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Syntheses of Intercalation Compounds of Layered Niobates with Methylviologen and Their Photochemical Behavior

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Intercalation of methylviologen (1,1′-dimethyl-4,4′-bipyridinium ion) into two layered niobates ($K_4Nb_6O_{17}$ and HNb_3O_8) and the photochemical behavior of the resulting compounds were investigated. UV irradiation of the intercalation compounds caused photoinduced electron transfer from the hosts to the guest; the formation of methylviologen radical cations was observed. This behavior was affected by the structure of the intercalation compounds. The radical cations were less stable in HNb_3O_8, where they were more densely packed, than in $K_4Nb_6O_{17}$. Co-intercalation of photoinactive species with methylviologen significantly stabilized the radical cations in both of the hosts. The differences in the photochemistry apparently arises from structural differences.

Introduction

Layered niobates and titanates are invaluable host materials for intercalation chemistry because their interlayer spaces in conjunction with their semiconducting properties enable them to act as photocatalysts for water splitting.[1–3] In particular, potassium niobate $K_4Nb_6O_{17}$ has two types of alternating interlayers (interlayers I and II).[4] The layered structure of $K_4Nb_6O_{17}$ consists of stacked $[Nb_6O_{17}]^{4-}$ layers (Figure 1). In the interlayer I, K^+ ions are present in "more open" cavities than those in the interlayer II. Chemical reactivity of interlayer K^+ ions in the interlayers I and II should be different. In fact, $K_4Nb_6O_{17}$ shows specific intercalation and photocatalytic properties; each interlayer type exhibits a different intercalating capability.[5] Overall photocatalytic water decomposition is achieved on the basis of the difference in the intercalating capability; two interlayers play different roles in the photocatalysis by loading of Ni or Pt which is intercalated only in the interlayer I.[1] Therefore, novel photofunctional intercalation compounds of these layered semiconductors can be produced by choosing suitable photo/electrofunctional guest species.

We have investigated the synthesis and the photochemistry of intercalation compounds formed between several layered niobates and titanates ($K_4Nb_6O_{17}$, $HTiNbO_5$, and $H_2Ti_4O_9$) and methylviologen (MV^{2+}). The photoinduced electron transfer from the hosts to the guest within these intercalation compounds has been observed.[6] The photochemistry of these solid systems has been characterized by the stability of methylviologen radical cations ($MV^{\bullet+}$) which form as the result of photoinduced host–guest electron transfer. Moreover, their stability has differed with the structure of the intercalation compounds.[6d] In the MV^{2+}–$K_xNb_6O_{17}$ intercalation compound, MV^{2+} was present only in the interlayer I. With this distribution of the guest species, $MV^{\bullet+}$ is stabilized probably by a restricted back reaction. In the MV^{2+}–H_xTiNbO_5, MV^{2+} was more densely packed than in the other intercalation compounds. It is inclined to $[TiNbO_5]^-$ layers and is less stable than in the other compounds.

Such a relationship between the photochemical behavior and the structures of the intercalation compounds is important. To spatially organize each chemical component to facilitate total photochemical reactions is important in the synthesis of novel photofunctional materials by intercalation reactions. However, only few studies have focused on the structural control of photochemical properties of intercalation compounds. Also in the MV^{2+}-layered semiconductors, further investigations using other related hosts is necessary to clarify the host–guest interactions in detail.

On the other hand, modification of the interlayer spaces by co-intercalation of other species should be regarded as a useful method to assist photoinduced energy/electron transfer in intercalation compounds. An electron-transport chain composed of three components has been organized at a molecular level in a zeolite matrix.[7] Thus, investigations aimed at altering the photochemical properties of MV^{2+}-niobate/titanate intercalation compounds by co-intercalation of other guests was also indicated.

