected the structure of the hybrid film.

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1. Introduction

Clay minerals are useful materials with layered structures. It is because they possess some interesting properties such as high surface area, cation exchange ability, intercalation, and swelling [1–4]. The clay minerals have been used in various industrial fields as adsorbent, filler, coating, and so on [1–4]. Montmorillonite is one of the clay minerals having stacking layer structures [1–3]. When montmorillonite is dispersed in water at a low concentration, the clay layers are exfoliated and suspended as the single clay layers (~1 nm thick and ~1 μm long, termed clay nanosheets hereafter) with negative charges. The surfaces of the clay nanosheets, which are hydrophilic, can be modified with alkylammonium cations to be hydrophobic. The hydrophobic clay nanosheets are well dispersed in organic polymers. The clay–polymer composite materials have been extensively investigated in these decades [3,5].

We have studied ultrathin clay films prepared by a modified Langmuir–Shaefer method [6–22]. When a solution of an amphiphilic alkylammonium salt is spread on a surface of an aqueous montmorillonite dispersion, the negatively charged clay nanosheets are adsorbed on a floating molecular layer of the amphiphilic alkylammonium cations by the electrostatic interaction. The Langmuir film of the ammonium cations and the clay nanosheets can be transferred on a substrate by horizontal dipping (or Schaefer's method). The outer surface of the transferred film has cation exchange ability because the density of the negative charge in the clay nanosheet is larger than that of the positive charge of the ammonium cation in the film. Any cationic molecules, therefore, can be introduced as a third component in the film through the cation exchange reaction, by immersing the film surface in an aqueous solution of the corresponding salt. A set of the three layers of the amphiphilic alkylammonium cations, the clay nanosheets and the third cationic molecules is termed a hybrid monolayer. One can prepare hybrid multilayers by repeating these procedures.

The hybrid films show various remarkable features. For example, (1) layered structures of the films are very stable, (2) densities of the alkylammonium cation and the third cationic component are controllable, and (3) second harmonic generation is active because of a noncentrosymmetric structure of the film [7,9–12,16]. Various applications of the hybrid films have been reported as photocatalytic films

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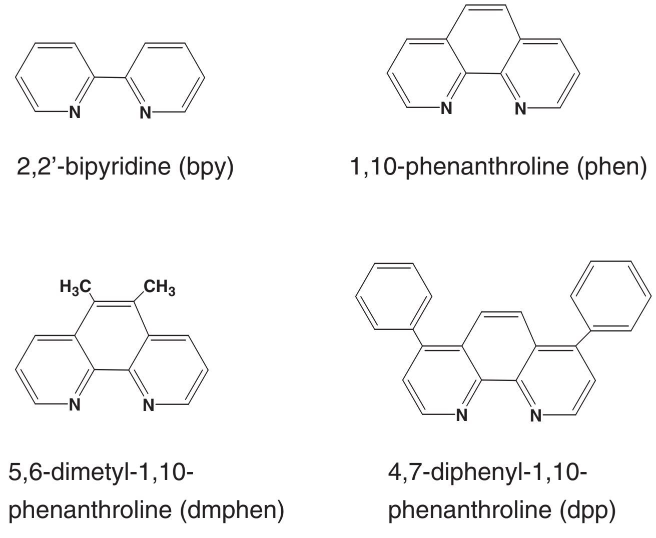
[14,16,21], electrode modifiers [22–25], photoswitchable magnetic films [19–21], and energy-transfer platforms [26,27]. The well-defined layer ordering at a nanometer level and the two-dimensional molecular alignment in the layer play important roles in these applications.

Ruthenium(II) complex cations are known as stable dyes and often used as photocatalysts [28] and light-emitting materials [29–32]. Hybrid films with Ru(II) complex cations would be applicable to visible-light working devices [16]. It is worthwhile to get information on film structures and, in particular, on packing state of the complex in the film. We prepared some hybrid films with $[RuL_3]^{2+}$ (L: bidentate ligand) complex cations in this work, and their properties were investigated by spectroscopic measurements. Orientation of the $[RuL_3]^{2+}$ cations in the film was the major interest in this work. Tilt angles of three-fold axes were determined for the Ru(II) complexes in the films and an orientation model of the complex cation was proposed.

2. Experimental details

A stock dispersion of montmorillonite (Kunipia P (Na^+-type), Kunimine Ind. Co., Ltd., Japan) was prepared by dispersing 1 g of the clay in 1 dm^3 of water (0.05 μS cm^{-1}). The stock dispersion at 1000 ppm (ppm = mg dm^{-3}) was diluted with water to 50 ppm just prior to use. An amphiphilic alkylammonium salt of octadecylammonium chloride [$(CH_3)(CH_2)_{17}NH_3Cl$: $ODAH^+Cl^-$] was synthesized from the corresponding amine by neutralization with hydrochloric acid. The crude salt was recrystallized from methanol twice. The purified salt was dissolved in a mixed solvent of chloroform and methanol (4:1 in volume) at 2.0×10^{-4} mol dm^{-3}. Ruthenium (II) complex salts, $[RuL_3]Cl_2$ [L = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 5,6-dimethyl-1,10-phenanthroline (dmphen), and 4,7-diphenyl-1,10-phenanthroline (dpp)] were synthesized according to literatures [33–35]. The molecular structures of the ligands are shown in Fig. 1. The Ru(II) salts of $[Ru(bpy)_3]Cl_2$, $[Ru(phen)_3]Cl_2$, and $[Ru(dmphen)_3]Cl_2$, were dissolved in water at 2×10^{-4} mol dm^{-3}. The other salt, $[Ru(dpp)_3]Cl_2$, was dissolved in water at 1×10^{-5} mol dm^{-3} because of its low solubility in water.

