Intercalation of a Free-base Porphyrin into Layered Tetratitanic Acid

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An intercalation compound of layered $H_2Ti_4O_9$ with 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin (H_2tmpyp^{4+}) was synthesised by a guest-exchange method using the $NPrH_3^+$–$H_xTi_4O_9$ intercalation compound as intermediate. The porphyrin is present as the free base without protonation. Its molecules are arranged with their planes inclined to the $[Ti_4O_9]^{2-}$ layers because of the high charge density of the host layers. Whereas the fluorescence spectrum of the intercalated H_2tmpyp^{4+} indicated that the porphyrin is present as a monomer without stacked aggregation, the fluorescence decayed as rapidly as that of solid powders of $H_2tmpyp^{4+}4I^-$, suggesting the porphyrin molecules interact with one another in the interlayer space.

'Intercalation compounds' are of interest as candidates for advanced materials based on molecular assembling.[1] Two-dimensional galleries of layered host materials are advantageous to take up large guest species which cannot be incorporated into intersecting channels of zeolites. In particular, the smectite group of clay minerals are versatile hosts and various functional molecules and ions have been intercalated into them. However, other kinds of layered compounds such as semiconductors have potential to exhibit novel photochemical properties in their intercalation compounds. We have already investigated intercalation compounds of layered titanates and niobates, and have found that the semiconducting properties of these layered materials allow the intercalation compounds to display photo-induced host–guest electron transfer, in contrast to intercalation compounds of clay minerals.[2,3] Nevertheless, there have been few studies on the intercalation chemistry of these oxides, especially focusing on their properties based on host–guest interactions.

Porphyrins have attracted much attention as photofunctional molecules. A number of studies have been reported on the use of porphyrins for artificial photosynthesis or photochemical hole burning.[4,5] Intercalation of porphyrins into layered materials is interesting as two-dimensional molecular assembling of photofunctional species. In addition, porphyrins can be a probe of the interlayer environment of host lattices because they undergo reversible protonation–deprotonation reactions depending on the acidity of the environment. Several intercalation compounds with porphyrins have been reported.[6–11] However, the host materials have been restricted to clay minerals except for one case where a layered double hydroxide was used.[11]

In the present study we prepared an intercalation compound of $H_2Ti_4O_9$ with 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin (H_2tmpyp^{4+}). Figs. 1 and 2 show the layered structure of $H_2Ti_4O_9$[12] and the molecular structure of H_2tmpyp^{4+}, respectively. Although the intercalating capability of $H_2Ti_4O_9$ is not as high as that of clay minerals, H_2tmpyp^{4+} was successfully intercalated through exchange with pre-intercalated propylammonium ions. In the intercalation compound, H_2tmpyp^{4+} was present as the free base in the interlayer of $H_2Ti_4O_9$, whereas all previous studies of clay–porphyrin systems have reported at least some degree of protonation.

Experimental

Materials.—The compound $H_2Ti_4O_9$ was prepared by acid treatment of $K_2Ti_4O_9$ (Ohtuka Chemical Co.) as described elsewhere.[2] The commercially available tetraiodide of H_2tmpyp^{4+} (Wako Pure Chemical Industries Co.) was used as received.

Synthesis of the Intercalation Compound.— A guest-exchange reaction was adopted for the following reasons. The compound $H_2Ti_4O_9$ can take up only small cations (*e.g.* alkali-metal cations) by ion exchange with the interlayer oxonium ions or protons,[12,13] and guest-exchange reactions are necessary in order to incorporate bulky organic cations such as methyl viologen (1,1'-dimethyl-4,4'-bipyridinium dichloride).[2] On the other hand, it intercalates organic bases by acid–base reactions. Non-ionic compounds exemplifed by alkylamines can be incorporated in this way, and the intercalated species are present as cations because during the incorporation process they are protonated with the interlayer protons by acid–base reactions.[14,15] The ion H_2tmpyp^{4+} can be protonated to form H_4tmpyp^{6+}, and this property might enable it to be directly incorporated. However, $H_2Ti_4O_9$ is a weak acid which can only take up organic bases having $pK_a > 9$.[14] The pK_a value of H_2tmpyp^{4+} has been reported to be 1–2,[16–19] indicating that the basicity is too low for protonation by $H_2Ti_4O_9$. Therefore, we considered that this ion could not be intercalated directly. It was therefore intercalated into $H_2Ti_4O_9$ through exchange of previously intercalated propylammonium ion with H_2tmpyp^{4+}. The reaction with the intercalated propylammonium, prepared as reported previously,[2] was carried out by heating a mixture of an excess of H_2tmpyp^{4+} (0.002 mol dm^{-3} aqueous solution) and the propylammonium intercalate in a glass ampoule at 60 °C for 2 weeks. The product was characterized after washing with methanol.

