# Preparation and Characterization of a Transparent Thin Film of the Layered Perovskite, $K_2La_2Ti_3O_{10}$, Intercalated with an Ionic Porphyrin

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An intercalation compound of the layered perovskite, $K_2La_2Ti_3O_{10}$, with 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)-21*H*,23*H*-porphin ($TMPyP^{4+}$), as the first example of a large molecule intercalation into this perovskite, was successfully prepared by a guest-exchange method using the *n*-$PrNH_3^+$–$H_xLa_2Ti_3O_{10}$ intercalation compound as an intermediate. Its structural characterization was carried out by means of X-ray diffraction, UV, and polarized spectroscopic investigations. The porphyrin molecules were revealed to be situated with their molecular planes inclined to the $(La_2Ti_3O_{10})^{2-}$ layers at an angle of 58° because of the high charge density of the host layers.

Nanoscale laminated materials obtained by the intercalation of porphyrins and metalloporphyrins into two-dimensional matrices have been investigated with the purpose of exploring novel photoprocesses and catalytic reactions.[1] Intercalation compounds of layered semiconductors, such as layered titanates and niobates, are able to exhibit unique photochemical and semiconducting properties, which allow these compounds to display a photoinduced host–guest electron transfer, in contrast to intercalation compounds of clay minerals.[2–5] In this study, we have designed and synthesized a novel intercalation compound of the layered perovskite $K_2La_2Ti_3O_{10}$ with 5,10,15,20-tetrakis(*N*-methylpyridinium-4-ly)-21*H*,23*H*-porphin ($TMPyP^{4+}$). The structural characterization analysis of this new hybrid, by means of X-ray diffraction, elemental analyses, polarized and UV–vis spectroscopy, has also been carried out. Figure 1 shows the layered perovskite structure of $K_2La_2Ti_3O_{10}$.[6] It belongs to the Ruddlesden–Popper family of layered pervoskites, and the general formulas are presented as $A'_2[A_{n-1}B_nO_{3n+1}]$, where A′ is the interlayer cation, A is the cation, which is surrounded by 12 oxygen atoms, B is Ti and/or Nb hexacoordinated by oxygen atoms, and *n* describes the thickness of the perovskite slab, as shown in Figure 1. The ion-exchange properties of the layered perovskite $K_2La_2Ti_3O_{10}$ and photocatalytic activity have been reported.[7,8] The exfoliation of the layered perovskite by addition of tetraalkylammmonium ion has also been reported,[9] while incorporation of bulky ions into the interlayer spaces of the layered perovskite $K_2La_2Ti_3O_{10}$ has not yet been reported, probably because of the stiffness and high charge density of the nanolayers. However, we have employed here a guest-exchange method and successfully incorporated a cationic porphyrin immobilized into the layered perovskite, $K_2La_2Ti_3O_{10}$ as the first example of intercalation into this perovskite.

$K_2La_2Ti_3O_{10}$ was prepared by a conventional solid-state reaction. Stoichiometric amounts of $La_2O_3$, $TiO_2$, and 20% excess of $K_2CO_3$ were mixed and maintained at a temperature of 900 °C for 5 h in air. The $K_2La_2Ti_3O_{10}$ powder obtained was ground, heated at 1050 °C in the furnace, with intermittent grinding, for 40 h and was then cooled. After the treatments, the product was washed with distilled water and dried at 100 °C. The powder sample was then treated with 2 mol/dm$^3$ HCl for 24 h three times at room temperature (100 cm$^3$ HCl per gram $K_2La_2Ti_3O_{10}$). The resultant $H_2La_2Ti_3O_{10}$ was washed thoroughly with deionized water, and then dried in air. Into the $H_2La_2Ti_3O_{10}$, propylammonium ions were incorporated through acid–base reaction with propylamime. The host material has enough acidity because of the interlayer $H^+$ ions. The $H_2La_2Ti_3O_{10}$ was sealed in an ampoule containing a 50% (v/v) *n*-propylamine aqueous solution, which was allowed to stand for three weeks at 50 °C. The product was then washed with alcohol and dried in air at 25 °C. The intermediate obtained, *n*-$PrNH_3^+$–$H_xLa_2Ti_3O_{10}$, was allowed to react further with an aqueous $TMPyP^{4+}$ solution. The propylammonium-$H_2La_2Ti_3O_{10}$ ($(PrNH_3^+)_xH_{2-x}La_2Ti_3O_{10}$) was again sealed with a 3 mmol/dm$^3$ $TMPyP^{4+}$ aqueous solution and allowed to stand for two weeks at 50 °C. The amount of porphyrin was 5 times greater than the ion-exchange capacity of the $H_2La_2Ti_3O_{10}$. The resultant product was washed with deionized water until the $TMPyP^{4+}$ absorption could not be detected at 422 nm in the filtrate solution. The intercalation compound was dispersed in deionized water with sonication and cast on quartz substrates, so that optically transparent $(TMPyP^{4+})_x H_{2-4x}La_2Ti_3O_{10}$ hybrid thin films were obtained. The optically transparent thin films were used for the structural characterization. The elemental analysis of the $(TMPyP^{4+})_x$-$H_{2-4x}La_2Ti_3O_{10}$ showed a 14% $TMPyP^{4+}$ ion-exchange with $H_2La_2Ti_3O_{10}$ (Calcd for $(TMPyP^{4+})_{0.07}H_{1.72}La_2Ti_3O_{10}\cdot 1.3H_2O$ was C, 5.65; H, 1.08; N, 1.20%. Found: C, 5.71; H, 1.08; N, 1.21%). Since the surface area of the perovskite is estimated to be 139 m$^2$/g (0.15 nm$^2$/anionic site), the occupied area of $TMPyP^{4+}$ can be calculated to be 4.34 nm$^2$ from the composition of the hybrid compound, $(TMPyP^{4+})_{0.07}H_{1.72}La_2Ti_3O_{10}\cdot 1.3H_2O$. The mean intermolecular distance between the porphyrins intercalated within the interlayer can thus be estimated to be around 2.08 nm.

