Reactivity of the Ruddlesden−Popper Phase $H_2La_2Ti_3O_{10}$ with Organic Compounds: Intercalation and Grafting Reactions

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A protonated form of the Ruddlesden−Popper-type ion-exchangeable layered perovskite $H_2La_2Ti_3O_{10}$ (H_2LaTi) has been modified with *n*-alkylamine and *n*-alcohols to yield intercalation compounds and alkoxy derivatives, respectively. As concerns the intercalation of *n*-alkylamines into H_2LaTi, no reaction of H_2LaTi with *n*-butylamine occurred in anhydrous solvent, and the addition of water was required for the successful intercalation of *n*-butylamine into H_2LaTi. The successful uptake of *n*-butylammonium ions from an *n*-butylammonium hydroxide aqueous solution suggests that the intercalation mechanism is of the ion-exchange type rather than the acid−base type. For interlayer surface modification with *n*-alcohol, no direct reaction of H_2LaTi with *n*-alcohol occurred, but the *n*-propoxy derivative of H_2LaTi formed by using the intercalation compound of H_2LaTi with *n*-butylamine as an intermediate. In addition, reactions between the *n*-propoxy derivative of H_2LaTi and *n*-alcohols (*n*-butanol, *n*-octanol, *n*-decanol, and *n*-dodecanol) led to the formation of various *n*-alkoxy derivatives via an alcohol-exchange-type reaction. As the model for *n*-alkoxy derivatives of H_2LaTi, a bilayer arrangement of the *n*-alkyl chain possessing an *all-trans* ordered state with a 75° tilting angle is proposed. The reaction mechanisms of these reactions are also discussed.

Introduction

Inorganic−organic hybrids are interesting materials, because they potentially exhibit a combination of the properties of organic materials with those of inorganic materials.[1−5] Various approaches have been developed for the preparation of inorganic−organic hybrids. Intercalation is one of the approaches for preparing two-dimensional inorganic−organic hybrids;[1−3] some inorganic layered materials consisting of stacked inorganic layers can uptake organic molecules/ions into the interlayer space to form two-dimensional inorganic−organic hybrids (so-called "intercalation compounds") where inorganic layers and organic molecules/ions are stacked alternately. Interaction between inorganic layers and organic molecules/ions leads to formation of the well-organized organic molecular assemblies in the interlayer space,[1] and the packing of organic molecules/ions is affected by various factors including the layer charge. Selection of the layered materials is therefore very important for tuning properties of inorganic−organic hybrids. Among layered materials, layered transition metal oxides are attractive host materials for intercalation, because the layered transition metal oxides exhibiting interesting properties, such as ferroelectricity and semiconductivity, could bring additional interaction between the inorganic layers and the organic molecules/ions.[6]

Among the layered materials capable of intercalation, ion-exchangeable layered perovskites are of particular interest, because the inorganic layers, which possess a perovskite-related structure, potentially exhibit attractive dielectric and optoelectronic properties as well as photocatalytic activities. Ion-exchangeable layered perovskites consist of perovskite-like slabs, $[A_{m-1}B_mO_{3m+1}]$ (where "*m*" expresses the thickness of the perovskite-like slabs) and interlayer cations, M, leading to the general formula $M_x[A_{m-1}B_mO_{3m+1}]$.[7] Acid treatment can easily convert these compounds into the corresponding protonated forms, $H_x[A_{m-1}B_mO_{3m+1}]$.[7] On the basis of the layer charge per $[A_{m-1}B_mO_{3m+1}]$, *x*, ion-exchangeable layered perovskites can be classified into two phases: the Dion−Jacobson phases, which possess one cation per $[A_{m-1}B_mO_{3m+1}]$ ($x = 1$),[8−10] and the Ruddlesden−Popper phases, which possess two cations per $[A_{m-1}B_mO_{3m+1}]$.[11]

Extensive research has been devoted to the intercalation of organic amines into the protonated forms of the Dion−Jacobson phases.[7,12−15] Various organic amines, such as

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n-alkylamine,[12,13,15] pyridine,[12] and aniline,[16] can be intercalated into the interlayer space of protonated forms of the Dion−Jacobson phases via acid−base reactions. Reactions between the Dion−Jacobson phases [$HLaNb_2O_7 \cdot xH_2O$ (HLaNb) and $HCa_2Nb_3O_{10} \cdot xH_2O$ (HCaNb)] and *n*-alcohols have also been reported.[17−20] These reactions with alcohols are not simple intercalation reactions. Instead, intercalation of *n*-alcohols and subsequent dissociative adsorption of *n*-alcohols yields *n*-alkoxy derivatives where *n*-alkoxy groups are bound to the perovskite-like slabs via covalent Nb−O−C bonds. In addition, reactions of the *n*-alkoxy derivatives of HLaNb and HCaNb with organic molecules possessing OH groups lead to the formation of various organic derivatives of HLaNb and HCaNb.[17,19,21−25] There is no report so far, however, on interlayer surface modification of the Ruddlesden−Popper phases.

