

Unidirectional Orientation of Methylene Blue Intercalated in $K_4Nb_6O_{17}$ Single CrystalRyozo Kaito[†] and Kazuyuki Kuroda^{†,‡}

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Intercalation of methylene blue into $K_4Nb_6O_{17}$ single crystals was investigated for the construction of hybrid materials with three-dimensional anisotropy. By the reaction of $K_4Nb_6O_{17}$ with a methylene blue aqueous solution in the presence of propylamine, methylene blue/ $K_4Nb_6O_{17}$ intercalation compounds were obtained. The basal spacing increased to 3.0 nm, and the macroscopic thickness of the crystal also increased. The regularity in the *ac* plane did not change by the reaction as evidenced by the in-plane X-ray diffraction measurements. Polarized absorption spectra showed a dichroism showing that the methylene blue/ $K_4Nb_6O_{17}$ intercalation compounds possess three-dimensionally confined nanostructures.

Introduction

The complexation of organic species with crystalline inorganic solids has extensively been investigated to construct inorganic–organic hybrids with unique microstructures controlled by host–guest and guest–guest interactions.^{1,2} The potential of inorganic–organic hybrids as advanced materials including adsorptive, catalytic, and optical ones has been proposed. The spatial distribution and the orientation of guest species must affect the physicochemical characteristics of the resulting hybrids; however, there remains much difficulty to control and evaluate them.

Intercalation of organic guest species into layered inorganic solids is a way of producing inorganic–organic hybrids with multilayered nanostructures. The properties of the intercalation compounds have been extensively investigated.^{2,3} Among known functions of intercalation compounds, those for optical applications are worth investigating because nanostructures significantly affect the performance. Accordingly, the organization of photoactive species on the surface of layered materials has been investigated.⁴ The products are composed of finite particles so that the anisotropic orientation of intercalated guest species is difficult to evaluate. The out-of-plane (tilted with respect to the layer) orientation of the guest species has been discussed from the expanded basal spacing by means of the geometrical consideration and one-dimensional Fourier syntheses of X-ray diffraction patterns.^{2–4}

To use the intercalation compounds for electronics and optics applications, hierarchical organization from microscopic to macroscopic scales is a key issue. For such purposes, oriented thin films of intercalation compounds have been prepared by simple casting of suspension.⁵ Langmuir–Blodgett⁶ (LB) and layer-by-layer deposition techniques⁷ have been applied to prepare multilayered films of intercalation compounds from

exfoliated layers. The electron spin resonance, infrared spectroscopy, and polarized UV–vis spectroscopy have been utilized to evaluate the out-of plane orientation of the guest species. The intercalation of organic cations into crystals of layered solids including vermiculite, FeOCl, and MnPS₃ and the crystallographic discussion about the products were conducted.^{8,9} Tetramethylammonium and cobaltocenium ions were successfully intercalated into the MnPS₃ single crystal, and their out-of-plane anisotropy in the interlayer space was evaluated by X-ray diffraction.^{9a} Intercalation of aniline into single crystals of FeOCl has been reported previously.^{9b} The orientation of polyaniline in the interlayer space of FeOCl has been evaluated by using single-crystal data. Concerning the in-plane anisotropy of the guest species, we have utilized an electric field to align the dipoles of *p*-nitroaniline in tetramethylammonium-saponite films and the resulting materials exhibit optical second harmonic generation.^{5a} However, to the best of our knowledge, in-plane anisotropy of guest orientation has not been observed for other intercalation compounds.