In the present study we have used two layered niobates, $K_4Nb_6O_{17}$ and HNb_3O_8, as hosts to form MV^{2+} intercalates. HNb_3O_8 has only one type of the interlayer (Figure 2). Two intercalation compounds of $K_4Nb_6O_{17}$ with MV^{2+} were synthesized; K^+ ions were co-intercalated with MV^{2+} in one compound and K^+ ions were almost removed in the other. Two types of MV^{2+}–$H_xNb_3O_8$ intercalation compounds were also prepared; one compound contained *n*-propylammonium ions (PA^+) with MV^{2+} and the other only contained MV^{2+}. The photochemical behavior of these intercalation compounds was investigated, and $MV^{\bullet+}$ was found to be extremely well stabilized by the co-intercalation of K^+ or PA^+. The results show that modification of interlayer spaces by co-intercalation of photoinactive guests alters the interlayer environment so

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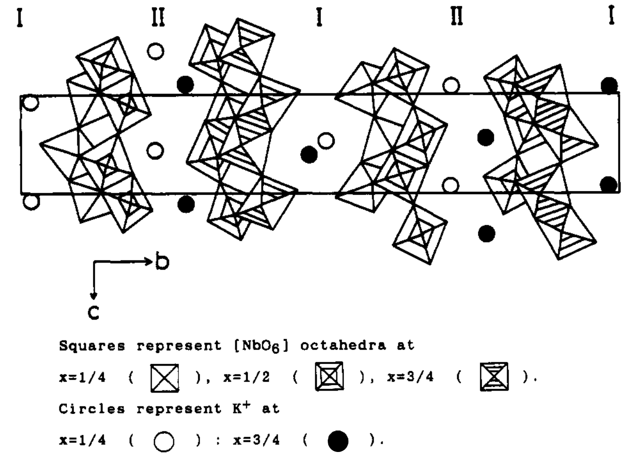

Figure 1. Structure of $K_4Nb_6O_{17}{\cdot}3H_2O$ showing the two the interlayer spaces.[4]

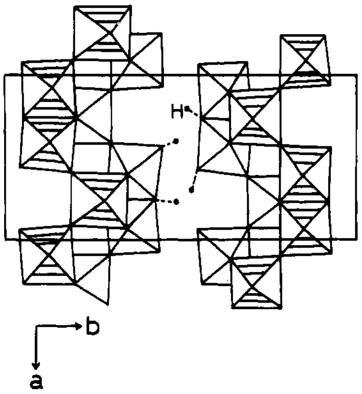

Figure 2. Structure of HNb_3O_8.[9]

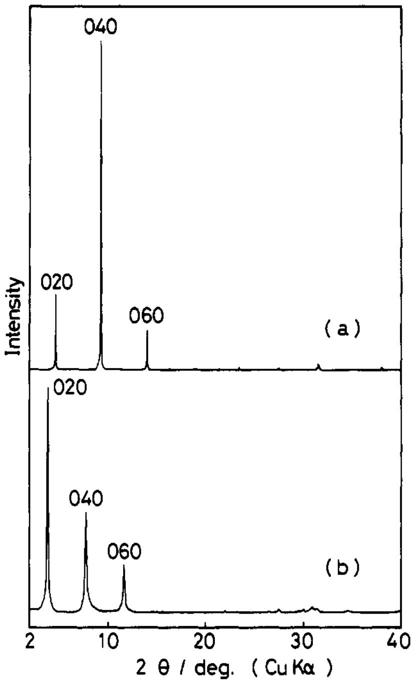

Figure 3. XRD patterns of (a) $K_4Nb_6O_{17}{\cdot}3H_2O$ and (b) MV^{2+}–$K_xNb_6O_{17}$ intercalation compound kept under ambient conditions (obtained by the reaction for 3 weeks).

changing the photochemical behavior of the intercalation compounds.

Experimental Section

Materials. $K_4Nb_6O_{17}$ and HNb_3O_8 were prepared by the methods reported previously.[8,9] $K_4Nb_6O_{17}{\cdot}3H_2O$ was obtained by heating a 2.1:3.0 molar mixture of K_2CO_3 (Kokusan Kagaku Co.) and Nb_2O_5 (Wako Pure Chemical Ind. Co.) at 1100 °C for 10 h. KNb_3O_8 was prepared by heating of a mixture of K_2CO_3 and Nb_2O_5 (2.1:1.0) under the same conditions. $HNb_3O_8{\cdot}H_2O$ was formed by the treatment of KNb_3O_8 with 6.5 N HNO_3. These oxide products were identified by XRD and ICP analyses. The acid treatment of KNb_3O_8 was shown by inductively coupled plasma emission spectroscopy (ICP) to remove 97% of K^+ ions. Commercially available methylviologen dichloride (Tokyo Kasei Co.) was used without further purification.

