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Intercalation of cationic phthalocyanines into layered titanates and control of the microstructures†

Ryozo Kaito,[a] Nobuyoshi Miyamoto,[a] Kazuyuki Kuroda[a,b] and Makoto Ogawa*[c]

[a]*Department of Applied Chemistry, Waseda University, Ohkubo-3, Shinjuku-ku, Tokyo 169-8555, Japan*
[b]*Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, Nishiwaseda 2, Shinjuku-ku, Tokyo 169-0051, Japan*
[c]*PRESTO, Japan Science and Technology Corporation and Department of Earth Sciences, Waseda University, Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, Japan*

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Two cationic phthalocyanines (Pc), a tetravalent Alcian Blue pyridine variant ($ABpy^{4+}$) and a monovalent iron(III) phthalocyanine ($FePc^{+}$), were intercalated into two layered titanates derived from $Na_2Ti_3O_7$ and $Cs_xTi_{2-x/4}\square_{x/4}O_4$ ($\square$ = vacancy, $x = 0.7$) by using the corresponding propylammonium titanates as the intermediates for guest displacement reactions. When $Na_2Ti_3O_7$ was used as a host, segregation occurred in the products, since it has a relatively higher layer charge density; some interlayer spaces accommodated Pc, but the others contained propylammonium cations. On the other hand, Pc cations were homogeneously intercalated into the interlayer spaces of $Ti_{2-x/4}\square_{x/4}O_4$ layers. $ABpy^{4+}$ formed agglomerates in the gallery between $Ti_{2-x/4}\square_{x/4}O_4$ layers, whereas $FePc^{+}$ was distributed molecularly. In the ABpy–$Ti_{2-x/4}\square_{x/4}O_4$ system, further $ABpy^{4+}$ was added or any remaining propylammonium cations were removed by thermal treatment under reduced pressure in order to vary the microstructure, which resulted in the formation of higher aggregated states of $ABpy^{4+}$. Electron transfer from $FePc^{+}$ to $Ti_{2-x/4}\square_{x/4}O_4$ induced by visible light irradiation was observed for FePc–$Ti_{2-x/4}\square_{x/4}O_4$ by fluorescence measurements.

Introduction

The interlayer spaces of layered materials afford effective two-dimensional environments for orientation and immobilization of intercalated guest species, which is very promising for the development of novel functional materials.[1] In particular, photoactive organic species are expected to exhibit unique properties due to the control that can be exerted on the orientations of species in the interlayer region. For example, controlled orientation of molecules with large polarizabilities by host–guest interactions enables the alignment of their dipole moments, yielding strong SHG signals.[2–5] Takagi *et al.* have performed stereoselective photoreactions by utilizing the confined space of host lattices.[6] One of us (M. O.) has reported on the aggregation of azobenzene derivatives in the interlayer region of montmorillonite and control of the orientation of the derivatives by dye–dye and dye–host interactions.[7,8] The adsorbed and associated states of cyanine dyes intercalated in various layered clay minerals depend on the kind of host material.[9] The orientation and aggregation of guest species are influenced by the charge density of layered materials. Decreasing the layer charge density has been shown to suppresses the agglomeration of Methylene Blue in the interlayer space of montmorillonites.[10] Consequently, it is very interesting and useful to organize ionic dyes into media with different charge densities.

Layered titanates with exchangeable alkali metal ions located in the interlayer region are a sort of layered transition metal oxide and can form intercalation compounds with various cationic species by ion exchange. Layered titanates can be easily prepared by solid-state reactions and are both thermally and chemically stable. In addition, the layers are semiconductive and photo-induced electron transfer between the host and guest species can occur.[11] Layered titanates can also act as photocatalysts[12] and are very useful as hosts for organizing guest species. The interlayer reactivities of layered titanates are relatively lower than those of the smectite group of clay minerals and the introduction of guests is relatively difficult. This drawback notwithstanding, the higher layer charge densities compared to the smectites are advantageous for the formation of higher aggregated states of guest species in the gallery.

Phthalocyanines are photochemically and thermally stable, and have attracted increasing interest as functional molecules for catalysis, photofunctional materials, and energy conversion.[13] In particular, immobilization of dyes and formation of their aggregated states are of importance for controlling the properties of materials, such as the photosensitization of TiO_2[14] and the photoconductivity of the aggregates.[15] Although intercalation of phthalocyanines into layered materials has been investigated using clays, layered double hydroxides, layered perovskites, and so on,[16–22] only the formation of dimers in the galleries[16–18] has been investigated and there have been no studies on the formation of aggregates.