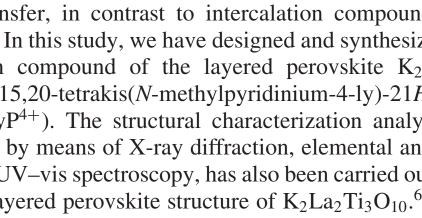

**Figure 1.** Schematic structure of $K_2La_2Ti_3O_{10}$.

The XRD pattern of $K_2La_2Ti_3O_{10}\cdot H_2O$ (Figure 2a) indicates that this compound was obtained as a single phase.[6] An exchange of $K^+$ with protons caused the basal spacings to be decreased to 1.57 nm (Figure 2b). The $2\theta$ angles of the (001) diffraction peaks of the hybrid materials, $(PrNH_3^+)_xH_{2-x}La_2Ti_3O_{10}$ and $(TMPyP^{4+})_xH_{2-4x}La_2Ti_3O_{10}$ were smaller than that for $H_2La_2Ti_3O_{10}$ (Figures 2c and 2d). These observations confirmed that the interlayers of $H_2La_2Ti_3O_{10}$ were topochemically expanded by the reaction with $PrNH_3^+$ and $TMPyP^{4+}$. It should be noted that peaks due to the perovskite-type slab ((100), (101), (107), and (110) peaks) do not shift after the reactions. The *d* values of the (00l) reflection peak of the intercalation compounds are listed in Table 1. Using the lattice parameters of $K_2La_2Ti_3O_{10}\cdot H_2O$, we can calculate out that the perovskite layer thickness of $[La_2Ti_3O_{10}]^{2-}$ is 1.16 nm.[6] By subtracting the thickness of the perovskite layer, we obtain the net interlayer height (clearance space). The results are also listed in Table 1. The interlayer height of the $(PrNH_3^+)_xH_{2-x}La_2Ti_3O_{10}$

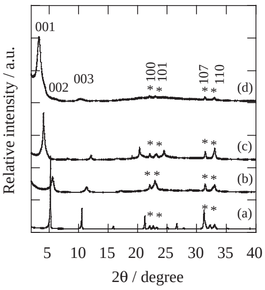

**Figure 2.** XRD patterns of (a) $K_2La_2Ti_3O_{10}\cdot H_2O$, (b) $H_2La_2Ti_3O_{10}$, (c) $(PrNH_3^+)_xH_{2-x}La_2Ti_3O_{10}$, and (d) $(TMPyP^{4+})_xH_{2-4x}La_2Ti_3O_{10}$.

**Table 1.** X-ray diffraction data

| Compound | $d_{001}$/nm | $\Delta d$/nm |
|---|---|---|
| $K_2La_2Ti_3O_{10}\cdot H_2O$ | 1.67 | 0.51 |
| $H_2La_2Ti_3O_{10}$ | 1.57 | 0.41 |
| $(PrNH_3^+)_xH_{2-x}La_2Ti_3O_{10}$ | 2.16 | 1.00 |
| $(TMPyP^{4+})_xH_{2-4x}La_2Ti_3O_{10}$ | 2.67 | 1.51 |