Syntheses of the Intercalation Compounds. Intercalation of $K_4Nb_6O_{17}$ by MV^{2+} was carried out by direct reaction. $K_4Nb_6O_{17}$ was reacted with an excess of MV^{2+} in an aqueous solution (1.0 mol dm^{-3}) in a glass ampule at 60 °C. By using different reaction times, two different samples were obtained; one was prepared by a 3-week reaction and the other by repeating the reaction for 2 weeks three times (total 6 weeks).

Two MV^{2+}–$H_xNb_3O_8$ intercalation compounds were obtained by different procedures. One was the guest-exchange method previously used to obtain the intercalation compounds of $H_2Ti_4O_9$ and $HTiNbO_5$ with MV^{2+}.[6a,b] $HNb_3O_8{\cdot}H_2O$ was sealed in a glass ampule containing an excess of 50% *n*-propylamine aqueous solution and allowed to stand for 1 week at 60 °C. The product was washed with acetone and dried under ambient conditions. Powder X-ray diffraction (XRD) and infrared spectroscopy (IR) analyses confirmed that an *n*-propylammonium (PA^+)–$H_xNb_3O_8$ intercalation compound had been formed.[10] The d_{020} spacing of the intercalation compound was 1.48 nm, being close to the value reported previously (1.466 nm). The PA^+–intercalate was then allowed to react at 110 °C with an excess amount of a 0.2 mol dm^{-3} MV^{2+} aqueous solution in a sealed Teflon bottle for 2 weeks. By the other method, HNb_3O_8 was intercalated with MV^{2+} by using a direct reaction. Such a method had not been successful with $H_2Ti_4O_9$ or $HTiNbO_5$. The reaction was carried out by heating a mixture of $HNb_3O_8{\cdot}H_2O$ and an excess amount of a MV^{2+} aqueous solution (0.2 mol dm^{-3}) in a sealed Teflon bottle at 110 °C for 2 weeks. All the products were thoroughly washed with methanol and dried under ambient conditions.

Analyses. All samples were characterized by XRD and IR. XRD patterns were obtained from Rigaku RADI-C (Ni-filtered Cu Kα radiation) and Rigaku RADII-A (Mn-filtered Fe Kα radiation) diffractometers. Powdered samples (<100 mesh) for XRD were used without any techniques to orient them. IR spectra were recorded on a Perkin-Elmer FTIR-1640 spectrometer (KBr disk technique). The composition of the samples was determined by ICP (Nippon Jarrell Ash ICAP-575-II) and conventional elemental (C, H, N) analyses.

Observation of Photochemical Behavior. The photochemical behavior of the MV^{2+} intercalates was observed spectroscopically. The intercalation compounds were dispersed into methanol and dropped onto inside window of a glass cell for visible spectroscopy. The cell coated with the powdered samples was irradiated by a 100-W super-high-pressure mercury lamp (Ushio USH-102D) and purged with oxygen, air, or argon. We did not estimate the thickness and uniformity of the coated samples. The absorption spectra of the samples in the visible region were measured by diffuse reflectance using either a Hitachi U-3200 or a Shimadzu UV-210A spectrometer equipped with integrating spheres.

Results and Discussion

Syntheses of MV^{2+}–$K_xNb_6O_{17}$ Intercalation Compounds. The XRD patterns, shown in Figure 3, indicated that the interlayer structure of $K_4Nb_6O_{17}$ was changed by the reaction with MV^{2+} because the relative intensities of the (020) and the (040) peaks altered. The relative in-

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Table I. Basal Spacings of the Samples

sample	basal spacing/nm	Δd/nm
$K_4Nb_6O_{17}$ (anhyd)	1.64	
$MV-K_2Nb_6O_{17}$[a]	2.05	0.41
$MV/K-K_2Nb_6O_{17}$[b]	2.07	0.43
HNb_3O_8 (anhyd)	0.93	
$MV-HNb_3O_8$[c]	1.42	0.49
$MV/PA-HNb_3O_8$[d]	1.47	0.54