In the present study, we used $Cs_xTi_{2-x/4}\square_{x/4}O_4$ ($\square$ = vacancy, x = 0.7) and $Na_2Ti_3O_7$ (Scheme 1) because they possess different layer charge densities and interlayer surroundings. Cationic Cu-type Alcian Blue pyridine variant ($ABpy^{4+}$) and Fe-type phthalocyanine ($FePc^{+}$) were used as the guest species.

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†Electronic supplementary information (ESI) available: CHN analytical data and amounts of PA and Pc intercalated in Ti_3O_7 (Table S1), and XRD patterns of products derived from $H_2Ti_3O_7$ (Fig. S1). See http://www.rsc.org/suppdata/jm/b2/b210237b/

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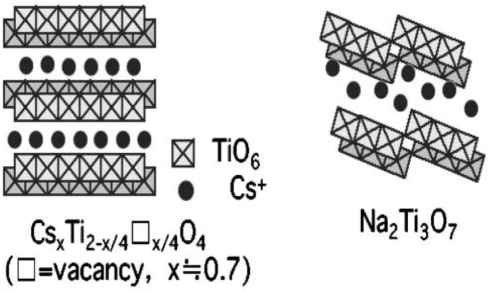
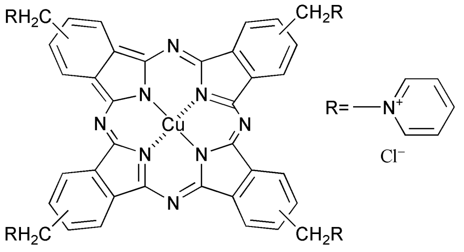
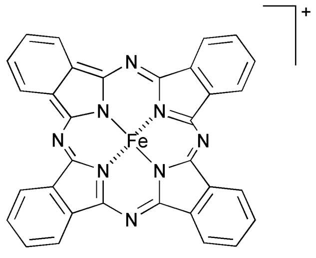


Scheme 1



[ABpy](Cl)$_4$



FePc$^+$

Their intercalation and immobilization into the titanates, as well as control of the microstructures, were examined. In view of the high layer charge densities of the titanates and the strong tendency towards aggregation of the phthalocyanines, the formation of highly aggregated states of the guests in the interlayer space was anticipated. Control of the microstructures with a view to the formation of higher aggregates by increasing the amount of intercalated phthalocyanines or by removing co-existing species by thermal treatment was also attempted. Electron transfer between the hosts and the guests as a result of the photosensitizing effect of the phthalocyanines and the semiconducting properties of the layered titanates was surveyed by fluorescence measurements. The central metal ion (Cu^{2+}) in $ABpy^{4+}$ shows quenching of the fluorescence and the degree of quenching of Fe^{3+} (in $FePc^+$) is weaker than that of Cu^{2+}. Furthermore, $Na_2Ti_3O_7$ cannot accommodate these phthalocyanines so homogeneously, as described below. Accordingly, photoinduced electron transfer in an FePc–$Ti_{2-x/4}\square_{x/4}O_4$ intercalation compound was examined by fluorescence measurements.

Experimental

Materials

[ABpy](Cl)$_4$ (purity *ca.* 95%) was purchased from Sigma Chemical Co. and [FePc]Cl (purity *ca.* 95%) was obtained from Aldrich Chemical Co. Propylamine (purity >98%.) was obtained from Tokyo Kasei Industry Co. Ltd. Anion exchange resin (Amberlite IRA-410) was used after being conditioned as OH-type.