Analyses.—All the samples were characterized by powder X-ray diffraction (XRD) and infrared spectroscopy. The XRD patterns were obtained on a Rigaku RADI-B diffractometer (nickel-filtered Cu-Kα radiation), and IR spectra were recorded

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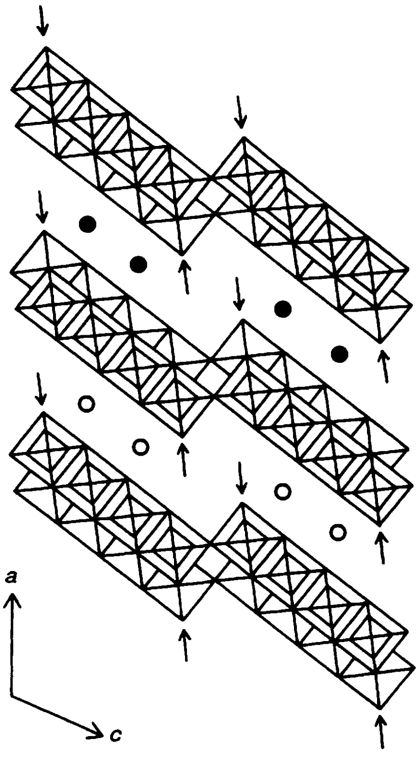

Fig. 1 The structure of $H_2Ti_4O_9$. Squares represent TiO_6 octahedra which are connected to one another to form $[Ti_4O_9]^{2-}$ layers. Circles and arrows indicate possible positions of protons and oxonium ions, respectively[12]

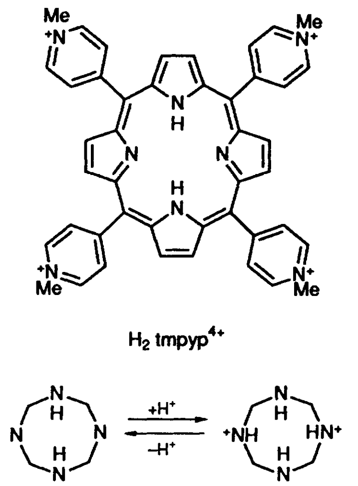

Fig. 2 Structural formula of H_2tmpyp^{4+} and protonation scheme

on a Perkin Elmer FTIR-1640 spectrometer (KBr disc technique). Visible and fluorescence spectra were measured by Shimadzu UV-210A and RF-5000 spectrometers, respectively. Fluorescence lifetimes were measured by a single-photon-counting technique on a Hitachi-Horiba NAES-1100 time-resolved spectrofluorometer under anaerobic conditions. The excitation source was a 10 atm (*ca.* 10^6 Pa) hydrogen lamp. The compositions of the products were determined by conventional elemental (C, H, N) analysis.

Table 1 X-Ray powder diffraction data

Compound	d_{200}/nm	Δd*/nm
$H_2Ti_4O_9$	0.85	
$NPrH_3{}^+$-$H_xTi_4O_9$	1.52	0.67
H_2tmpyp^{4+}-$H_xTi_4O_9$	1.90	1.05

* The increase in d_{200} from that of $H_2Ti_4O_9$.