[a] $MV^{2+}-K_2Nb_6O_{17}$ intercalation compound obtained by three times of the treatment for 2 weeks. [b] $MV^{2+}-K_2Nb_6O_{17}$ intercalation compound obtained by the reaction for 3 weeks. [c] $MV^{2+}-H_xNb_3O_8$ intercalation compound obtained by the direct reaction. [d] $MV^{2+}-H_xNb_3O_8$ intercalation compound obtained by the guest-exchange reaction.

Table II. Composition of the Intercalation Compounds

compound[a]	MV/mol	K or PA/mol	Nb/mol
$MV-K_2Nb_6O_{17}$	0.4	2.1	6.0
$MV/K-K_2Nb_6O_{17}$	0.3	2.7	6.0
$MV-HNb_3O_8$	0.3		3.0
$MV/PA-HNb_3O_8$	0.2	0.3	3.0

[a] Abbreviations of the intercalation compounds are the same as those in Table I.

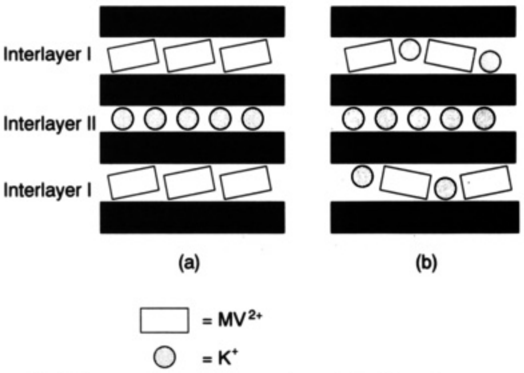

Figure 4. Schematic representation of the interlayer structure of (a) $MV-K_2Nb_6O_{17}$ and (b) $MV/K-K_2Nb_6O_{17}$.

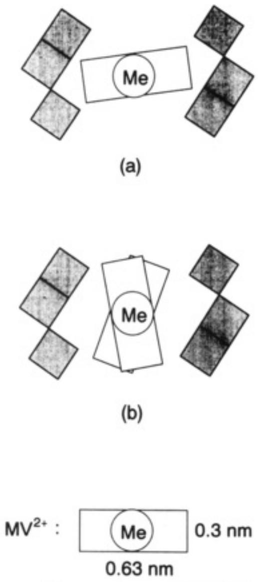

Figure 5. Possible conformations of MV^{2+} ions (a) with keying into the cavity provided by $[Nb_6O_{17}]^{4-}$ layers and (b) inclined with respect to the layers without keying in the interlayer of $K_4Nb_6O_{17}$.

tensities of these two peaks reflect a difference in the X-ray scattering by the interlayers I and II. For example, in $K_4Nb_6O_{17}$ (anhydrous), the two interlayers are indistinguishable from each other, so the (020) diffraction peak does not occur.[8] In the XRD pattern of $K_4Nb_6O_{17}\cdot 3H_2O$, the usual hydration state under ambient conditions, the (020) peak appears with a low intensity because water molecules are intercalated only into the interlayer I (Figure 3a).[8] But, if the difference between the interlayers becomes large, e.g. by intercalation of a bulky guest species only into the interlayer I, the intensity of the (020) peak would be larger that that of the (040) peak. In the XRD pattern of the reaction products formed between MV^{2+} and $K_4Nb_6O_{17}$, the (020) peak is strong, indicating a large difference between the two interlayers (Figure 3b, the two products with the different reaction time showed similar XRD patterns). Thus, the exchange of K^+ by MV^{2+} should occur only in the interlayer I.