$Cs_xTi_{2-x/4}\square_{x/4}O_4$ was synthesized by repeated calcination of a mixture of $CsCO_3$ and TiO_2 (anatase) in the molar ratio 5.2 : 1 at 800 °C for 20 h (twice) in a Pt crucible.[23] $Na_2Ti_3O_7$ was synthesized from a mixture of Na_2CO_3 and TiO_2 in the molar ratio 1.1 : 3 by calcination at 900 °C for 1 day (twice).[24] Acid-treated products ($H_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$ and $H_2Ti_3O_7$) were prepared by stirring the titanates with aqueous hydrochloric acid (1 M) for 1 day, a procedure which was repeated three times. The powder XRD patterns of the $Cs_xTi_{2-x/4}\square_{x/4}O_4$ and $H_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$ samples prepared coincided with those given on the relevant JCPDS card[25] and in the report by Sasaki *et al.*, respectively.[23] The XRD patterns of the $Na_2Ti_3O_7$ and $H_2Ti_3O_7$ samples were in good agreement with those reported by Andersson and Wadsley,[26] and Izawa *et al.*,[24] respectively. The protonic titanates were added to 20-fold excesses of propylamine and the mixtures sealed in glass ampoules and reacted at 60 °C for 6 days produce propylammonium (PA)-exchanged titanates (PA–$Ti_{2-x/4}\square_{x/4}O_4 \cdot H_2O$ and PA–Ti_3O_7).

Intercalation of Pc

Intercalation of the cationic phthalocyanines into PA–$Ti_{2-x/4}\square_{x/4}O_4$ was conducted as follows. Aqueous solutions of [ABpy](Cl)$_4$ (4×10^{-3} M, pH = 2.7) and [ABpy](OH)$_4$ (3.3×10^{-3} M, pH = 10.3) were used. [ABpy](OH)$_4$ was prepared by treatment of an aqueous solution of [ABpy](Cl)$_4$ with OH-type anion exchange resin. PA–$Ti_{2-x/4}\square_{x/4}O_4$ was dispersed in an aqueous solution of [ABpy](Cl)$_4$ or [ABpy](OH)$_4$. The amounts of the guest species added were 1.5 times larger than requied for stoichiometric ratios. The mixtures were sealed in glass ampoules and allowed to react at 60 °C for 6 days. The products were washed with methanol until the supernatants became colorless.

[FePc]Cl was dissolved in DMSO to form a solution (1.4×10^{-3} M). PA–$Ti_{2-x/4}\square_{x/4}O_4$ was mixed with an equivalent amount of the DMSO solution of [FePc]Cl and the mixture was sealed in a glass ampoule and allowed to react at 60 °C for 6 days. In this case, water was added to the DMSO solution (1 : 10 by volume) to expand the interlayer region of the titanate. The product was washed with DMSO until the supernatant became colorless and the DMSO was removed by washing with ethanol.

When PA–Ti_3O_7 was used as the intermediate, an alkaline aqueous solution of [ABpy](OH)$_4$ and a DMSO solution of [FePc]Cl were employed, and the reaction mixtures allowed to react under the same conditions as described above.

Control of the microstructures

In order to control the microstructures of the intercalation compounds, the following two methods were employed. To further agglomerate $ABpy^{4+}$ in ABpy–$Ti_{2-x/4}\square_{x/4}O_4$, intercalation of additional $ABpy^{4+}$ cations was carried out by reacting the initial intercalation compound with an aqueous solution of [ABpy](OH)$_4$ (3.3×10^{-3} M). Thermal treatment of the intercalation compound *in vacuo* at 200 °C for 3 h to remove co-existing PA was also conducted.

Analysis

XRD patterns were obtained with a Mac Science MO3X-HF[22] diffractometer using Mn-filtered Fe-Kα radiation. CHN analysis was performed with a Perkin Elmer PE2400II instrument. UV-Vis absorption spectra of suspensions containing samples were recorded on a Shimadzu UV2500PC spectrometer. The samples (*ca.* 1 mg) for the measurements were prepared by mixing the materials with a solvent (10 ml water and DMSO for ABpy and FePc systems, respectively) and sonicating the mixtures for 10 min to provide suspensions. Fluorescence spectra of the same suspensions were obtained using a Hitachi F4500 spectrometer. The reason for using fluorescence to estimate the photoinduced electron transfer is that this method