Ruddlesden−Popper phases are interesting as the host materials for intercalation, because the layer charge of Ruddlesden−Popper phases is twice that of Dion−Jacobson phases. Earlier studies on the intercalation behavior of the Ruddlesden−Popper phases, on the other hand, have been contradictory. Uma et al. first reported that no reaction occurred between *n*-alkylamines and $H_2La_2Ti_3O_{10}$ (H_2LaTi) using *n*-heptane solvent as a result of the low reactivity of H_2LaTi.[26] The low reactivity of H_2LaTi was interpreted on the basis of the assumption that the displacement of adjacent perovskite-like slabs in the Ruddlesden−Popper phases along the *a* and *b* direction leads to the "nesting" of protons in a cavity. (It is worth noting that the protonated forms of Dion−Jacobson phases, on the contrary, exhibit no displacement of perovskite-like slabs in their stacking sequence.) A few recent reports have, however, described intercalation reactions of Ruddlesden−Popper-type tantalates. Schaak and Mallouk reported that *n*-decylamine was intercalated into $H_2CaNaTa_3O_{10}$ using hexane solvent,[27] while Shimizu et al. reported the intercalation of *n*-alkylamines into $H_2SrTa_2O_7$ using water solvent.[28] Recently, moreover, the reaction of an *n*-propylamine−water mixture and the Ruddlesden−Popper-type titanate H_2LaTi was reported to form an intercalation compound.[29] Thus, it has been established that some Ruddlesden−Popper phases do undergo intercalation reactions, but the discrepancy concerning the reactivity of H_2LaTi in terms of the intercalation of *n*-alkylamine remains unsolved.

We report here the reaction of H_2LaTi with two types of organic compounds: *n*-alkylamine for intercalation and *n*-alcohol for interlayer surface modification. The mechanism of intercalation of *n*-butylamine into H_2LaTi is discussed with an emphasis on the role of water. Interlayer surface modification of H_2LaTi with *n*-propanol, alcohol-exchange-type reactions, and structural characterization of the resulting products with *n*-alcohols are also described.

Experimental Section

Materials. The ion-exchangeable layered perovskite, $K_2La_2Ti_3O_{10}$ (K_2LaTi), was prepared by the conventional ceramic method.[11] The lattice parameters calculated from the X-ray diffraction (XRD) pattern by the Rietveld refinement were $a = 0.38746(5)$ and $c = 2.9808(4)$ nm with a tetragonal cell (space group, *I*4/*mmm*), which showed good consistency with the reported values ($a = 0.3874(1)$ and $c = 2.978(2)$ nm).[11] Its protonated form, $H_2La_2Ti_3O_{10}$ (H_2LaTi), was prepared by acid treatment of K_2LaTi with an excess of 1 M HNO_3, as reported elsewhere.[11,29] The XRD pattern of the acid-treated product was indexed with a tetragonal cell, and the lattice parameters were calculated by the least-squares method to be $a = 0.38129(9)$ and $c = 2.748(2)$ nm, which were consistent with the values in an earlier report ($a = 0.3820(9)$ and $c = 2.766(7)$ nm).[11] The elimination of K^+ ions was demonstrated by inductively coupled plasma emission spectrometry. Distillation of *n*-butylamine was conducted over potassium hydroxide, and tetrahydrofuran (THF) was distilled over sodium and benzophenone under ambient pressure. The *n*-butylammonium hydroxide aqueous solution was prepared from an *n*-butylammonium chloride aqueous solution via ion exchange using an anion-exchange resin, Amberlite IRA402BL OH AG. Complete exchange of the Cl^- ions for the OH^- ions was confirmed by ion chromatography.

Instrumentation. The XRD patterns were obtained using a Rigaku RINT-1100 diffractometer with Mn-filtered Fe Kα radiation. The lattice parameters of the products with *n*-alcohols were refined by the least-square method using all the observed reflections. The solid-state ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL CMX-400 spectrometer operated at 100.54 MHz with cross polarization and magic angle spinning techniques (CP/MAS) at a spinning rate of about 5 kHz. The contact time was 1.5 ms, and the pulse delay was 5 s. Chemical shifts were reported with respect to external tetramethylsilane. Liquid-state ^{13}C NMR measurements were performed using a JEOL JNM-Lambda 500 spectrometer operated at 125.65 MHz with tetramethylsilane employed as an external standard. The amounts of carbon and nitrogen were determined by an internal service at the Waseda University Materials Characterization Central Laboratory. Infrared (IR) absorption spectra of the products were recorded on a JASCO FT/IR-460 Plus instrument using the KBr disc technique. The thermogravimetry (TG) curves were obtained using a Perkin-Elmer TGA7 in the range from room temperature to 900 °C (heating rate: 10 °C/min) under air flow.

Reactions of H_2LaTi with *n*-Butylamine and *n*-Butylammonium Hydroxide. The manipulations for the reaction between H_2LaTi and *n*-butylamine were performed using standard Schlenk techniques under a protective nitrogen atmosphere.[30] For the reaction between H_2LaTi and *n*-butylamine, 0.3 g of H_2LaTi and 3

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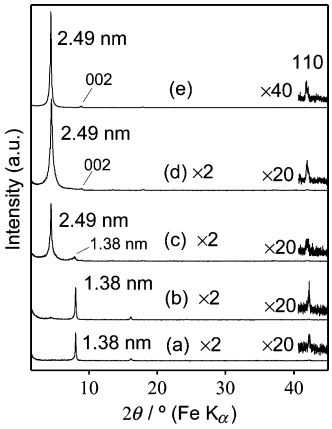

Figure 1. XRD patterns of (a) H_2LaTi, the products of the reaction between H_2LaTi and *n*-butylamine with (b) THF (*n*-butylamine/THF/H_2LaTi), (c) a water−THF mixture (*n*-butylamine/water−THF/H_2LaTi), and (d) water (*n*-butylamine/water/H_2LaTi) and (e) the product of the reaction between H_2LaTi and *n*-butylammonium hydroxide.

mL of distilled *n*-butylamine were allowed to react in 27 mL of water, distilled THF, or a THF−water mixture (5 vol % water) at room temperature for 5 d under a nitrogen atmosphere. After centrifugation and washing with acetone, the product was dried under reduced pressure (abbreviated as *n*-butylamine/water/H_2LaTi, *n*-butylamine/THF/H_2LaTi, and *n*-butylamine/THF−water/H_2LaTi).