Table I shows the basal spacings of the samples and the Δd values (increase in the basal spacing following intercalation). These values were obtained after dehydration of the samples at 60 °C under reduced pressure, whereas Figure 3b shows the XRD pattern of the product kept under ambient conditions. The d_{020} values, corresponding to the sum of the two interlayer spacings, were adopted as the basal spacings. On the other hand, it was a problem that what spacing should be subtracted from the basal spacing of the products. The *b* parameter of $K_4Nb_6O_{17}$ (anhydrous) is the same as that of $Rb_4Nb_6O_{17}$ (anhydrous) although the ionic radius of K^+ is smaller than that of Rb^+.[4] Therefore, the basal spacing of $K_4Nb_6O_{17}$ (anhydrous) (d_{020} = 1.64 nm) should reflect the narrowest interlayer spacing, and we adopted this value.

The composition of the intercalation compounds is shown in Table II. Since the negative charge of a $[Nb_6O_{17}]^{4-}$ layer is not completely balanced by K^+ and MV^{2+} ions, protons (or oxonium ions) may also be present in the interlayers. In the intercalation compound obtained by the three repeated 2-week reaction, half the K^+ ions remained. Thus, the reaction product incorporated MV^{2+} only in the interlayer I, where almost all the K^+ ions were removed. On the other hand, the intercalation compound formed during the 3-week reaction period had a larger amount of K^+ than in the product given by three repeated 2-week reaction. Therefore, this intercalation compound contained K^+ ions not only in the interlayer II but because of incomplete exchange of K^+ also in the interlayer I. Namely, K^+ ions were co-intercalated with MV^{2+} in the interlayer I. Thus we designate the intercalation compound obtained by three times the treatment for 2 weeks as $MV-K_2Nb_6O_{17}$ and the intercalation compound given by the 3-week reaction as $MV/K-K_2Nb_6O_{17}$. The interlayer structure of these two intercalaction compounds are illustrated in Figure 4.

The arrangement of MV^{2+} is inferred from the basal spacings. Intercalation of a flat monolayer of MV^{2+} was reported to increase the basal spacings of clay minerals and MPS_3 (M = Mn, Cd, and Fe) by 0.28–0.33 nm.[11] If $K_4Nb_6O_{17}$ intercalated MV^{2+} into both of its interlayers, the Δd value would be larger than ca. 0.6 nm. Although $[Nb_6O_{17}]^{4-}$ layers are not flat and have cavities accommodating K^+ ions in the interlayer I, bulky MV^{2+} ions (0.63 nm × 1.34 nm × 0.3 nm)[11b] cannot be oriented to give a smaller Δd value than 0.3 nm even if they keyed into the cavities as shown in Figure 5a. Therefore, the Δd values in Table I reveal that MV^{2+} was intercalated into only one interlayer, agreeing with the intensity ordering of the (020) and the (040) peaks. The values also indicate that the arrangement of MV^{2+} ions are not flat with respect to the

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layers. Possible conformations are represented in Figure 5. Twist of two pyridyl rings of MV^{2+} with respect to each other is also possible (Figure 5b).

The compositions of the intercalation compounds agree with this assumption. The area of the $[Nb_6O_{17}]^{4-}$ layer surface per charge is calculated as 0.126 nm^2,[4] and the area of a molecular plane of MV^{2+} is estimated as 0.734 nm^2.[11b] If MV^{2+} is recognized as a rectangular shape, the area is calculated as 0.63 nm × 1.34 nm = 0.844 nm^2.[11b] Thus, the maximum amount of MV^{2+} which can be intercalated as a flat monolayer in the interlayer I is estimated as 0.34 mol of MV^{2+} per $[Nb_6O_{17}]^{4-}$. Therefore, MV^{2+} cannot be arranged in flat monolayer in $MV–K_2Nb_6O_{17}$. MV^{2+} ions should be inclined to reduce their projected area to 0.63 nm^2 because the amount of MV^{2+} is 0.4 mol per $[Nb_6O_{17}]^{4-}$. The tilt angle of MV^{2+} is calculated as 43° from the Δd value when its 0.63-nm side is inclined, and then the projected area of MV^{2+} is calculated as 0.62 nm^2 for the rectangular shape of MV^{2+}. If the size of methyl groups of MV^{2+} is accurately estimated, the value becomes 0.54 nm^2. The former value agrees with the required projected area. These results lead to the conclusion that the surface of $[Nb_6O_{17}]^{4-}$ layers is almost covered with closely packed MV^{2+} except the neighborhood of its methyl groups. On the other hand, the amount of MV^{2+} in $MV/K–K_2Nb_6O_{17}$ reveals that MV^{2+} can be accommodated flat. However, MV^{2+} is supposed to be inclined by taking into account co-intercalated K^+ ions.