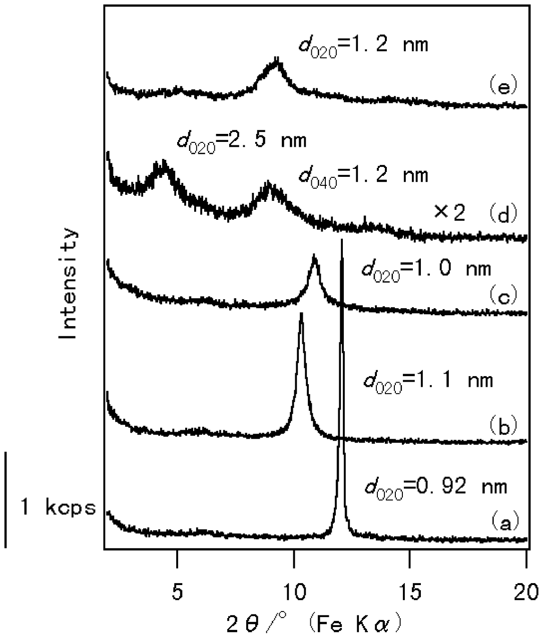


Fig. 1 XRD patterns of (a) $H_xTi_{2-x/4}\square_{x/4}O_4{\cdot}H_2O$, (b) PA–$Ti_{2-x/4}\square_{x/4}O_4$, (c) PA–$Ti_{2-x/4}\square_{x/4}O_4$ + [ABpy](Cl)$_4$, (d) PA–$Ti_{2-x/4}\square_{x/4}O_4$ + [ABpy](OH)$_4$, and (e) PA–$Ti_{2-x/4}\square_{x/4}O_4$ + [FePc]Cl.

allows the electron transfer efficiency to be evaluated. The electron transfer efficiency cannot be estimated from photocurrent spectra or by detection of both Pc radical cations and $Ti_{2-x/4}\square_{x/4}O_4$ radical anions.[27]

A swelling clay mineral, Na-type fluorotetrasilicic mica, $NaMg_{2.5}(Si_4O_{10})F_2$ (NaTSM; cation exchange capacity *ca.* 124 meq. per 100 g clay, *i.e.* 0.96 nm^2 per unit charge), was also used as an insulating host for the intercalation of $FePc^+$ to compare the photoinduced electron transfer reaction. The characterization data of NaTSM has been reported previously.[28] A DMSO solution of [FePc]Cl was mixed with NaTSM, with the amount of $FePc^+$ added set at half the cation exchange capacity of the host. Water was also added (1 : 10 by volume of DMSO). The mixture was sealed in an ampoule and allowed to react at 60 °C for 6 days.

Results and discussion

Intercalation of Pc into PA–$Ti_{2-x/4}\square_{x/4}O_4$

Because $Cs_xTi_{2-x/4}\square_{x/4}O_4$ and $Na_2Ti_3O_7$ do not intercalate $ABpy^{4+}$ and $FePc^+$ cations by direct cation exchange reactions, the intercalation was realized by displacement reactions of pre-intercalated propylammonium cations for the Pc cations. The interlayer alkali metal cations in $Cs_xTi_{2-x/4}\square_{x/4}O_4$ and $Na_2Ti_3O_7$ were exchanged for protons by acid treatment;[23,24] the proton-exchanged titanates can react with propylamine *via* acid–base reactions to form PA-titanates with enlarged interlayer spacings.[29,30]

The XRD patterns of the products derived from the lepidocrocite-type material are shown in Fig. 1. The basal spacing of H-type $H_xTi_{2-x/4}\square_{x/4}O_4{\cdot}H_2O$ (0.92 nm) increased to 1.1 nm after reaction with propylamine. The CHN data (Table 1), as well as the increase in the basal spacing, confirm the intercalation of PA. When PA–$Ti_{2-x/4}\square_{x/4}O_4$ was allowed to react with an acidic aqueous solution of [ABpy](Cl)$_4$, an increase in the basal spacing of the titanate was not observed, suggesting intercalation of protons. The size of the basal spacing (1.0 nm) suggests a different hydration state for the H-type titanate. The small amount of $ABpy^{4+}$ observed in this sample (Table 1) is ascribed to adsorption of the dye onto the outer surfaces of the titanate. When PA–$Ti_{2-x/4}\square_{x/4}O_4$ was allowed to react with a basic aqueous solution of [ABpy](OH)$_4$, the basal spacing of the product increased to 2.5 nm, strongly suggesting that the intercalation of $ABpy^{4+}$ had taken place. The gallery height, calculated by subtraction of the layer thickness (0.66 nm[31]) from the basal spacing, was *ca.* 1.9 nm. Considering the size of $ABpy^{4+}$ (2 nm × 2 nm × 1 nm) and possible twisting of its pyridinium groups, the cations could form a perpendicular monomolecular layer or be arranged bimolecularly parallel to the layers.