For investigation of the reaction mechanism, 0.3 g of H_2LaTi was dispersed in 30 mL of a 0.1 M *n*-butylammonium hydroxide aqueous solution at room temperature for 5 d. After centrifugation and washing with acetone, the product was dried under reduced pressure.

Interlayer Surface Modification with *n*-Alcohols. For the direct reactions with *n*-alcohols (*n*-propanol, ethanol, and methanol), 0.3 g of H_2LaTi and 15 mL of an *n*-alcohol−water mixture (containing 10 mass % water) were reacted in an autoclave for 5 d (at 180 °C for *n*-propanol, 150 °C for ethanol, 100 °C for methanol). After centrifugation and washing with acetone, the product was dried under reduced pressure. For the reaction using an intermediate, 0.3 g of the product of the reaction between H_2LaTi and an *n*-butylamine−water mixture was sealed with 15 mL of *n*-propanol in an autoclave and heated at 180 °C for 5 d. The product was centrifuged, washed with acetone, and dried under reduced pressure (*n*-propanol/H_2LaTi).

For the modification with *n*-alcohols, $C_nH_{2n+1}OH$ ($n = 4$, 8, 10, or 12), 0.3 g of *n*-propoxy/H_2LaTi, and 15 mL of *n*-alcohol were reacted in an autoclave at 150 °C for 5 d. After centrifugation, the product was washed with acetone. The product was then dried at ambient temperature (product with *n*-butanol; *n*-butanol/H_2LaTi) or 150 °C [(products with $C_nH_{2n+1}OH$ ($n = 8$, 10 or 12; *n*-octanol/H_2LaTi, *n*-decanol/H_2LaTi, or *n*-dodecanol/H_2LaTi)].

Results and Discussion

Intercalation of *n*-Alkylamine into H_2LaTi. The intercalation of *n*-butylamine into H_2LaTi was performed using three different types of solvents (anhydrous THF, a THF−water mixture, and water). Figure 1 demonstrates the XRD patterns of H_2LaTi and the products of the reactions between H_2LaTi and *n*-butylamine in the three solvents. In the XRD pattern of the product obtained with anhydrous THF (*n*-butylamine/THF/H_2LaTi, Figure 1b), only the reflection at 1.38 nm, which corresponds to the interlayer distance of H_2LaTi (Figure 1a), is observed, indicating the absence of intercalation. The XRD patterns of the products obtained with

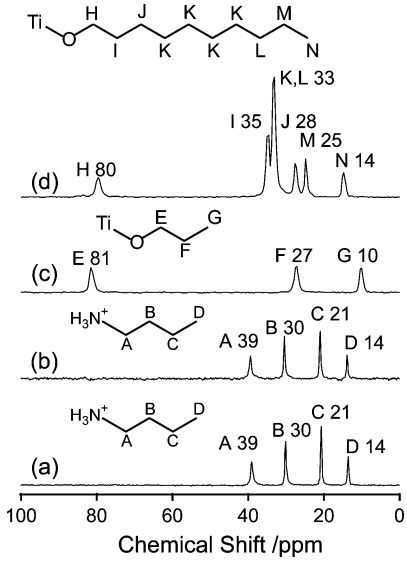

Figure 2. Solid-state ^{13}C CP/MAS NMR spectra of (a) the product of the reaction between H_2LaTi and *n*-butylamine with water (*n*-butylamine/water/H_2LaTi), (b) the product of the reaction between H_2LaTi and *n*-butylammonium hydroxide, (c) the product of the reaction between *n*-butylamine/water/H_2LaTi and *n*-propanol (*n*-propanol/H_2LaTi), and (d) the product of the reaction between *n*-propanol/H_2LaTi and *n*-decanol (*n*-decanol/H_2LaTi).

a THF−water mixture (*n*-butylamine/THF−water/H_2LaTi, Figure 1c) and water (*n*-butylamine/water/H_2LaTi, Figure 1d), on the contrary, show new reflections corresponding to interlayer distances at 2.49 nm. In Figure 1c, a weak reflection is also observed at 1.38 nm, and no reflection is observed at 1.38 nm in Figure 1d, indicating *n*-butylamine/water/H_2LaTi is a single-phase product. The (110) reflection of H_2LaTi at 2.70 nm (due to perovskite-like slabs) does not shift, indicating the preservation of a perovskite-like slab structure. These observations clearly indicate the successful intercalation of *n*-butylamine into H_2LaTi. These results exhibit good consistency with the reported successful intercalation of *n*-propylamine using 50 vol % aqueous solution[29] and no intercalation of *n*-alkylamines in heptane.[26]

The requirement that water be added to achieve successful intercalation suggests that H_2LaTi cannot undergo an acid−base reaction; a possible route is one in which *n*-butylammonium ions (*n*-$C_4H_9NH_3^+$), formed by protonation of *n*-butylamine, are accommodated in H_2LaTi via ion exchange between H^+ in H_2LaTi and *n*-butylammonium ions. To confirm this assumption, an ion-exchange reaction between H_2LaTi and *n*-butylammonium hydroxide was performed at pH ∼ 12. In the XRD pattern of the product of the reaction between H_2LaTi and *n*-butylammonium hydroxide (Figure 1e), a reflection appears at 2.49 nm, indicating the occurrence of intercalation of *n*-butylammonium into H_2LaTi; the proposed ion-exchange mechanism is strongly suggested.