Recently, we have reported the adsorption of cationic cyanine dyes on $K_4Nb_6O_{17}$ single crystals to create unidirectional orientation of the dyes on the crystal surface by means of the in-plane anisotropy of $K_4Nb_6O_{17}$.¹⁰ The ion exchange properties of $K_4Nb_6O_{17}$ have long been recognized.¹¹ $K_4Nb_6O_{17}$ has an anisotropic surface with regularly arranged NbO^- groups which act as cation-exchangeable sites as shown in Figure 1.¹² It is thought that the difference in the periodic distances between the *a* and *c* axes of $K_4Nb_6O_{17}$ matches the distance of the positive charges in the cyanine dye aggregates which leads to unidirectional orientation of the adsorbed dyes. Although the presence of unidirectionally oriented cyanine dye aggregates was revealed by polarized visible absorption spectroscopy, the basal spacing did not change by the dye adsorption. This fact indicated that the adsorbed cyanine dyes were located at the external surface of the host and/or that the adsorbed dye amounts were too low to detect the expansion of the interlayer spacing. The increase in the loading dye amounts is worth conducting o

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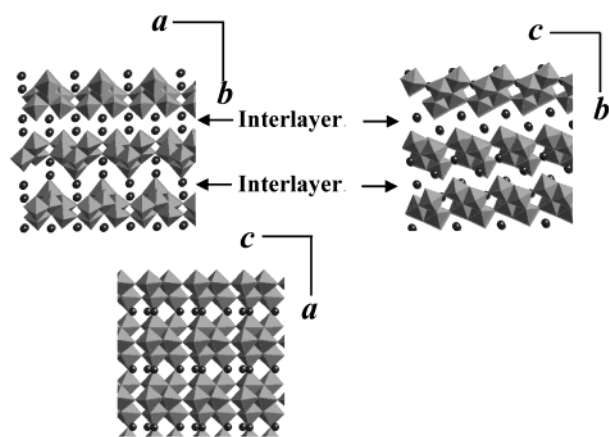


Figure 1. The surface structures of $K_4Nb_6O_{17}$ cleaved from “interlayer I”.

construct intercalation compounds with single crystal like three-dimensionally confined nanostructures.

In this study, we investigated the intercalation of methylene blue into $K_4Nb_6O_{17}$ single crystals. The adsorption of methylene blue in various heterogeneous systems has been investigated for the characterization of the surface as well as to construct photo- and electrofunctional supramolecular systems. The intercalation of methylene blue into layered materials,^{13,14} mainly clay minerals, has been reported previously. Depending on the hosts and the doped methylene blue amounts, methylene blue forms aggregates with different types on the layer surface as revealed by the visible absorption spectra. In the present study, we succeeded in the intercalation of methylene blue into $K_4Nb_6O_{17}$ single crystals without loss of the *ac* plane anisotropy. The microstructures of resulting methylene blue/ $K_4Nb_6O_{17}$ intercalation compounds were deduced. X-ray diffraction as well as conventional and polarized visible absorption spectroscopy was employed to conceive the microstructures of the methylene blue/ $K_4Nb_6O_{17}$ intercalation compounds.

Experimental Section

Materials. K_2CO_3 (purity ca. 95%) was obtained from Kokusan Chem. Co., and Nb_2O_5 (purity ca. 99.9%) was obtained from Wako Pure Chemical Industries Ltd. Methylene blue (purity higher than 98.5%) and *n*-propylamine were obtained from Tokyo Kasei Industry Co. Ltd. All the reagents were used as received. Single crystals of $K_4Nb_6O_{17}$ were grown by a flux method reported previously.^{11,12} Transparent single crystals of $K_4Nb_6O_{17}$ were obtained by calcination of the mixture of K_2CO_3 and Nb_2O_5 at the molar ratio of 2.7:3.0 with acetone at 1150 °C for 10 h in a Pt crucible.

Intercalation of Methylene Blue. Single crystals of $K_4Nb_6O_{17}$ were cleaved along the *ac* plane into platy rectangular

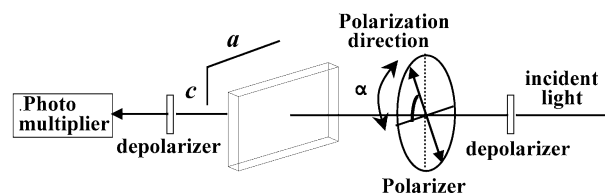


Figure 2. Experimental setup for polarized absorption spectra. Samples were mounted in the sample holder, while the polarizer was rotated so that the angle between the *a* axis of the crystal and the polarized direction of the incident light was varied.