On the basis of these results, it can be stated that the intercalation of $ABpy^{4+}$ is strongly dependent on pH. The amounts of methylamine and propylamine intercalated into $H_2Ti_3O_7$ *via* acid–base reactions have been shown to strongly depend on the pH of the starting solution.[30] Consequently, the pH is a key factor for the intercalation of guest species into layered titanates. As stated above, under acidic conditions (pH = 2.7), using an [ABpy](Cl)$_4$ solution, only protons were intercalated and a significant amount of propylammonium ions were released. Under basic conditions (pH = 10.3), prepared by adding NaOH to a solution of [ABpy](Cl)$_4$, the basal spacing was 0.96 nm, smaller than that of PA–$Ti_{2-x/4}\square_{x/4}O_4$ (1.1 nm), which also indicates that $ABpy^{4+}$ was not intercalated, but that Na^+ was. Therefore, an anion exchange resin was used in order to avoid the addition of NaOH to the chloride solution. An aqueous solution of [ABpy](Cl)$_4$ was allowed to react with an anion exchange resin to yield an aqueous solution of [ABpy](OH)$_4$ (pH = 10.3), and the aqueous solution was reacted with PA–$Ti_{2-x/4}\square_{x/4}O_4$ to form an ABpy–$Ti_{2-x/4}\square_{x/4}O_4$ intercalation compound. The amount of $ABpy^{4+}$ adsorbed was larger than the amount of PA released, suggesting that intermolecular interactions between $ABpy^{4+}$ cations are also a driving force for the intercalation. The difference in pH between the intercalation of PA and the exchange with $ABpy^{4+}$ is another possible reason for the difference in the amounts of $ABpy^{4+}$ adsorbed and PA released.

On the other hand, when PA–$Ti_{2-x/4}\square_{x/4}O_4$ was allowed to react with a DMSO solution of [FePc]Cl containing a small amount of water, $FePc^+$ was intercalated and the basal spacing increased to 1.2 nm. Subtracting the layer thickness (0.66 nm) gives a gallery height of about 0.54 nm. Given that the dimensions of $FePc^+$ are 1.2 nm × 1.2 nm × 4.6 nm, the intercalated guest species probably form a monomolecular arrangement with an inclined alignment of the molecular axes. The lower driving force for $FePc^+$ intercalation, due to its lower charge density, probably explains the fact that the amount of intercalated monovalent $FePc^+$ was lower than the amount of tetravalent $ABpy^{4+}$ intercalated.

Intercalation of Pc into PA–Ti_3O_7

The XRD patterns of the products derived from $H_2Ti_3O_7$ (Fig. S1, ESI) revealed partial intercalation of Pc. The formation of PA–Ti_3O_7 was confirmed by the increase in the basal spacing

Table 1 Amounts of propylammonium (PA) and phthalocyanine (Pc) cations intercalated into the interlayer space of $Ti_{2-x/4}\square_{x/4}O_4$

	C/wt%	N/wt%	Pc intercalated/mol per mol host	PA intercalated/mol per mol host
$H_xTi_{2-x/4}\square_{x/4}O_4{\cdot}H_2O$	—	—	—	—
PA–$Ti_{2-x/4}\square_{x/4}O_4$	6.56	2.41	—	0.302
ABpy–$Ti_{2-x/4}\square_{x/4}O_4$ (pH = 2.7)	9.44	2.45	0.025	0.034
ABpy–$Ti_{2-x/4}\square_{x/4}O_4$ (pH = 10.3)	24.46	6.27	0.085	0.074
FePc–$Ti_{2-x/4}\square_{x/4}O_4$	13.94	4.37	0.058	0.179

of PA–Ti_3O_7 (1.2 nm) from that of $H_2Ti_3O_7$ (0.79 nm) and the CHN analytical data (Table S1, ESI). Similarly to the lepidocrocite-type material, an alkaline aqueous solution of $[ABpy](OH)_4$ was allowed to react with PA–Ti_3O_7. Although a small diffraction peak at $d = 2.5$ nm appeared due to the intercalation of $ABpy^{4+}$, the major phase detected was PA–Ti_3O_7. Even when a DMSO solution of $FePc^+$ and a small amount of water were allowed to react with PA–Ti_3O_7, PA largely remained in the reaction mixture, though a peak ascribable to the phase intercalated with $FePc^+$ was observed at $d = 1.3$ nm.