The solid-state ^{13}C CP/MAS NMR spectra of *n*-butylamine/water/H_2LaTi and the product of the reaction between H_2LaTi and the *n*-butylammonium hydroxide aqueous solution are shown in Figure 2. Both the spectra show four signals assignable to CH_3-, CH_3-CH_2-, $CH_2-CH_2-CH_2-N$, and $-CH_2-N$ environments at 14, 21, 30, and 39 ppm, respectively. The profiles of these two spectra are essentially identical, indicating that the organic species in *n*-butylamine/water/H_2LaTi and in the product of the reaction between

Table 1. Amounts of Organic Species per [$La_2Ti_3O_{10}$] in *n*-Butylamine/Water/H_2LaTi, the Product of the Reaction between H_2LaTi and *n*-Butylammonium Hydroxide, *n*-Propanol/H_2LaTi, *n*-Butanol/H_2LaTi, *n*-Octanol/H_2LaTi, *n*-Decanol/H_2LaTi, and *n*-Dodecanol/H_2LaTi

sample	carbon content, mass %	nitrogen content, mass %	amount of *n*-butylammonium per [$La_2Ti_3O_{10}$]	amount of *n*-alkoxy group per [$La_2Ti_3O_{10}$]
n-butylamine/water/H_2LaTi	6.1	1.7	0.81	
product of the reaction between H_2LaTi and *n*-butylammonium hydroxide	6.5	1.8	0.88	
n-propanol/H_2LaTi	5.8	0.0	0	1.0
n-butanol/H_2LaTi	6.9	0.0	0	0.94
n-octanol/H_2LaTi	13.5	0.0	0	0.97
n-decanol/H_2LaTi	16.9	0.0	0	1.0
n-dodecanol/H_2LaTi	20.0	0.0	0	1.0

H_2LaTi and *n*-butylammonium ions are identical. In the liquid-state ^{13}C NMR spectrum of *n*-butylamine in D_2O (Figure S1a, Supporting Information), four signals are observed at 14 (CH_3-), 21 (CH_3-CH_2-), 37 ($CH_2-CH_2-CH_2-N$), and 43 ($-CH_2-N$) ppm. Thus, the signals of the β-carbon atom ($CH_2-CH_2-CH_2-N$) and the α-carbon atom ($-CH_2-N$) shift upfield (β-carbon atom, 37 → 30 ppm; α-carbon atom, 43 → 40 ppm) after intercalation. To interpret these upfield shifts, the ^{13}C NMR spectrum of the *n*-butylamine−hydrochloric acid mixture, whose pH was 1.3, was measured. The spectrum of the *n*-butylamine−hydrochloric acid mixture shows signals at 13, 19, 29, and 39 ppm (Figure S1b, Supporting Information), and the chemical shifts of the α- and β-carbon signals show good consistency with those in the solid-state ^{13}C CP/MAS NMR spectra of the intercalation compounds. Since the upfield shifts of these two signals in *n*-butylammonium ions were attributed to the conversion of $-NH_2$ groups into $-NH_3^+$ groups,[31] the upfield shifts of the α- and β-carbon signals upon intercalation also indicate the *n*-butylamines are present as *n*-butylammonium ions in the interlayer space.

The amount of *n*-butylammonium ions in *n*-butylamine/water/H_2LaTi and the product of the reaction between H_2LaTi and *n*-butylammonium are estimated from the carbon content as listed in Table 1. In both the products, the estimated amount of *n*-butylammonium ions are 0.9 per [$La_2Ti_3O_{10}$]. These results suggest that approximately half the protons in H_2LaTi reacts with *n*-butylamine. Similar results were reported for intercalation into the interlayer space of $H_{1.8}Bi_{0.2}Sr_{0.2}Ta_2O_7$ and were attributed to the relationship between the cross-sectional area of *n*-alkylamine and the interlayer surface geometry of [$Bi_{0.2}Sr_{0.8}Ta_2O_7$]; only every other cavity can be occupied by *n*-alkylamine because of spatial limitations.[32] Because the surface geometry of [$La_2Ti_3O_{10}$] is essentially identical to that of [$Bi_{0.2}Sr_{0.8}Ta_2O_7$], the present results can be explained in a similar fashion.