TABLE 1: Chemical Compositions of the Products

reaction period/days	C/mass %	N/mass %	mol of <i>n</i> -propylamine/ Nb_6O_{17}	mol of methylene blue/ Nb_6O_{17}
3	2.1	0.48	0.0011	0.10
7	2.61	0.59	0.030	0.12
14	4.27	1.09	0.23	0.17

solids with a size of several square millimeters and a thickness of ca. 0.05 mm. Single crystals of $K_4Nb_6O_{17}$ (0.05 g) were added in an aqueous solution of *n*-propylamine and 5×10^{-3} M methylene blue. The molar ratio of methylene blue/*n*-propylamine/K was 1.5:1:1. The mixture was sealed in a glass ampule and allowed to react at 60 °C for 3, 7, 14, and 28 days. The products were washed with ethanol until the supernatant became colorless. For the intercalation of *n*-propylamine into a single crystal of $K_4Nb_6O_{17}$, single crystals of $K_4Nb_6O_{17}$ were allowed to react with an aqueous *n*-propylamine solution. The molar ratio of *n*-propylamine/K in the reaction was 3:1. The mixtures were allowed to react at 25 °C for 1 day. The reason for the reaction at 25 °C for 1 day is to prevent swelling of $K_4Nb_6O_{17}$.

Characterization. X-ray diffraction (XRD) patterns were obtained with a Mac Science MO3X-HF22 diffractometer using Mn-filtered Fe $K\alpha$ and graphite-monochromated Cu $K\alpha$ radiation. CHN analysis was performed with a Perkin-Elmer PE2400 II instrument. Visible absorption spectra were obtained with a Shimadzu UV2500PC spectrometer. Polarized absorption spectra were measured by using of polarizer and depolarizer. The experimental setup for obtaining polarized absorption spectra is shown in Figure 2. Polarized microscopic images were obtained with a universal microscope, Olympus BX60-33MU, with a polarizer. Polarizing angle was defined by the angle between the *a* axis of the crystal and the polarized direction of the incident light, when the incident light was radiated vertically to the *ac* plane of the crystal.

Results and Discussion

Since the direct intercalation of methylene blue into $K_4Nb_6O_{17}$ crystals is difficult, the methylene blue intercalation was

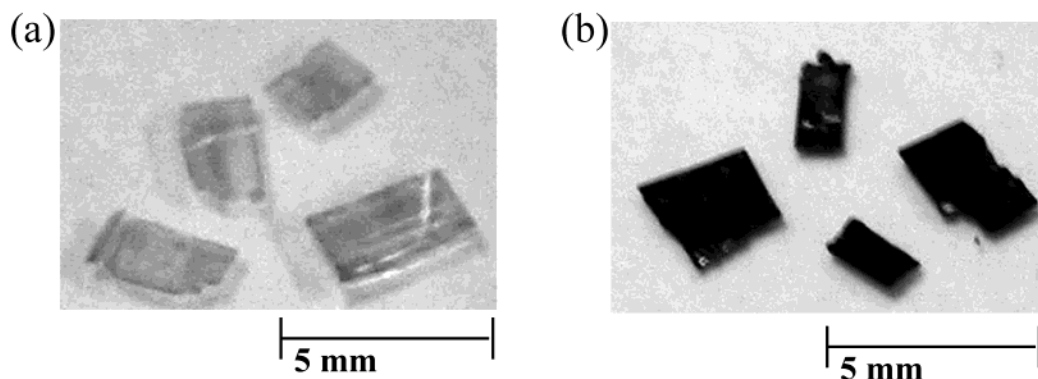


Figure 3. Photographs of the $K_4Nb_6O_{17}$ crystal before (a) and after (b) the reaction with methylene blue.