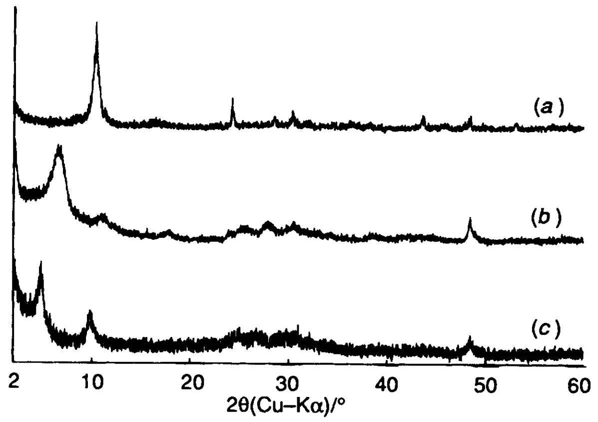

Fig. 3 Powder X-ray diffraction patterns of (*a*) $H_2Ti_4O_9$, (*b*) $NPrH_3{}^+$-$H_xTi_4O_9$ intercalation compound, and (*c*) H_2tmpyp^{4+}-$H_xTi_4O_9$ intercalation compound

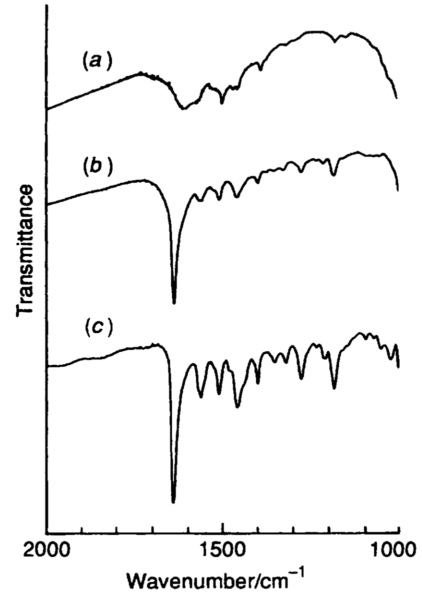

Fig. 4 Infrared spectra of (*a*) $NPrH_3{}^+$-$H_xTi_4O_9$ intercalation compound, (*b*) H_2tmpyp^{4+}-$H_xTi_4O_9$ intercalation compound, and (*c*) H_2tmpyp$^{4+}4I^-$ in KBr

Results and Discussion

Formation of the Intercalation Compound.—The XRD pattern of the reaction product is shown in Fig. 3. The (020) diffraction peak appeared at almost the same 2θ angle as for $H_2Ti_4O_9$, indicating retention of the layered structure of $H_2Ti_4O_9$. In contrast, the 2θ angle of the (200) diffraction peak was lower than that of $H_2Ti_4O_9$ or the $NPrH_3{}^+$-$H_xTi_4O_9$ intercalation compound. These observations confirmed that the interlayer spacing of the $H_2Ti_4O_9$ was topochemically expanded by the reaction of the $NPrH_3{}^+$-$H_xTi_4O_9$ intercalation compound with H_2tmpyp^{4+}. The basal spacing and the Δd value of the product are shown in Table 1.

The exchange of propylammonium ions for H_2tmpyp^{4+} was revealed by infrared spectroscopy (Fig. 4). The IR spectrum of the product exhibited no absorption bands due to propylammonium ions of the $NPrH_3{}^+$-$H_xTi_4O_9$ intercalation compound [1570 and 1502, δ(N-H) of NH_3; 1470, δ(C-H) of