Interlayer Surface Modification with *n*-Alcohols. Because the protonated forms of a few Dion−Jacobson phases, $HLaNb_2O_7 \cdot xH_2O$ and $HCa_2Nb_3O_{10} \cdot xH_2O$, can react with *n*-alcohols to form *n*-alkoxy derivatives,[18,19] direct reaction of H_2LaTi with *n*-propanol was attempted. The XRD pattern of the product (not shown) showed only reflections due to H_2LaTi, indicating no direct reaction with *n*-propanol. Similar results were obtained with less bulky methanol and ethanol. When *n*-butylamine/water/H_2LaTi is used as an intermediate, on the contrary, the XRD pattern of the product of the reaction with *n*-propanol (*n*-propanol/H_2LaTi) shows a decrease in the interlayer distance from 2.49 to 2.20 nm (Figure 3a). The (110) reflection at 2.70 nm due to perovskite-like slabs does not shift, indicating the preservation of a perovskite-like slab structure.

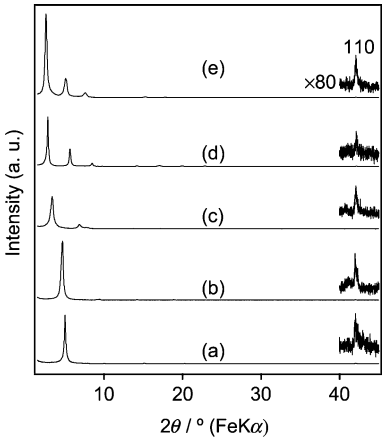

Figure 3. XRD patterns of (a) the product of the reaction between the *n*-butylamine−H_2LaTi intercalation compound and *n*-propanol (*n*-propanol/H_2LaTi), (b) the product of the reaction between *n*-propoxy−H_2LaTi and *n*-butanol (*n*-butanol/H_2LaTi), (c) the product of the reaction between *n*-propoxy-H_2LaTi and *n*-octanol (*n*-octanol/H_2LaTi), (d) the product of the reaction between *n*-propoxy−H_2LaTi and *n*-decanol (*n*-decanol/H_2LaTi), and (e) the product of the reaction between *n*-propoxy−H_2LaTi and *n*-dodecanol (*n*-dodecanol/H_2LaTi).

The solid-state ^{13}C CP/MAS NMR spectrum of *n*-propanol/H_2LaTi is shown in Figure 2c. In the spectrum, no signals due to *n*-butylamine are observed, and signals due to *n*-propoxy groups are detected at 10 (CH_3-), 27 ($CH_3-CH_2-CH_2$), and 81 ($-CH_2-O-$) ppm. As compared to the α-carbon signal of *n*-propanol in the liquid-state NMR spectrum (63 ppm), the α-carbon signal (signal E, 81 ppm) shifts downfield by ∼18 ppm. In the ^{13}C NMR spectra of titanium alkoxides, α-carbon signals of titanium *n*-butoxide and titanium *iso*-propoxide were observed at 76 ppm[33] and 78 ppm,[34] respectively, and these chemical shifts are very close to that of signal E. Similar downfield shifts (∼20 ppm) were also reported, moreover, for the *n*-alkoxy derivative of $HLaNb_2O_7 \cdot xH_2O$ and $HCa_2Nb_3O_{10} \cdot xH_2O$.[18,19,21] The observed downfield shift of α-carbon signals can therefore be taken as evidence for the formation of Ti−O−C bonds; the solid-state ^{13}C CP/MAS NMR spectrum clearly demonstrates the formation of an *n*-propoxy derivative of H_2LaTi.

Thermal decomposition behavior, studied by TG, provides further support for the formation of a Ti−O−C bond. The TG curve of *n*-propanol/H_2LaTi (Figure S2, Supporting Information) is very different from that of *n*-butylamine/

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Table 2. Lattice Parameters (*a* and *c* for Tetragonal Cells) of *n*-Propanol/H_2LaTi, *n*-Butanol/H_2LaTi, *n*-Octanol/H_2LaTi, *n*-Decanol/H_2LaTi, and *n*-Dodecanol/H_2LaTi

sample	*a* lattice parameter, nm	*c* lattice parameter, nm
n-propanol/H_2LaTi	0.3820(7)	2.211(5)
n-butanol/H_2LaTi	0.3823(1)	2.373(1)
n-octanol/H_2LaTi	0.3819(8)	3.238(7)
n-decanol/H_2LaTi	0.38093(3)	3.9183(7)
n-dodecanol/H_2LaTi	0.3816 (4)	4.391(8)

water/H_2LaTi; while the TG curve of *n*-butylamine/water/H_2LaTi shows the onset of decomposition at approximately 80 °C, *n*-propanol/H_2LaTi begins to decompose at approximately 300 °C. This high stability shown by *n*-propanol/H_2LaTi is thought to be attributable to the formation of strong covalent bonds between the organic groups and the surfaces of the inorganic layers.[35] Similar decomposition behavior was reported for the products of grafting reactions between Dion−Jacobson phases, $HLaNb_2O_7 \cdot xH_2O$ and $HCa_2Nb_3O_{10} \cdot xH_2O$, and *n*-alcohol.[18,19,21]