The solution of $ODAH^+Cl^-$ was dropped on a surface of the montmorillonite dispersion in a Langmuir trough (KSV Minitrough) after impurities on the surface of the dispersion were removed by suction. About 15 min later, a surface pressure–molecular area (π–A) isotherm curve was measured upon compression of the floating film (at 3 mm min^{-1}) from both sides with barriers. The surface pressure change was monitored by the Wilhelmy method using a filter paper [36]. The floating film was deposited on a glass plate (non-fluorescence slide glass S-0313, Matsunami Glass Ind., Ltd., Japan) at 10 mN m^{-1} by horizontal dipping (Fig. 2). (Just before use, the glass surface was washed by supersonication in ethanol for 30 min and then rinsed with water. The glass surface was hydrophobic.) After the deposition, the film surface was washed with water very well, and then it was immersed in the $[RuL_3]Cl_2$ solution for 30 s. The film surface was washed with water again, and dried under a N_2 gas flow. In this way, one hybrid monolayer, composed of $ODAH^+$, clay nanosheets, and Ru(II) complex cations, was prepared. A hybrid multilayer was fabricated by repeating these procedures.


2,2'-bipyridine (bpy)

1,10-phenanthroline (phen)

5,6-dimetyl-1,10-phenanthroline (dmphen)

4,7-diphenyl-1,10-phenanthroline (dpp)

Fig 1. Structures of ligands.

Electronic spectra and IR spectra of the films were recorded in a transmission mode with a spectrophotometer U-3310 (Hitachi, Japan) and a Fourier transform infrared spectrometer Spectrum One (PerkinElmer Inc., USA), respectively. A glass plate was used as a reference. Polarized electronic spectra were measured by using a Glan-Taylor prism made of α-BBO. The s- and p-polarized beams transmitted the film samples at various incident angles (inset in Fig. 8b) [12,37–40]. Out-of-plane X-ray diffraction (XRD) patterns of the films were obtained with an X'Pert MRD (PANalytical B. V., the Netherlands) using the Cu Kα line.

3. Results and discussion

3.1. **π**–A isotherm curves of $ODAH^+$

We previously investigated adsorption mechanism of the clay nanosheets onto a floating molecular film of alkylammonium cations in detail [17]. The adsorption rate depends on the clay concentration in the subphase. Fifteen minutes of the waiting time, from spreading some drops of an amphiphilic salt solution to starting compression, is good enough for attainment of the adsorption equilibrium for a clay dispersion at 50 ppm. π–A isotherm curves of $ODAH^+Cl^-$ on water and on the clay dispersion at 50 ppm were shown in Fig. 3. The figure exhibited rise in surface pressure with the decrease in molecular area (or upon film compression). The isotherm curve for $ODAH^+$ on water rose steeply from a molecular area of ~0.2 nm^2 $molecule^{-1}$ and gave a collapse point at a surface pressure of 62 mN m^{-1}. On the contrary, the curve for $ODAH^+$ on the 50-ppm clay dispersion indicated a gradual rise from ~1.5 nm^2 $molecule^{-1}$ and a low collapse pressure (~30 mN m^{-1}), which was the characteristic behavior for a floating film adsorbed by the clay nanosheets [7,8,10,11]. The floating film of $ODAH^+$ and the clay was deposited on a glass plate by horizontal dipping at a surface pressure of 10 mN m^{-1}, where the molecular area was about 1.2 nm^2 $molecule^{-1}$. The transferred film surface was subsequently immersed in a $[RuL_3]Cl_2$ solution to form a hybrid monolayer of $ODAH^+$ cations, the clay nanosheets, and the Ru(II) complex cations.

3.2. IR and electronic spectra of hybrid films

IR and electronic spectra were measured after almost every deposition of the hybrid monolayer. IR spectra for the films of $[Ru(phen)_3]^{2+}$ (2, 4, 5, 6, and 7 layers) were shown in Fig. 4a. The peaks around 2853 and 2926 cm^{-1} were assigned to the symmetric and antisymmetric stretching vibrations of $-CH_2-$ in $ODAH^+$, respectively [41,42]. Conformational ordering of alkylchains is sensitively reflected on the peak positions of the $-CH_2-$ stretching modes [43]. The peak positions for the vibration modes of $ODAH^+$ in the films suggested formation of gauche rotomers, in other words, disorder of the chains in the films. (If the alkylchains were in all-trans conformation, the peak positions should have appeared at 2850 ± 1 and 2918 ± 1 cm^{-1}, or at even lower wavenumbers.) The absorbance intensities at 2926 cm^{-1} were plotted as a function of layer number in Fig. 4b. The absorbance increased linearly with the increase in the layer number, showing layer-by-layer deposition of the hybrid monolayers. For the other film systems of $[Ru(bpy)_3]^{2+}$, $[Ru(dmphen)_3]^{2+}$, and $[Ru(dpp)_3]^{2+}$, similar IR spectral data were

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