Segregated phases were formed, comprising small amounts of phases intercalated with $ABpy^{4+}$ or $FePc^+$ and unreacted PA-intercalated phase, whereas PA–$Ti_{2-x/4}\square_{x/4}O_4$ intercalates both $ABpy^{4+}$ and $FePc^+$. This finding is a result of the layer charge densities of the layered titanates: the charge density of PA–Ti_3O_7 ($2ab$/charge) is 0.17 nm^2 per unit charge, which is high, thus, the mutual attraction of the layers is too strong for phthalocyanines to be intercalated. The charge density of PA–$Ti_{2-x/4}\square_{x/4}O_4$ ($2ac$/charge) is 0.32 nm^2 per unit charge, lower than that of PA–Ti_3O_7, which may induce intercalation of bulky guest species like phthalocyanines. Sasaki *et al.* reported that $H_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$ has one of the lowest layer charge densities of any layered material, except for smectite-type clay minerals, and that it is expected to accommodate large molecules in the interlayer region.[23]

Control of microstructures

In order to control the microstructures of the intercalation compounds, the following two treatments for ABpy–$Ti_{2-x/4}\square_{x/4}O_4$ were carried out. The first involved increasing the amount of $ABpy^{4+}$ in the interlayer space by adding an aqueous solution of $[ABpy](OH)_4$ and the other attempted to desorb only co-adsorbed PA by thermal treatment (200 °C for 3 h *in vacuo*).

Fig. 2 shows the XRD patterns of the products obtained by adding an aqueous solution of $[ABpy](OH)_4$ to ABpy–$Ti_{2-x/4}\square_{x/4}O_4$ and by thermal treatment. The basal spacing of the $[ABpy](OH)_4$-treated product did not change, indicating that the layer structure was retained and the arrangement of $ABpy^{4+}$ was virtually unchanged by this treatment. On the other hand, the basal spacing decreased slightly for the thermally treated material, suggesting that the arrangement of $ABpy^{4+}$ had been affected to some extent. Table 2 lists the amounts of adsorbed $ABpy^{4+}$ and PA per 1 mol of the host, calculated from the C/N ratio, for ABpy–$Ti_{2-x/4}\square_{x/4}O_4$ and the products after the treatments. An increase in the amount of adsorbed $ABpy^{4+}$ and a decrease in the amount of adsorbed PA were observed for the product resulting from further addition of aqueous $[ABpy](OH)_4$ solution, relative to the initial ABpy–$Ti_{2-x/4}\square_{x/4}O_4$ material. The percentage of the area occupied by $ABpy^{4+}$ (volume occupied by adsorbed $ABpy^{4+}$/interlayer volume) was calculated to be 86% for ABpy–$Ti_{2-x/4}\square_{x/4}O_4$ and 96% for the product of further $[ABpy](OH)_4$ addition, almost reaching maximum adsorption. For the thermally treated product, the amount of $ABpy^{4+}$ adsorbed did not change, while the amount of intercalated PA decreased.

In the visible spectrum of an aqueous solution of $ABpy^{4+}$, a peak at 616 nm due to the π–π^* transition of the $ABpy^{4+}$ dimer is the main feature. The spectrum of ABpy–$Ti_{2-x/4}\square_{x/4}O_4$ is very different from that of an aqueous solution of $ABpy^{4+}$, implying the formation of aggregated states. On inclusion of further $ABpy^{4+}$, the peaks at 633 and 695 nm were shifted to longer wavelengths (642 and 701 nm) with increasing $ABpy^{4+}$ content (Fig. 3). While the absorbances at 633 and 642 nm are more intense than those at 695 and 701 nm, the intensity of the peak at longer wavelength increases relative to the peak at shorter wavelength on intercalation of more $ABpy^{4+}$. These results suggest that the peaks at the longer wavelengths are due to higher order aggregates of $ABpy^{4+}$. When co-adsorbed PA was desorbed by thermal treatment *in vacuo* at 200 °C for 3 h, the spectral profile was again shifted to longer wavelengths