Table 2 shows the amounts of carbon and nitrogen in the product and the estimated amount of *n*-propoxy groups per $[La_2Ti_3O_{10}]$. Because no nitrogen is present in *n*-propanol/H_2LaTi, all the *n*-butylamine in the interlayer space must have been removed during the reaction with *n*-propanol, a result consistent with the solid-state ^{13}C NMR result. The amount of *n*-propoxy groups per $[La_2Ti_3O_{10}]$ is therefore calculated from the carbon content (5.8%) to be 1.0. This can be interpreted based on the arrangement of *n*-propoxy groups on the interlayer surface (Figure 4). On the interlayer surface of H_2LaTi, all the octahedra possess protons for formation of $HOTiO_5$ sites. When one $HOTiO_5$ site reacts with *n*-alcohol to form an $(RO)TiO_5$ site, the four nearest $HOTiO_5$ sites (indicated by the triangles in Figure 4) cannot react with *n*-alcohol, because the cross-sectional area of the *n*-alkyl chain (0.186 nm^2, diameter 0.48 nm)[36] is larger than the area of a perovskite-like slab per $[La_2Ti_3O_{10}]$, approximately 0.144 nm^2 ($= a \times a = 0.382 \times 0.382$ nm^2). The ideal amount of alkoxy groups per $[La_2Ti_3O_{10}]$ is therefore estimated to be 1.0, which corresponds to the maximal value for Dion−Jacobson-type $HLaNb_2O_7 \cdot xH_2O$ and $HCa_2Nb_3O_{10} \cdot xH_2O$, where every other octahedron bears protons ($NbO_6/HONbO_5 = 1:1$) on the interlayer surface; 1.0 *n*-propoxy groups per $[La_2Ti_3O_{10}]$ is therefore considered to be maximal based on the surface area of the perovskite-like slabs and the cross-sectional area of the *n*-alkyl chain.

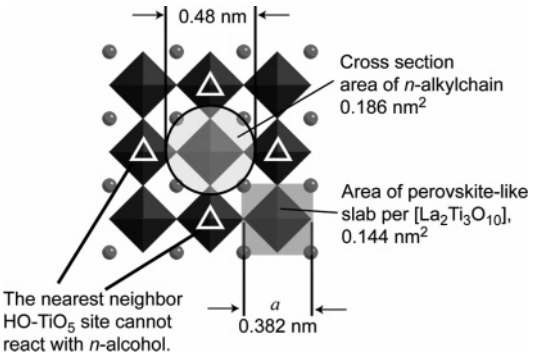

Figure 4. Relationship between the area of the HO−TiO_5 site and that of the *n*-alkyl chain.

Alcohol-Exchange-Type Reaction. Because the *n*-alkoxy derivative of the protonated forms of Dion−Jacobson phases, $HLaNb_2O_7 \cdot xH_2O$ and $HCa_2Nb_3O_{10} \cdot xH_2O$, can be reacted with alcohols to form various organic derivatives via alcohol-exchange-type reactions,[19,21] we conducted reactions of an *n*-propoxy derivative of H_2LaTi with excess amounts of *n*-alcohols, *n*-$C_nH_{2n+1}OH$ ($n = 4$, 8, 10, 12). The XRD patterns of the products are shown in Figure 3b−e, and Table 2 lists their lattice parameters (*a* and *c*) calculated from the XRD patterns for the tetragonal cells. The interlayer distances increase after the reactions with *n*-alcohols, *n*-$C_nH_{2n+1}OH$ ($n = 4$, 8, 10, 12), suggesting the occurrence of substitution reactions.

The solid-state ^{13}C CP/MAS NMR spectrum of the product of the reaction between *n*-propanol/H_2LaTi and *n*-decanol is shown in Figure 2d. No signals due to *n*-propoxy groups are observed, and new signals assignable to *n*-decoxy groups are detected at 14, 25, 28, 33, 35, and 80 ppm. The downfield shift of the α-carbon signal (from 63 ppm observed in a liquid-state ^{13}C NMR spectrum of *n*-decanol to 80 ppm) indicates the formation of Ti−O−C bonds. The solid-state ^{13}C CP/MAS NMR spectra of the products of the reactions between *n*-propanol/H_2LaTi and *n*-$C_nH_{2n+1}OH$ ($n = 4$, 8 and 12, not shown) exhibited similar results: no signals due to *n*-propoxy groups and new signals due to *n*-butoxy, *n*-octoxy, or *n*-dodecoxy groups. The α-carbon signals of *n*-butoxy, *n*-octoxy, and *n*-dodecoxy groups were detected at 80 ppm, indicating the formation of Ti−O−C bonds. The XRD and solid-state ^{13}C CP/MAS NMR results therefore indicate the successful occurrence of alcohol-exchange-type reactions.

The amounts of *n*-alkoxy groups per $[La_2Ti_3O_{10}]$ are estimated from the carbon contents and are listed in Table 1. The estimated amounts of the alkoxy groups on the interlayer surface are approximately 1.0, which can be interpreted in the method described for starting *n*-propanol/H_2LaTi; the maximal amount of *n*-alkoxy groups per $[La_2Ti_3O_{10}]$ is 1.0, as indicated by the interlayer surface structure of the perovskite-like slabs and the cross-sectional area of the *n*-alkyl chain.