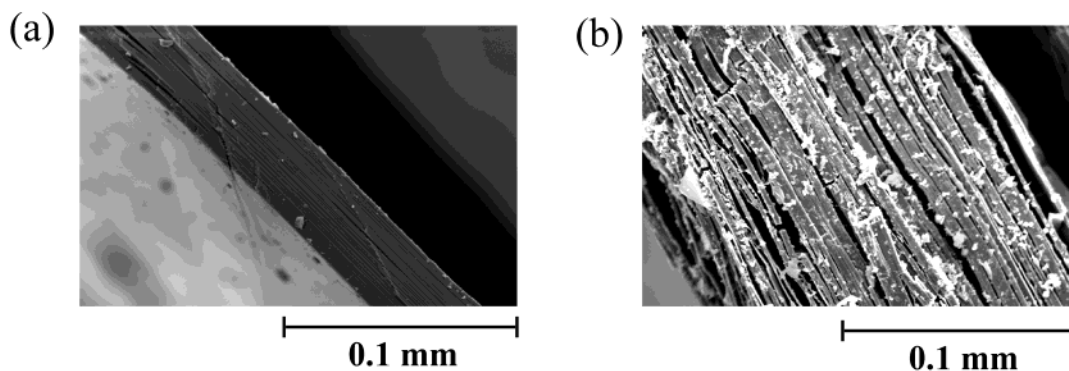


Figure 4. Scanning electron micrographs of $\text{K}_4\text{Nb}_6\text{O}_{17}$ crystal (cross-sectional view) before (a) and after (b) the reaction with methylene blue.

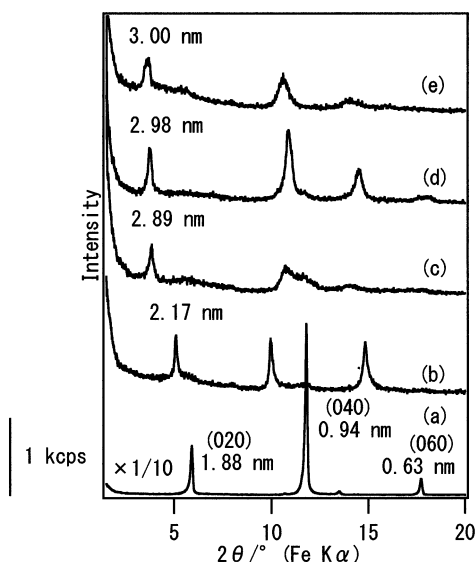


Figure 5. The X-ray diffraction patterns of (a) $\text{K}_4\text{Nb}_6\text{O}_{17}$ hydrate, (b) propylammonium/ $\text{K}_4\text{Nb}_6\text{O}_{17}$, and (c–e) methylene blue/ $\text{K}_4\text{Nb}_6\text{O}_{17}$ prepared by the reactions for (c) 3, (d) 7, and (e) 14 days.

conducted in the presence of *n*-propylamine. When finite particles of $\text{K}_4\text{Nb}_6\text{O}_{17}$ were used, alkylamines with short alkyl chains have been intercalated by direct ion exchange reaction. On the other hand, the guest displacement method has been required to introduce other cationic compounds such as bulky alkylammonium ions and dyes into the interlayer space. In our separate study on the reaction of a $\text{K}_4\text{Nb}_6\text{O}_{17}$ single crystal with *n*-propylamine, exfoliation of $\text{K}_4\text{Nb}_6\text{O}_{17}$ layers was observed. To avoid exfoliation, the intercalation of methylene blue was conducted by a one-step reaction where $\text{K}_4\text{Nb}_6\text{O}_{17}$ was allowed to react with a solution containing methylene blue and *n*-propylamine.

The photographs and scanning electron micrographs of the $\text{K}_4\text{Nb}_6\text{O}_{17}$ crystals before and after the reaction with methylene blue are shown in Figures 3 and 4, respectively. After the reaction, the crystal became pale blue and the crystal morphology changed, showing expansion only in the *b* axis. These observations suggested the intercalation of methylene blue into $\text{K}_4\text{Nb}_6\text{O}_{17}$ single crystals.

