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Two-dimensional molecular ordering of Os(II) complexes in organo-clay hybrid ultrathin films†

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An ordered structure of $[OsL_3]^{2+}$ (L = 2, 2′-bipyridine or 1, 10-phenanthroline) layer in an ultrathin film composed of the complex cations, clay nanosheets and alkylammonium cations is reported on the basis of its in-plane X-ray diffraction and polarized electronic spectral data.

One of the characteristic properties of clay minerals is the adsorption of cationic compounds into their interlayer spaces (intercalation).[1,2] The intercalation of metal complexes into the clay is of interest. For example, a racemic mixture of $[Ru(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) is adsorbed up to the cation-exchange capacity (CEC) of the clay, whereas the corresponding enantiomer is adsorbed up to two times in excess of the CEC.[3–5] The difference in the adsorption structure of the racemic and enantiomeric metal complexes has been investigated by various methods.[5–8] However, some ambiguities have remained in those results because, with a few exceptions (vermiculite clays), it is impossible to prepare single crystals of the clay–metal complex adducts.[1]

Smectite clays are exfoliated into single clay nanosheets with negative charges in their aqueous suspensions at a low concentration.[9] When amphiphilic alkylammonium cations are spread onto an air–clay suspension interface, a positively charged monolayer of the alkylammonium cations is hybridized with the negatively charged clay nanosheets at the interface.[10–11] The hybrid monolayer of the ammonium cations and the clay can be transferred onto a solid surface by horizontal dipping. The outer surface of the transferred film possesses a cation-exchange capacity because some exchangeable metal cations such as Na^+ remain on the surface. Therefore, any cationic compound is introduced into the hybrid film by immersing the film surface into an aqueous solution of the compound.[11] A hybrid multilayer of the alkylammonium cations, the clay nanosheets and the cationic compound can be fabricated by repeating the above procedure.

In this work, we prepared hybrid multilayers of octadecylammonium cation ($ODAH^+$), montmorillonite (Kunipia P, from Kunimine Ind. Co. Ltd., Japan) and $[OsL_3]^{2+}$ (L = 2, 2′-bipyridine (bpy) or 1,10-phenanthroline (phen)) on glass plates (see ESI†). This type of organo-clay hybrid film would be a relevant model system to investigate the two-dimensional (2D) structure of the metal complex layer in the clay–metal complex adduct. We report here the first example of the hybrid film which gives a diffraction peak due to the 2D-ordering of the metal complex in its X-ray diffraction (XRD) pattern recorded in an in-plane mode. Together with results from electronic spectra of the films measured with polarized lights, the 2D-structure of the Os(II) complex layer in the hybrid film is discussed.

The hybrid films of $ODAH^+$, the clay and $[Os(bpy)_3]^{2+}$ ($[Os(bpy)_3]^{2+}/clay/ODAH^+$) showed absorption bands peaked at 442 and 499 nm in their electronic spectra (see ESI†), which were assigned to the metal-to-ligand charge transfer bands of the complex.[12] The absorption intensities of these peaks increased as the hybrid monolayers (a set of three layers of $ODAH^+$, the clay and Os(II) complex cation) were deposited. A linear relation between the absorbance at 499 nm and the layer number (see ESI†) indicated that the multilayer of the hybrid film was fabricated layer-by-layer. The XRD pattern measured in a θ–2θ mode for the film of $[Os(bpy)_3]^{2+}/clay/ODAH^+$ (see ESI†) gave diffraction peaks at 2θ = 4.9, 9.8, 15.0, 20.0 and 25.2° at ~5° intervals. This pattern meant that the hybrid film possessed a layered structure. The five peaks observed in the XRD pattern from 2θ = 4.9 to 25.2° were assigned to (001), (002), (003), (004) and (005), respectively. From the (001) peak (2θ = 4.9°), the basal spacing was calculated to be 1.80 ± 0.02 nm. The thickness of the clay nanosheet is 0.96 nm, and the thickness of the $ODAH^+$ layer in the film was negligible because the density of $ODAH^+$ in the film was low (1.4 nm^2 per cation, estimated from the molecular area–surface pressure isotherm curve).[11] Taking these things into consideration, a thickness of the $[Os(bpy)_3]^{2+}$ layer in the film should be 0.84±0.02 nm. This indicates that the complex cations form monomolecular layers in the hybrid film.[4,5]

Similar results were obtained for the hybrid films of $[Os(phen)_3]^{2+}/clay/ODAH^+$ in the characterization by the electronic spectroscopy and the θ–2θ XRD measurements. Interestingly, the diffraction peaks in the XRD pattern for $[Os(phen)_3]^{2+}/clay/ODAH^+$ were observed at the same positions as those for $[Os(bpy)_3]^{2+}/clay/ODAH^+$. This suggests that the hydrogen atoms at 5- and 6-positions in 1,10-phenanthroline of the complex in the film may not be associated with the thickness of the complex layer.