Structural Model for the *n*-Alkoxy Derivative of H_2LaTi. The relationship between the *c* lattice parameter and the number of carbon atoms, n_c, is plotted in Figure 5. The linear relationship, $d = 0.244n_c + 1.40$, indicates that the conformation of *n*-alkyl chains in all *n*-alkoxy derivatives of H_2LaTi is the same. The presence of the same conformation of *n*-alkyl chains in all the derivatives is also evidenced by the IR spectra of *n*-octanol/H_2LaTi, *n*-decanol/H_2LaTi, and *n*-dodecanol/H_2LaTi (Figure S3, Supporting Information); the absorption bands due to CH_2 chains are observed at the same wavenumbers (2955 cm^{-1}, $\nu_{as}(CH_3)$; 2918 cm^{-1}, $\nu_{as}(CH_2)$; 2872 cm^{-1}, $\nu_s(CH_3)$; 2850 cm^{-1}, $\nu_s(CH_2)$).[37] The positions of the $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ bands (2918 and 2850 cm^{-1}) suggest that the conformation of *n*-alkyl chains is an

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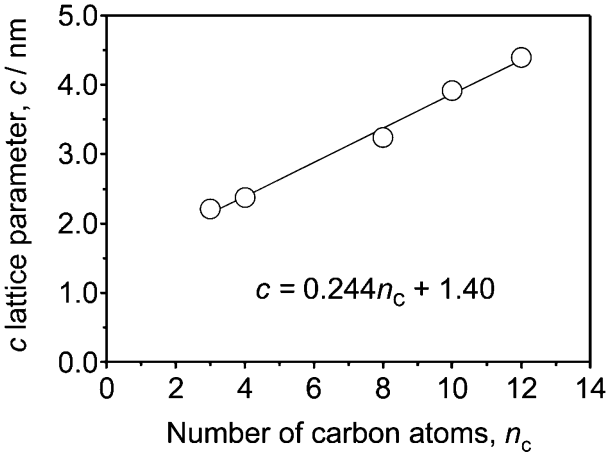


Figure 5. Relationship between the number of carbon atoms, n_c, and the *c* lattice parameter, *c*.

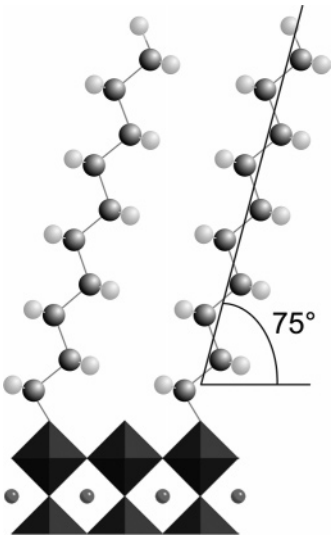


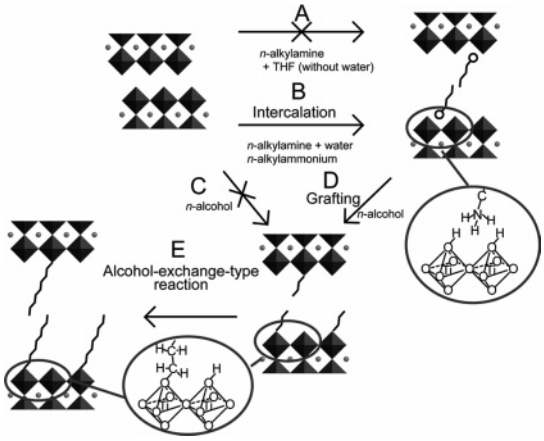
Figure 6. Proposed model for the *n*-alkoxy derivative of H_2LaTi.

all-trans ordered state in the interlayer space of the *n*-alkoxy derivatives of H_2LaTi.[38,39] (It should be noted that this type of discussion of IR spectra is not possible for the products with shorter *n*-alkyl chains, *n*-propanol/H_2LaTi and *n*-butanol/H_2LaTi.)

The length of the *all-trans* ordered *n*-alkyl chain per one CH_2 group is 0.127 nm,[40,41] which is smaller than the increment of the *c* lattice parameter per one CH_2 group, 0.244 nm (the slope of the linear relationship), indicating a bilayer arrangement. The tilt angle of the *all-trans* ordered *n*-alkyl chains is therefore calculated from the slope to be 75°.[40] The proposed structure of the *n*-alkoxy derivative of H_2LaTi is illustrated in Figure 6.

Reactivity of a Protonated Ruddlesden−Popper Phase, $H_2La_2Ti_3O_{10}$. We have demonstrated both the intercalation of *n*-butylamine in the interlayer space of H_2LaTi and the conversion of the resultant intercalation compound into *n*-alkoxy derivatives of H_2LaTi. The reactions explored in the present study are summarized in Scheme 1. No reaction of H_2LaTi with *n*-butylamine took place via the acid−base mechanism (Scheme 1, route A), but intercalation of *n*-butylammonium via the ion exchange mechanism was likely to occur (Scheme 1, route B). To date, there have been several reports on the intercalation of *n*-alkylamine into the Ruddlesden−Popper phases and related compounds via the acid−base mechanism in anhydrous systems. $H_2CaNaTa_3O_{10}$ possesses the capability of accommodating *n*-decylamine using hexane as a solvent.[27] In addition, intercalation of *n*-alkylamine into $H_{1.8}Bi_{0.2}A_{0.8}NaNb_3O_{10}$ (A = Sr or Ca) and $H_{1.8}Bi_{0.2}Sr_{0.8}Ta_2O_7$ (derived from the Aurivillius phases via selective leaching of bismuth oxide sheets), whose proton density is similar to that of the Ruddlesden−Popper phase, was achieved by using *n*-alkylamine−heptane mixtures ($H_{1.8}Bi_{0.2}A_{0.8}NaNb_3O_{10}$ (A = Sr or Ca)) and *n*-alkylamine−THF mixture ($H_{1.8}Bi_{0.2}Sr_{0.8}Ta_2O_7$).[17,32,42] These results can be interpreted on the basis of the effect of the B-site cations on the intercalation behavior via the acid−base mechanism, since niobates and tantalates generally exhibit stronger acidity than titanates.[12,13,27,43−46]