Synthesis of MV^{2+}-$H_xNb_3O_8$ Intercalation Compounds. Intercalation of MV^{2+} was confirmed by XRD and IR. Since HNb_3O_8 contains only one type of interlayer, its XRD patterns can be easily interpreted. The XRD patterns of the intercalation products indicated that the basal spacings (d_{020} values) had increased from 0.93 nm for HNb_3O_8 (anhydrous) as shown in Table I. The Δd values were obtained on the basis of the basal spacing of HNb_3O_8 (anhydrous) which reflects the lowest interlayer spacing of the HNb_3O_8 system. In addition, many absorption bands due to MV^{2+} were observed in the IR spectra of both the samples.

On the other hand, the basal spacing of the guest exchanged product was close to that of the $PA^+–H_xNb_3O_8$ intercalation compound (1.48 nm). The (020) peak of the product had a symmetrical shape, in accord the compound having a homogeneous composition. Therefore, we assume that PA^+ remains after the reaction of the $PA^+–H_xNb_3O_8$ intercalation compound with MV^{2+}. IR and elemental analyses supported this assumption. In the IR spectrum, absorption bands for PA^+ were observed in addition to those for MV^{2+}. The C:N atomic ratio of the sample was 4.5:1, which was an intermediate value between the ratios of PA^+ (3:1) and MV^{2+} (6:1). Therefore, we conclude that PA^+ is co-intercalated with MV^{2+} in this intercalation compound. We designate the intercalation compound obtained by the direct reaction and the guest exchanged product as $MV–HNb_3O_8$ and $MV/PA–HNb_3O_8$, respectively.

The arrangement of MV^{2+} in HNb_3O_8 was deduced from the intercalate's basal spacings and the composition. Table II lists the composition of the intercalation compounds. The organic contents of $MV/PA–HNb_3O_8$ were divided into the amounts of PA^+ and MV^{2+} on the basis of the C:N ratio. The Δd values were larger than those for $MV^{2+}–K_2Nb_6O_{17}$ intercalation compounds, indicative of inclined arrangements for MV^{2+}. Although $[Nb_3O_8]^-$ layers have small cavities, MV^{2+} cannot be keyed into the cavities as in the case of the $MV^{2+}–K_4Nb_6O_{17}$ system. Bilayer arrangements are not possible because the Δd values are too small. The area of $[Nb_3O_8]^-$ layer surface per one charge is calculated as 0.171 nm^2.[9] Hence, the amount of MV^{2+} (0.734 nm^2) must be below 0.23 mol per $[Nb_3O_8]^-$ if the arrangement is a flat monolayer. If HNb_3O_8 contains 0.3 mol of MV^{2+} per $[Nb_3O_8]^-$ as it does in $MV–HNb_3O_8$, the projected area of MV^{2+} onto the layer surface must be smaller than 0.57 nm^2. On the other hand, the tilt angle of MV^{2+} molecular plane to the host layer is calculated as 51° when 0.63 nm side of the rectangle is inclined. In this situation, the projected area of MV^{2+} is estimated as 0.53 nm^2 for rectangular MV^{2+}. It is also estimated as 0.46 nm^2 if the size of methyl groups of MV^{2+} is accurately estimated. These values are smaller than the maximum projected area. The fraction of the $[Nb_3O_8]^-$ layer surface covered by MV^{2+} is estimated as 80%.

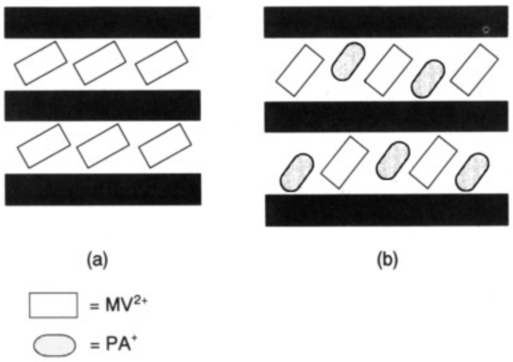

Figure 6. Schematic representation of the interlayer structure of (a) $MV–HNb_3O_8$ and (b) $MV/PA–HNb_3O_8$.