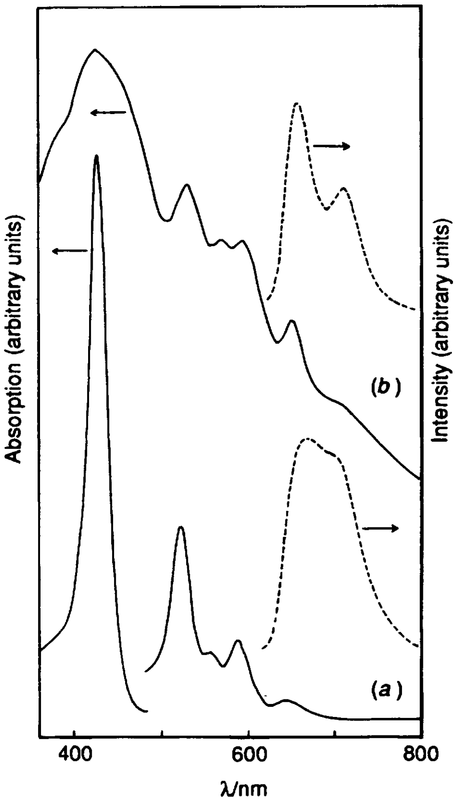

Fig. 5 Visible absorption (solid line) and fluorescence (broken line) spectra of H_2tmpyp^{4+} (*a*) in water (4.2×10^{-6} mol dm^{-3}, transmission spectrum) and (*b*) in the interlayer of $H_2Ti_4O_9$ (diffuse reflectance spectrum). The fluorescence spectra were obtained by excitation at 420 nm

Table 2 Fluorescence decay lifetimes of H_2tmpyp^{4+}

Sample	τ_1/ns (I_1)[a]	τ_2/ns (I_2)[a]
H_2tmpyp^{4+}–$H_xTi_4O_9$	6.0 (0.36)	1.2 (0.64)
$H_2tmpyp^{4+}4I^-$	5.7 (0.32)	1.2 (0.68)
H_2tmpyp^{4+} in water	4.1[b]	
H_2tmpyp^{4+} in MeOH	7.2[b]	
H_2tmpyp^{4+} in glycerol	10.8[b]	

[a] The relative contribution to the fluorescence intensity. [b] From ref. 22.

CH_2; 1180 cm^{-1}, δ(C–N), *etc.*], but many absorption bands due to H_2tmpyp^{4+} [1640, ν(C–N) of pyridyl substituent; 1560, ν(C–C) of pyrrole ring, 1455 and 1355 cm^{-1}, ν(C–N) of pyrrole ring, *etc.*][20] were observed. The C:N atomic ratio of the product (5.6:1) also agreed with that of H_2tmpyp^{4+} (5.5:1).

Interlayer State.—The colour of the intercalation compound was maroon, indicating that H_2tmpyp^{4+} is present as the free base. The visible diffuse reflectance spectrum of the intercalation compound (Fig. 5) is nearly identical to that of H_2tmpyp^{4+} free base in water. In addition, the absorption bands in the infrared region also appear at the same positions as those of the free base tetraiodide in KBr (Fig. 4). The spectrum clarifies the presence of H_2tmpyp^{4+}, not further protonated because the C–N stretching bands (1455 and 1355 cm^{-1}) are not affected by the intercalation.[7]

This is noteworthy because free-base porphyrins are protonated by Brønsted acid-base reactions with hydrated interlayer metal cations in clay minerals.[6] In clay–porphyrin intercalates the degree of protonation depends on the acidity of the cations. As described in the Experimental section, $H_2Ti_4O_9$ also has Brønsted acidity, and donates its interlayer protons to basic compounds. Alkylamines are protonated in the interlayer of the titanic acid. The protons remain in the $NPr^nH_3{}^+$–$H_xTi_4O_9$ intercalation compound because the amount of propylammonium is only 0.67 mol per mol $[Ti_4O_9]^{2-}$, *i.e.* $(NPrH_3)_{0.67}H_{1.33}Ti_4O_9$.[2] The final product should also contain protons because the composition of the sample (described later) indicates that the negative charge of the $[Ti_4O_9]^{2-}$ layers cannot be compensated only by H_2tmpyp^{4+}. Hence, the present results confirm that the acidity of $H_2Ti_4O_9$ is too weak to protonate H_2tmpyp^{4+} which is a weak base with a pK_a value of 1–2 as mentioned above. This property of $H_2Ti_4O_9$ shows that the layered titanate is capable of immobilizing guest species with weak chemical interactions.

The arrangement of H_2tmpyp^{4+} was inferred from the XRD data. The increase in the basal spacing upon intercalation was calculated to be 1.05 nm (Table 1). When H_2tmpyp^{4+} or its metal complexes are intercalated in clay minerals the basal spacing increases by 0.4–0.5 nm for a flat monolayer arrangement[8–10] and by 1.05 nm for an inclined orientation.[10] Consequently, the value of 1.05 nm indicates an inclined or a bilayer arrangement. However, the latter is ruled out because it would cause interactions of H_2tmpyp^{4+} with other molecules to form dimers or with the host lattice, which is not spectroscopically evidenced as described later.