Table 1 summarizes the chemical composition of the products. The amounts of *n*-propylamine and methylene blue were derived from the N and C contents of the products using different C:N ratios of the two compounds. The adsorbed methylene blue amounts increased with the increase in the reaction period, and the ion exchange reaction reached an equilibrium state 14 days after the reaction. No further increase in the methylene blue amount was observed when the reaction was prolonged to 28

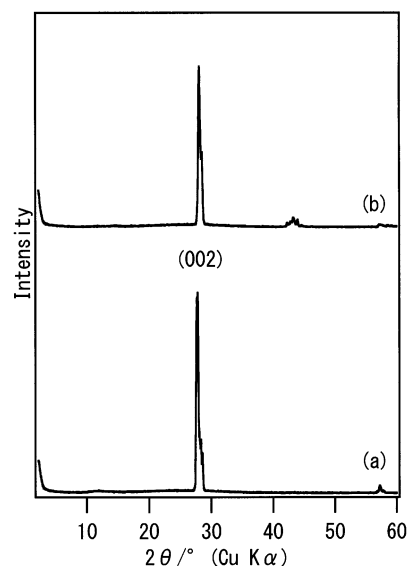


Figure 6. The *ab* plane X-ray diffraction patterns of methylene blue/ $\text{K}_4\text{Nb}_6\text{O}_{17}$.

days. At the equilibrium state, the adsorbed methylene blue amount was 0.17 mol/ Nb_6O_{17} . Hereafter the product obtained after 14 days of reaction is designated as methylene blue/ $\text{K}_4\text{Nb}_6\text{O}_{17}$, and further characterization was conducted for the sample.

The ion exchange reaction was confirmed by the change in the X-ray diffraction pattern shown in Figure 5. The basal spacing of $\text{K}_4\text{Nb}_6\text{O}_{17} \cdot 3\text{H}_2\text{O}$ (1.9 nm) increased to 3.0 nm, indicating the intercalation of methylene blue. The reflection due to a basal spacing of *n*-propylamine/ $\text{K}_4\text{Nb}_6\text{O}_{17}$ (2.2 nm, which was determined in the present study) was not observed. The guest displacement method has previously been conducted to introduce bulky cationic dyes into the interlayer space of $\text{K}_4\text{Nb}_6\text{O}_{17}$ powders and relating layered titanates and niobates.¹⁵ These layered materials are semiconducting, so that the optical applications including the photocatalytic ones have been investigated extensively.¹⁶ The immobilization of dyes for the sensitization to visible light has been conducted. The present one-step reaction is feasible because of the ease of operation and an alternative way for the cationic dye intercalation.

It has been reported that $\text{K}_4\text{Nb}_6\text{O}_{17}$ possess two interlayer environments (named interlayer I and II) with different reactivities.^{15,17} The potassium ions in interlayer I can be easily exchanged while those in interlayer II are relatively difficult to replace. Supposing that the adsorbed methylene blue exists only in the interlayer I, the gallery height of the methylene blue intercalated interlayer is determined by subtracting the basal spacing of 1.64 nm for dehydrated $\text{K}_4\text{Nb}_6\text{O}_{17}$ from the observed

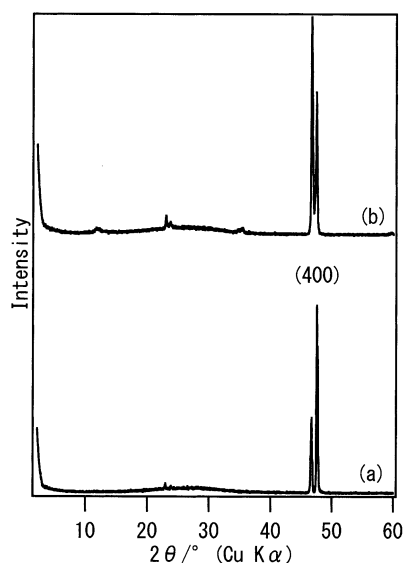


Figure 7. The *bc* plane X-ray diffraction patterns of methylene blue/ $\text{K}_4\text{Nb}_6\text{O}_{17}$.

basal spacing for the methylene blue/ $\text{K}_4\text{Nb}_6\text{O}_{17}$ (3.0 nm) to be 1.36 nm. Taking the molecular size of methylene blue¹⁸ as well as intercalated water into consideration, the intercalated methylene blue is thought to take a bilayer with their molecular planes parallel to the niobate layers or to form a monolayer with their molecular plane and the longer axis almost perpendicular to the layers.