Table III. Half-Lives of $MV^{\bullet +}$ in Various Intercalation Compounds

	in oxygen	in air	in argon
$MV–K_2Nb_6O_{17}$[a]	15 min	45 min	2 h
$MV/K–K_2Nb_6O_{17}$	2 h	6 h	
$MV–HNb_3O_8$	3 min	4 min	10 min
$MV/PA–HNb_3O_8$	1 h	4 h	
$MV^{2+}–H_xTiNbO_5$[a]	3 min	4 min	20 min

[a] Reference 6d.

For $MV/PA–HNb_3O_8$ the basal spacing was close to that of the $PA^+–H_xNb_3O_8$ intercalation compound as described above. This indicates that the arrangement of PA^+ was not greatly altered by the reaction with MV^{2+}. Since PA^+ ions are arranged transversally in the $PA^+–H_xNb_3O_8$ intercalation compound, they can be regarded as "pillars" in $MV/PA–HNb_3O_8$. Therefore, we deduce that MV^{2+} is present among the pillars of PA^+ in $MV/PA–HNb_3O_8$. The interlayer structure of these intercalation compounds is represented in Figure 6 schematically.

Photochemical Behavior of $MV^{2+}–K_xNb_6O_{17}$ Intercalation Compounds. We have already reported the photochemical behavior of $MV–K_2Nb_6O_{17}$; electron transfer occurred from the $[Nb_6O_{17}]^{4-}$ layers to the intercalated MV^{2+} when the intercalation compound was irradiated by UV.[6d] The photochemical behavior was characterized by high stability of $MV^{\bullet +}$ which formed as the result of the photoinduced electron transfer. $MV^{\bullet +}$ was highly stabilized in $K_4Nb_6O_{17}$ as compared with it in $H_2Ti_4O_9$ and $HTiNbO_5$.

In the present study, we found that the stability of $MV^{\bullet +}$ was markedly enhanced in $MV/K–K_2Nb_6O_{17}$. Table III compares the stability of $MV^{\bullet +}$ in various intercalation compounds. The half-lives were determined by the decay of the optical density at 620 nm, the characteristic absorption band of $MV^{\bullet +}$, as measured by diffuse reflectance spectroscopy. The photochemical behavior of intercalated MV^{2+} is only significantly affected by co-intercalated small

Figure 7. Visible diffuse reflectance spectra after UV irradiation of (a) MV/PA-HNb_3O_8 and (b) MV-HNb_3O_8. These spectra were measured in air after 2 min of irradiation.

photoinactive ions such as K^+. Co-intercalation however had little effect upon the arrangement. This indicates that there are some guest-guest interactions in the photochemical reaction of the intercalation compounds in addition to host-guest interactions. Co-intercalation of K^+ should alter the guest-guest interactions. On the other hand, we could not observe obvious differences in the intensity of the absorption band of $MV^{\bullet+}$ between the two intercalation compounds both of which contained similar amount of MV^{2+}. This indicates that there are no significant differences in the photostationary states of the intercalation compounds, and we presume that co-intercalation of K^+ ions influences only the back reaction ($MV^{\bullet+} + h^+ \rightarrow MV^{2+}$).

Photochemical Behavior of MV^{2+}-$H_xNb_3O_8$ Intercalation Compounds. Both MV-HNb_3O_8 and MV/PA-HNb_3O_8 exhibited a blue color by UV irradiation, as do the other compounds of layered niobate and titanate intercalated with MV^{2+}. Figure 7 shows the visible diffuse reflectance spectra of MV^{2+}-$H_xNb_3O_8$ intercalation compounds after the irradiation. They are typical spectra of $MV^{\bullet+}$ monomers.[12] Thus the spectra confirmed that on UV irradiation HNb_3O_8 donated electrons to intercalated MV^{2+} as do the other layered niobates and titanates.