Scheme 1. Overview of the Modification of the Ion-Exchangeable Layered Perovskite H_2LaTi with *n*-Alkylamine and *n*-Alcohol



While direct reactions of H_2LaTi and *n*-alcohols did not occur (Scheme 1, route C), the protonated forms of the Dion−Jacobson phases $HLaNb_2O_7 \cdot xH_2O$ and $HCa_2Nb_3O_{10} \cdot xH_2O$ can react directly with *n*-alcohols.[18,19] According to an earlier report, water molecules both in the reaction system and in the interlayer space play a key role in the alcohol uptake.[19] Hydrated H_2LaTi ($H_2La_2Ti_3O_{10} \cdot yH_2O$) appears to be somewhat unstable in solvents and was actually converted into anhydrous H_2LaTi upon dispersal in *n*-alcohol−water mixtures. The interlayer water molecules in $HLaNb_2O_7 \cdot xH_2O$ and $HCa_2Nb_3O_{10} \cdot xH_2O$ are, on the contrary, relatively stable, so that these hydrated phases were detected when the grafting reaction was intentionally stopped at a very early stage.[47] Anhydrous $HLaNb_2O_7$ or $HCa_2Nb_3O_{10}$ can be readily rehy-

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drated in water to form $HLaNb_2O_7 \cdot xH_2O$ and $HCa_2Nb_3O_{10} \cdot xH_2O$, moreover, while anhydrous H_2LaTi cannot be rehydrated in water. These facts clearly indicate that the stability of the interlayer water molecules in H_2LaTi differs considerably from that in $HLaNb_2O_7$ and $HCa_2Nb_3O_{10}$. The stability of the interlayer water molecules appears to be the dominant factor for the occurrence of direct reactions with *n*-alcohol.

The preparation of an *n*-propoxy derivative of H_2LaTi was achieved using the *n*-alkylamine−H_2LaTi intercalation compound as an intermediate (Scheme 1, route D). Use of the *n*-butylamine/water/H_2LaTi with a larger interlayer distance (H_2LaTi, 1.38 nm; *n*-butylamine/water/H_2LaTi, 2.49 nm) appears to be advantageous for inducing a reaction of H_2LaTi with *n*-alcohol. Similar behavior has been reported for the surface modification of layered silicates with silylation agent;[48,49] H-magadiite, a layered crystalline silicate, was not able to react directly with silylation agents, but the use of intermediates possessing larger interlayer distances, such as intercalation compounds with dimethylsulfoxide and *N*-methylformamide, enabled the silylation.[48,49] In the surface modification of silica with silylation agents, moreover, $-NH_3^+$ groups are known to behave as catalysts for silylation; interaction between ≡SiOH groups and $-NH_2$ groups leads to the formation of more reactive $\equiv Si-O^-$ groups interacting with $-NH_3^+$ groups.[50] Thus, it might be possible to create a similar environment with higher reactivity in the present system. One or both of these two possible factors, larger interlayer distance and catalytic behavior of $-NH_3^+$ groups, could account for the successful interlayer surface modification with *n*-propanol.

Furthermore, *n*-propoxy groups on the interlayer surface can be replaced with different *n*-alkoxy groups (Scheme 1, route E). The reaction mechanism of the alcohol-exchange-type reaction between the *n*-alkoxy derivatives of $HLaNb_2O_7 \cdot xH_2O$ and $HCa_2Nb_3O_{10} \cdot xH_2O$ was reported to involve two steps, hydrolysis and esterification.[17,19,21] Thus, a similar mechanism is thought to be in effect in the present study. The reaction process can therefore be expressed as follows:

$$C_3H_7O-TiO_5 \xrightarrow{+H_2O} HO-TiO_5 \xrightarrow{+ROH} RO-TiO_5$$

In summary, we have demonstrated that Ruddlesden−Popper-type H_2LaTi can form two kinds of two-dimensional inorganic−organic hybrids. As reported earlier, H_2LaTi does not possess reactivity with *n*-alkylamines. The addition of water leads to the successful intercalation of *n*-butylamine into H_2LaTi, and an ion-exchange reaction with *n*-butylammonium ions is consequently proposed for the intercalation mechanism of H_2LaTi. Use of an intermediate possessing *n*-butylammonium in the interlayer space leads to the occurrence of a reaction with *n*-propanol, and the resulting *n*-propoxy groups on the interlayer surface can be further replaced with various *n*-alkoxy groups by alcohol-exchange-type reactions. This study provides strong evidence that various new inorganic−organic hybrids can be prepared from ion-exchangeable Ruddlesden−Popper phases.

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Supporting Information Available: Liquid-state ^{13}C NMR spectra of *n*-butylamine and an *n*-butylamine−hydrochloric acid mixture in D_2O, TG curves of H_2LaTi, *n*-butylamine/water/H_2LaTi, and *n*-propanol/H_2LaTi, and IR spectra of *n*-octanol/H_2LaTi, *n*-decanol/H_2LaTi, and *n*-dodecanol/H_2LaTi (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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