$\Delta d$ is gallery height

is larger than the chain length of the corresponding propylamine (0.72 nm). The phenomenon can be explained by the formation of a bilayer of alkyl chains, which made the interlayer height larger than the chain length. The insertion of $TMPyP^{4+}$ into the layered $H_2La_2Ti_3O_{10}$ resulted in an interlayer expansion up to 1.51 nm. A tilt angle ($\gamma$) of approximately 61° with respect to the interlayers was estimated on the basis of the gallery height (1.51 nm), the van der Waals radii of the two terminal oxygen atoms of the perovskite sheet, the molecular size of $TMPyP^{4+}$ (ca. 3 $nm^2$), and the van der Waals radii of the two terminal hydrogen atoms of the porphyrin molecule.[10] On the assumption that the $TMPyP^{4+}$ molecules are regularly aligned in the thin films of the layered $H_2La_2Ti_3O_{10}$, the angles $\gamma$ between the normal to the plane of the glass plate and the molecular axis were evaluated by employing spectroscopic studies using polarized light.[11,12] Here, the angles $\gamma$ can be expressed as depicted in Eq 1, where $R$ is the dichroic absorption intensity ratio of $A_y$ to $A_x$, where $x$ and $y$ denote the horizontally and vertically polarized incident light, respectively. The film exhibits an optical anisotropy due to the organized alignment of the molecules, since the $R$ values varied with the incident angle $\alpha$ to the glass plate. Thus, the angle $\gamma$ was determined by observing the correlation of $R$ with $\alpha$, as expressed by Eq 1. Here, the angle $\theta$ between the molecular axis and the optical transition moment was determined to be 90° by use of the transition moments deduced from MO calculations (both $PM_3$ and ZINDO/S). Figure 3 shows the dependence of the $R$ values of the hybrid sample on the $\alpha$ values, with a maximum at $\alpha = 0°$. The angle $\gamma$ was estimated by use of Eq 1; it indicates that the intercalated $TMPyP^{4+}$ molecular plane has a tilt angle of 58°, which corresponds well to the result estimated above (61°) by use of XRD measurements.

$$R = A_y/A_x = \frac{2[\sin^2\theta + \sin^2\alpha(3\cos^2\theta - 1)] - (3\sin^2\alpha - 1)(3\cos^2\theta - 1)\sin^2\gamma}{2\sin 2\theta + (2 - 3\sin 2\theta)\sin 2\gamma} \tag{1}$$

The $(TMPyP^{4+})_xH_{2-4x}La_2Ti_3O_{10}$ hybrid has a brown color and an electronic absorption spectrum similar to that of the free base $TMPyP^{4+}$ (Figure 4a). The Soret and Q bands did not show significant shifts when compared to the $TMPyP^{4+}$ absorption bands in water (422, 518, 551, 585, and 641 nm). The small red shift of the Soret and Q bands observed for the hybrid suggests a small interaction between the host surfaces and the guest molecules. Figure 4b shows the fluorescence spectrum. The spectrum of the intercalation compound, having maxima at 665 and 718 nm, corresponds to those of the $TMPyP^{4+}$ monomer without aggregation. Stacked $TMPyP^{4+}$ dimers have completely different $\lambda_{max}$ values (670 and 700 nm) in water.[13] It is noteworthy that the intercalated $TMPyP^{4+}$ behaves photophysically as the monomer, which is well correlated with the intermolecular distance (2.08 nm) between the porphyrins, as estimated above from their occupation areas.

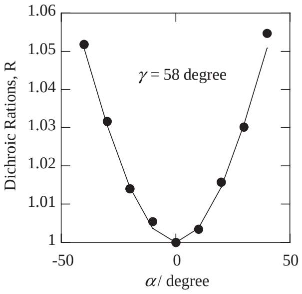

**Figure 3.** Dependence of the incident angle, $\alpha$, on the dichroic rations $R$ of the $(TMPyP^{4+})_xH_{2-4x}La_2Ti_3O_{10}$ hybrid thin film.

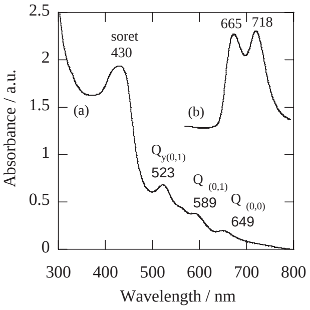

**Figure 4.** (a) Electronic absorption spectrum of $(TMPyP^{4+})_xH_{2-4x}La_2Ti_3O_{10}$ hybird and (b) emission spectrum of $(TMPyP^{4+})_xH_{2-4x}La_2Ti_3O_{10}$ hybird ($\lambda_{exc} = 30$ nm, $T = 298$ K).

In conclusion, the present study has demonstrated for the first time, to the best of our knowledge, that a cationic porphyrin can be immobilized within the layered perovskite, $K_2La_2Ti_3O_{10}$. The porphyrin was found to be tilted with an angle of 58° within the interlayers of the layered $[La_2Ti_3O_{10}]^{2-}$ sheets. Spectroscopic investigations confirmed that the porphyrin behaves like the monomeric ion. These results establish the importance of the layered perovskite $K_2La_2Ti_3O_{10}$ as an excellent layered host matrix, which can retain porphyrin in the free-base form and in a monomeric state.

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