In-plane XRD patterns for the hybrid films of $[Os(phen)_3]^{2+}/clay/ODAH^+$ and $[Os(bpy)_3]^{2+}/clay/ODAH^+$ were measured. These patterns exhibited similar characteristics. The in-plane XRD pattern of $[Os(phen)_3]^{2+}/clay/ODAH^+$ (47 hybrid layers) is shown in Fig. 1(a) (see ESI†), together with that for a 36-layered film of $clay/ODAH^+$ (Fig. 1(b), see ESI†) that was prepared by depositing the floating hybrid monolayers without immersion into the Os(II) complex salt solution. The in-plane XRD pattern for the hybrid film of $[Os(phen)_3]^{2+}/clay/ODAH^+$ in Fig. 1(a) gives an intense peak at

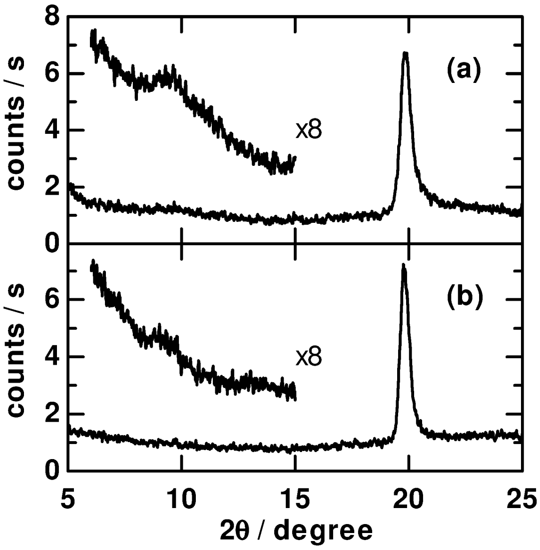

Fig. 1 In-plane XRD patterns for (a) $[Os(phen)_3]^{2+}/clay/ODAH^+$ and (b) $clay/ODAH^+$.

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† Electronic supplementary information (ESI) available: ESI Figs. 1–5. See http://www.rsc.org/suppdata/cc/b4/b402258k/

2θ = 19.8° and a weak one around 2θ = 9.5°. The former peak can be seen in the XRD pattern of clay/ODAH$^+$ in Fig. 1(b). The peak at 2θ = 19.8° is also observable in an in-plane XRD pattern of mica as the (110) diffraction peak. Therefore, this peak is due to the clay nanosheet in the hybrid film.[13] The latter peak at 2θ = 9.5° in Fig. 1(a) is not seen in the XRD pattern of clay/ODAH$^+$ (Fig. 1(b)), although the pattern of clay/ODAH$^+$ shows a very weak peak around 2θ = 8.8°. The peak at 2θ = 8.8° comes from the glass substrate because an in-plane XRD pattern of a glass plate indicated a weak peak at the same position. Comparing the XRD pattern for $[Os(phen)_3]^{2+}$/clay/ODAH$^+$ with that for clay/ODAH$^+$ (Fig. 1(a) and (b)), it is clear that the Os(II) complex layers in the hybrid film give rise to the diffraction peak at 2θ = 9.5°. This implies that the adsorbed Os(II) complex cations are ordered on the clay layer in the hybrid film with a distance of ~0.93 nm between the complexes; the distance of 0.93 nm is indicative of a closely packed ordering of the complex.