The amount of intercalated H_2tmpyp^{4+} is in accord with the XRD result: by elemental analysis, 0.12 mol per mol $[Ti_4O_9]^{2-}$. The area of the $[Ti_4O_9]^{2-}$ layer surface is calculated to be 0.225 nm^2 per mol $[Ti_4O_9]^{2-}$ from the lattice constant of $H_2Ti_4O_9$,[12] while the area of the molecular plane of H_2tmpyp^{4+} is approximately 3 nm^2.[10,11] The maximum amount of H_2tmpyp^{4+} which could be intercalated in a flat arrangement is therefore estimated to be 0.075 mol per mol $[Ti_4O_9]^{2-}$. Since the actual amount is 0.12 mol the H_2tmpyp^{4+} must be present in an inclined arrangement. Judging from the increase in the basal spacing, the maximum tilt angle of the H_2tmpyp^{4+} molecular plane is estimated to be about 35°.

Such an inclined arrangement of the porphyrin was observed previously in the interlayer of a highly charged fluorohectorite clay mineral.[10] The reciprocal of the layer charge density of fluorohectorite is 0.27 nm^2 per charge[10] while that of $H_2Ti_4O_9$ is 0.113 nm^2.[12] However, the tilt angle of H_2tmpyp^{4+} in $H_2Ti_4O_9$ is less than that in the fluorohectorite (*ca.* 45°). This is explained by the composition of the intercalation compound. Since intercalation of H_2tmpyp^{4+} occurs through exchange of propylammonium ions, the amount is restricted to that contained in the intermediate guest species. In fact the amount of propylammonium ions in the intermediate (0.67 mol per mol $[Ti_4O_9]^{2-}$) is smaller than the amount of protons in the original $H_2Ti_4O_9$. In other words, the density of the exchangeable sites for H_2tmpyp^{4+} is about 1/3 of the proton density in $H_2Ti_4O_9$. Therefore, the reciprocal of the layer charge density of the propylammonium intercalate is effectively 0.34 nm^2, and H_2tmpyp^{4+} cannot be arranged more densely in $H_2Ti_4O_9$ than in fluorohectorite. This is a general feature of guest-exchange systems, and leads to the fact that the orientation of H_2tmpyp^{4+} can be controlled by using suitable intermediates (*e.g.* bulkier intermediates should be intercalated to a smaller extent). In contrast, the arrangement of the guest species in clay minerals depends primarily on their layer charge density, because the hosts take up guest cations quantitatively by direct ion exchange of the interlayer cations.

Fluorescence Behaviour.—Fig. 5 also shows the fluorescence spectra. The spectrum of the intercalation compound having maxima at 660 and 710 nm corresponds to that of the H_2tmpyp^{4+} monomer without aggregation, whereas the spectrum in water [Fig. 5(*a*)] having maxima at 670 and 700 nm indicates formation of stacked H_2tmpyp^{4+} dimers.[21,22] It is noteworthy that intercalated H_2tmpyp^{4+} behaves photophysically as the monomer although it is densely packed with an inclined arrangement.

The fluorescence lifetimes of the H_2tmpyp^{4+}–$H_xTi_4O_9$ intercalation compound and the free base tetraiodide are shown in Table 2. The fluorescence decay curves of both the solid samples could be fitted by a double-exponential model. These lifetimes are very similar, but shorter than those of H_2tmpyp^{4+} in methanol or glycerol where the base molecules are present as monomeric ions. In addition, the solid samples have shorter lifetime components (τ_2) in contrast to the solutions of H_2tmpyp^{4+}. These facts lead us to assume that self-quenching of H_2tmpyp^{4+} occurred in the interlayer of $H_2Ti_4O_9$ as well as in the tetraiodide crystal because the porphyrin molecules are densely packed and easily interact with neighbouring molecules. Since the luminescence decay of the intercalation compound is similar to that of the free-base tetraiodide, the contribution of the $[Ti_4O_9]^{2-}$ layers to the decay can be neglected. Although we do not have direct evidence for self-quenching because samples in which the amount of H_2tmpyp^{4+} intercalated was varied could not be prepared, many previous studies on the photophysics of luminescence probes intercalated in layered materials (clay minerals and zirconium phosphates) have reported this phenomenon.[23–28] This phenomenon has been observed for luminescent species with short-lived excited states such as methyl viologen, in addition to species which emit from long-lived excited states as exemplified by tris(2,2′-bipyridine)ruthenium(II), $[Ru(bipy)_3]^{2+}$.