However, the absorption intensity due to $MV^{\bullet+}$ apparently is lower in MV-HNb_3O_8 than that in MV/PA-HNb_3O_8, and the stability of $MV^{\bullet+}$ was also much lower in MV-HNb_3O_8 than in MV/PA-HNb_3O_8. The stability is summarized in Table III. The decaying behavior of $MV^{\bullet+}$ in MV-HNb_3O_8 is comparable to that in the MV^{2+}-H_xTiNbO_5 intercalation compound, being characterized by unstable $MV^{\bullet+}$ even under an argon flow. This similarity should be related to the structural resemblance of the two intercalation compounds. Both compounds contain rather large amounts of MV^{2+} with the guest ions are arranged so that their molecular planes are inclined to the host layer. Such inclined orientations of MV^{2+} reduce the distance between adjacent MV^{2+} sites and enable the bipyridine rings to partially face one another. Therefore, we suppose that electron hopping occurs between adjacent MV^{2+} sites and then $MV^{\bullet+}$ decays faster. The lower absorption intensity of MV-HNb_3O_8 than that of MV/PA-HNb_3O_8 can also be explained by guest-guest interactions; total efficiency of the photoreduction may be decreased through prompt decay of $MV^{\bullet+}$ by interactions with neighboring MV^{2+}. On the other hand, since the diffuse reflectance spectrum showed only the presence of $MV^{\bullet+}$ monomers, the interactions did not cause dimerization of $MV^{\bullet+}$, as observed in electrochemical reduction of MV^{2+} in montmorillonite.[13] Electrostatic interactions between $[Nb_3O_8]^-$ layers and MV^{2+} should restrict conformational changes by the photochemical reaction.

On the other hand, $MV^{\bullet+}$ formed in MV/PA-HNb_3O_8 was much more stable than that in MV-HNb_3O_8. The stability was comparable to that in MV/K-$K_2Nb_6O_{17}$. In MV/PA-HNb_3O_8, MV^{2+} is regarded as diluted by PA^+ although the inclined conformation of MV^{2+} itself to the host layer is similar to that in MV^{2+}-$H_xNb_3O_8$. PA^+ can not be considered as playing an essential role, e.g., act as donor or acceptor in the reaction, in the host-guest electron transfer. In addition, *n*-propylamine (not propylammonium), which can act as an electron donor, is scarcely present as it is removed during the washing of the PA^+-$H_xNb_3O_8$ intercalate and the following reaction with MV^{2+}. Therefore, we suppose that the electron hopping between adjacent MV^{2+} sites is restricted by PA^+ pillars. Namely, MV-MV interactions which make $MV^{\bullet+}$ unstable are restrained by PA^+ ions which are present among MV^{2+}. The role of PA^+ is essentially the same as that of K^+ in MV/K-$K_2Nb_6O_{17}$. The slow decay of $MV^{\bullet+}$ in MV/K-$K_2Nb_6O_{17}$ also reflects the inability of photoinactive K^+ to interfere with MV-MV interactions.

Conclusion

We demonstrated that the photochemistry of intercalation compounds formed between the layered niobates $K_4Nb_6O_{17}$ and HNb_3O_8 with MV^{2+} can be controlled by changing the interlayer structures in these compounds. Two types of intercalation compounds were prepared for each host; one type contained only MV^{2+} in their interlayers and the other co-intercalated photoinactive species with MV^{2+}. All the intercalation compounds formed $MV^{\bullet+}$ in the interlayers by photoinduced host-guest electron transfer. The presence of co-intercalated species significantly affected the decay of $MV^{\bullet+}$. This difference was explained by guest-guest interactions which varied with the co-intercalation of photoinactive guests. The results have shown that the modification of photochemical properties can be effected by introducing various guest species into two-dimensional spaces. The concept is of importance to the design of highly organized photochemical systems based on layered matrices.

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Registry No. $MVCl_2$, 1910-42-5; PA, 107-10-8; $MV^{\bullet+}$, 25239-55-8; $K_4Nb_6O_{17}$, 12142-45-9; HNb_3O_8, 67724-84-9; K_2CO_3, 584-08-7; Nb_2O_5, 1313-96-8.

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