Supposing that the methylene blue was intercalated both in interlayers I and II, the gallery height is derived by subtracting 0.82 nm, the thickness of each niobate layer, from the basal spacing of the methylene blue/ $\text{K}_4\text{Nb}_6\text{O}_{17}$ (3.0 nm) to be 2.18 nm. To satisfy the value, methylene blue should form a bilayer with their molecular plane of the longer axis inclined to the *ac* plane.

As shown in Table 1, the intercalation compounds contain *n*-propylamine co-intercalated with methylene blue. It is very difficult to determine the orientation of the intercalated meth-

ylene blue precisely. The orientation of the intercalated methylene blue was discussed further from the polarized absorption spectra.

The regularity of the *ac* plane did not change after the methylene blue intercalation as revealed by the X-ray diffraction profiles in the *ab* and *bc* planes (Figures 6 and 7 for the *ab* and *bc* planes, respectively). The (002) and (400) diffractions were observed in Figures 6 and 7, and the positions did not change before and after the methylene blue intercalation. Thus, the *ac* plane regularity was preserved after the intercalation of methylene blue.

The visible absorption spectra were recorded after the products were cleaved into a thinner section to make optical density close to 1.0. The absorption spectrum of methylene blue/ $\text{K}_4\text{Nb}_6\text{O}_{17}$ showed a broad absorption band at around 600 nm, which can be ascribed to the methylene blue dimer, and the band at around 500 nm, which is ascribable to higher aggregates.¹⁹ No protonation occurred as revealed by the absence of the absorption band at 750 nm, which has previously been observed for methylene blue in acidic environments and assigned to the protonated methylene blue. This fact indicates the weak acidity of the interlayer surface of $\text{K}_4\text{Nb}_6\text{O}_{17}$.

The polarized microscopic images are shown in Figure 8, where α represents the angle between the polarization direction and the *a* axis of the crystal. When the plane of the polarization is rotated, the color changes dramatically as shown in Figure 9. The pale blue was seen for the photograph taken at $\alpha = 0^\circ$, while the photograph taken at $\alpha = 90^\circ$ is lighter in color. The polarized absorption spectra of methylene blue/ $\text{K}_4\text{Nb}_6\text{O}_{17}$ are shown in Figure 9. The absorbance at 600 nm, due to methylene blue dimer, varied depending on α , while the wavelength of the absorption maximum was almost constant. The maximum oscillator strength was obtained when $\alpha = 0^\circ$. These observations indicate that the intercalated methylene blue is oriented in one direction in the *ac* plane of $\text{K}_4\text{Nb}_6\text{O}_{17}$. Taking the geometrical consideration mentioned above, it was thought that the intercalated methylene blue formed a dimer and the dimer arranged in a direction in the *ac* plane to align the molecular longer axis to the *a* axis of $\text{K}_4\text{Nb}_6\text{O}_{17}$. In contrast to the dichroic absorption at 600 nm, the band at 550 nm, which can be ascribed