Double-exponential (and non-exponential including more than three components) decay of luminescence has often been observed for luminescent species within layered compounds.[23–33] Such behaviour has often been explained by the presence of two specific adsorption sites (or more than two sites when the decay curve is analysed by use of more than two components), which have sometimes been ascribed to interlayer spaces and external surfaces, for the luminescent probes.[23,25,27,28,30,31,33] However, this interpretation is not valid in the present system since the interlayer environment of $H_2Ti_4O_9$ should be almost uniform and the sample was washed thoroughly. It is unrealistic to consider that the interlayer microenvironment is divided into two specific types of environments. In contrast, another interpretation of double-exponential luminescence decay has been proposed for the luminescence of $[Ru(bipy)_3]^{2+}$ incorporated in a silk fibroin membrane.[34] The presence of shorter lifetime components was explained by self-quenching. Further, luminescence of tris(4,7-diphenyl-1,10-phenanthrolinedisulfonato)ruthenate(II) ions within a layered double hydroxide showing a double-exponential decay has also been explained by self-quenching.[24] Therefore, the double-exponential fluorescence decay of our system may be due to self-quenching.

However, it is possible to consider a variety of microenvironments in the interlayer space because the guest species, including co-intercalated water molecules, is probably not arranged in a strictly uniform manner. The low crystallinity of the sample (see Fig. 3) supports this supposition. Recently, the non-linearity of decay curves has sometimes been ascribed to immobility, resulting in spatial heterogeneity of the dynamics of photoreactions, of the luminescent species in layered matrices.[26,35] In particular, Colón *et al.*[26] have recently reported that the luminescence decay of $[Ru(bipy)_3]^{2+}$ incorporated in a derivative of α-zirconium phosphate can be fitted by a dispersed kinetics model which assumes a continuous distribution of rate constants as well as by the double-exponential model. The continuous distribution of decay rates implies a continuous distribution of chemical microenvironments within the matrix. This means that a double-exponential decay in heterogeneous systems does not always indicate two distinct chemical microenvironments. Our results fitted by the double-exponential model might be explained by a variety of interlayer microenvironments. Nevertheless, we would like to suggest for the reasons given above (*e.g.* the short lifetime of the intercalated H_2tmpyp^{4+}) that self-quenching could explain the emission decay of the present system better than heterogeneity of the microenvironments. To obtain additional information on the self-quenching, we have also measured the fluorescence lifetimes of the intercalation compound with changing incident light intensity using neutral density filters, and found that the lifetime did not vary with light intensity. This result indicates that the fluorescence of H_2tmpyp^{4+} is self-quenched by other H_2tmpyp^{4+} molecules in the ground state.

Conclusion

The H_2tmpyp^{4+}–$H_xTi_4O_9$ intercalation compound has been synthesised by a guest-exchange technique using a $NPrH_3{}^+$–$H_xTi_4O_9$ intercalation compound as intermediate. The porphyrin was intercalated with an inclined arrangement in the interlayer of $H_2Ti_4O_9$. Spectroscopic investigations confirmed that it was present as the monomeric free-base ion. These results establish the importance of $H_2Ti_4O_9$ as an excellent layered host matrix which can retain porphyrin in free-base form and monomeric state. On the other hand, the rapid fluorescence decay, which can be analysed by the double-exponential model, of the densely intercalated H_2tmpyp^{4+} suggests interactions between porphyrin molecules result in self-quenching. This behaviour is usual for the luminescence of species such as $[Ru(bipy)_3]^{2+}$ intercalated within layered materials.

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