In order to get further information on the 2D-structure of the complex layer in the hybrid film, electronic spectra of the films were recorded with polarized lights. Fig. 2(a) shows the electronic spectra for $[Os(phen)_3]^{2+}$/clay/ODAH$^+$ (47 layers) measured with the p- and s-polarized beams at an incident angle (ϕ) of 70° from the surface normal. Both of the absorption peaks at 440 and 498 nm in Fig. 2(a) are assigned to the metal-to-ligand charge transfer bands. Their transition moments are perpendicular to the 3-fold axis of the complex.[12] The absorption intensity of the p-polarized spectrum is smaller than that of the s-polarized one. Here, the dichroic ratio at 440 nm (D_{440}) is defined as the ratio of absorbance at 440 nm recorded with the p-polarized beam (A_p) to that with the s-polarized one (A_s): $D_{440} = A_p/A_s$. The dichroic ratio, D_{440}, is plotted as a function of the incident angle, ϕ, in Fig. 2(b). Theoretically, a relation between D_{440} and ϕ is provided as follows:[14]

$$D_{440} = \frac{2 - 2\sin^2\phi + (3\sin^2\phi - 1)\sin^2\alpha}{2 - \sin^2\alpha} \qquad (1)$$

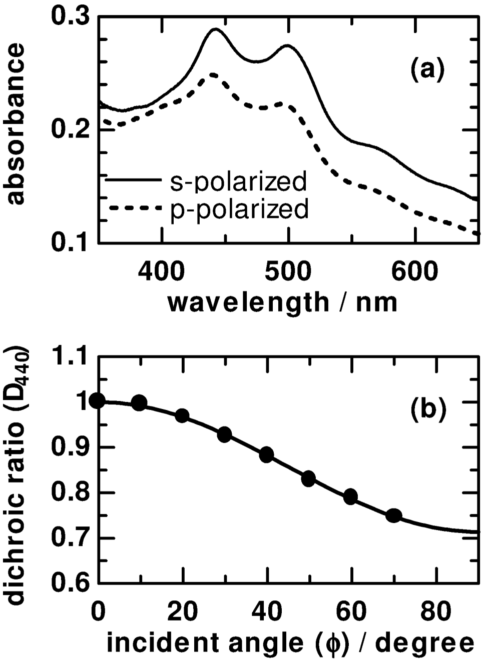

Fig. 2 (a) Electronic spectra for $[Os(phen)_3]^{2+}$/clay/ODAH$^+$ recorded with s- and p-polarized lights. (b) Plot of dichroic ratio against incident angle. The solid line indicates the result of the fitting analysis (see the text).

where α is a tilt angle from the surface normal for the 3-fold axis of the complex. By fitting the equation to the experimental data in Fig. 2(b), the tilt angle is determined to be α = 46°. In a similar way, a tilt angle for the Os(II) complex in the hybrid film of $[Os(bpy)_3]^{2+}$/clay/ODAH$^+$ was evaluated to be α = 44°. The value for $[Os(phen)_3]^{2+}$ is in accord with that for $[Os(bpy)_3]^{2+}$ within the experimental error.

Judging from the whole data obtained in this work, there is no remarkable difference in the molecular packing and orientation of $[Os(phen)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ in the hybrid film. If one of the three ligands in $[Os(phen)_3]^{2+}$ is perpendicular to the film surface and the 2-fold axis in this ligand is parallel to the surface (see ESI†), the H atoms at the 3- and 8-positions in this ligand are in touch with the clay layers on both sides and the other two ligands do not touch the clay layers. In this orientation, the 3-fold axis of the complex is inclined at 35° from the surface normal. Suppose that the complex is rotated along the 2-fold axis as the H atoms at the 4- and 5-positions in the other two ligands are in contact with the clay layers (see ESI†). The 3-fold axis of the complex is inclined at 45° from the surface normal. In this structure model, the 5- and 6-H atoms in the ligands play minor roles to maintain the layer thickness, which is consistent with the θ–2θ XRD results. If the 3-fold axis is perpendicular to the film surface, it is true that the thickness of the complex layer in the hybrid film is thinner than that in the structure model proposed above. However, the Os(II)–Os(II) distance between the adjacent complexes is longer than that in the proposed model. This suggests that the structure of the complex layer in the hybrid film would be dominated not by the layer thickness but by the packing between the neighbouring complexes in the layer. The Os(II) complexes employed in this work were racemic mixtures. The molecular packing between Δ- and Λ-forms should be different from that between the enantiomers (Δ–Δ or Λ–Λ) in the hybrid film. Further experimental data is necessary not only to support the proposed model but also to discuss the molecular packing with respect to the optical isomers.

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