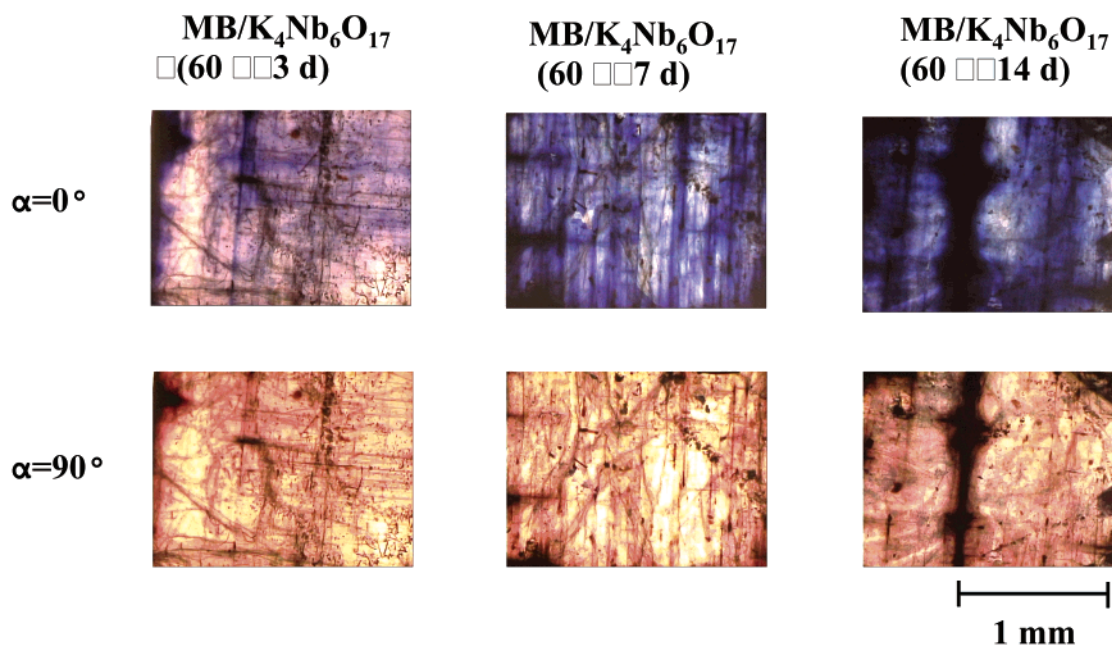


Figure 8. Polarized microscopic images of methylene blue/ $\text{K}_4\text{Nb}_6\text{O}_{17}$.

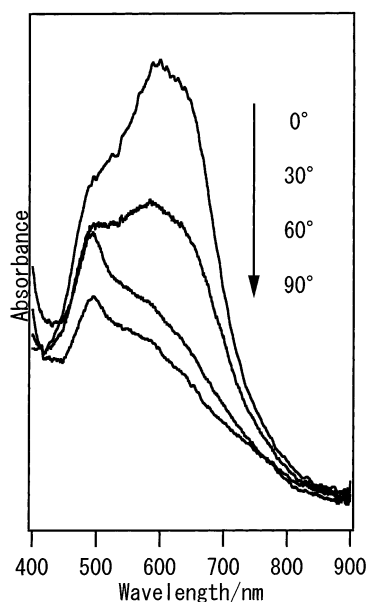


Figure 9. Polarized absorption spectra of methylene blue/ $K_4Nb_6O_{17}$.

to higher aggregates, did not depend on α so clearly. This fact suggests that the higher aggregates of methylene blue did not align so much in the *ac* plane. Since the structures of the higher aggregates have not been clarified, further discussion on the absorption band at 550 nm is difficult at the present stage.

In-plane anisotropy of organic molecules in macroscopically layered systems has been achieved in such systems as those formed on rubbing treated substrates^{20,21} and LB films in a dipping direction.²² If compared with these systems, the present system comprised of $K_4Nb_6O_{17}$ crystals is unique from the following viewpoints: it is composed of alternating semiconducting inorganic oxide ultrathin layers and layered assemblies of organic molecular species, the thickness of the materials can be controlled by simple cleaving before and after the complexation, and they are mechanically and chemically stable. Accordingly, the intercalation of organic species into a $K_4Nb_6O_{17}$ crystal are worth investigating further to construct functional hybrid materials.

Conclusions

Methylene blue/ $K_4Nb_6O_{17}$ intercalation compounds were synthesized by the reaction of methylene blue with a $K_4Nb_6O_{17}$ single crystal in the presence of *n*-propylamine. The intercalation of methylene blue was confirmed by the change in the color (from colorless to pale blue), the increase in basal spacing (from 1.9 to 3.0 nm), and the expansion of the crystal in the crystallographic *b* axis. The products retained the regularity in the *ac* plane, and the intercalated methylene blue ions were arranged in a manner governed by the anisotropy in the *ac* plane so that the dichroic visible absorption spectra were observed. This is the first successful example of an intercalation compound with in plane anisotropy of the intercalated guest species.

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