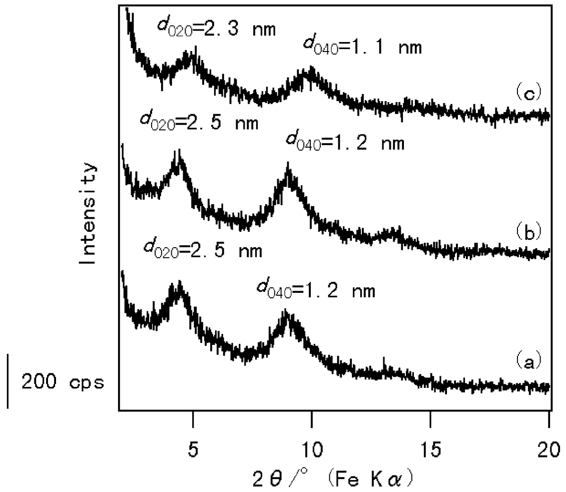


Fig. 2 XRD patterns of (a) ABpy–$Ti_{2-x/4}\square_{x/4}O_4$ and the products of (b) further addition of $ABpy^{4+}$ and (c) thermal treatment *in vacuo*.

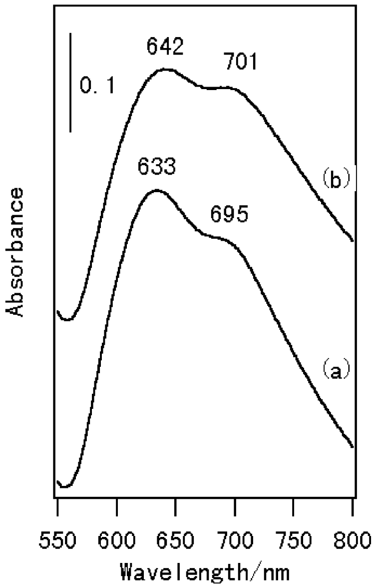


Fig. 3 Visible spectra of (a) ABpy–$Ti_{2-x/4}\square_{x/4}O_4$ and (b) the product obtained by further addition of $ABpy^{4+}$.

Table 2 Amounts of propylammonium (PA) and $ABpy^{4+}$ cations intercalated into the interlayer space of $Ti_{2-x/4}\square_{x/4}O_4$ before and after further treatments

	C/wt%	N/wt%	$ABpy^{4+}$ intercalated/mol per mol host	PA intercalated/mol per mol host
ABpy–$Ti_{2-x/4}\square_{x/4}O_4$ (pH = 10.3)	24.46	6.27	0.085	0.074
After further addition of $ABpy^{4+}$	26.68	6.68	0.101	0.005
After thermal treatment	24.02	5.97	0.085	0.005

and the absorbance at the longer wavelength region increased in intensity (Fig. 4). This suggests that the desorption of PA, which suppresses the formation of higher order aggregates, and the thermal treatment tend to induce intermolecular interactions between the $ABpy^{4+}$ cations to form higher aggregates. Attempts were made to induce aggregation of $FePc^+$ in the interlayer region of FePc–$Ti_{2-x/4}\square_{x/4}O_4$ by addition of further $FePc^+$. However, $FePc^+$ appears to molecularly dispersed in monomolecular coverage, with its molecular plane parallel to the layers, and such an arrangement is thought to be unsuitable for the formation of aggregates.

A schematic structure of ABpy–$Ti_{2-x/4}\square_{x/4}O_4$ based on the basal spacing and the visible absorption spectrum is shown in Fig. 5. The gallery height, calculated from the subtraction of the layer thickness from the basal spacing, and the size of $ABpy^{4+}$ suggests that the cations form a monomolecular layer with the molecular axis perpendicular to the layer or a bimolecular layer with the molecular axis parallel to the layer. Because the visible spectrum shows the presence of higher aggregates, monolayer coverage is more plausible.

For comparison, a swelling clay, NaTSM, which is an insulator, was used to form an FePc–TSM intercalation compound. The basal spacing was 1.43 nm, subtracting the layer thickness (0.96 nm) gives a gallery height of 0.47 nm. The gallery height is quite similar to the thickness of $FePc^+$ (0.46 nm), suggesting that the guest species are arranged parallel to the silicate sheets. Fig. 6 shows the visible absorption spectra of suspensions of FePc–TSM and FePc–$Ti_{2-x/4}\square_{x/4}O_4$, and a DMSO solution of [FePc]Cl (1×10^{-5} M). In the spectrum of the DMSO solution of $FePc^+$, a peak and a shoulder due to the π–π^* transition are observed at 654 and 600 nm, respectively.[16] In the spectra of the suspensions of FePc–TSM and FePc–$Ti_{2-x/4}\square_{x/4}O_4$, the peak at 654 nm is predominant, indicating that $FePc^+$ is mainly present in the monomeric state. Based on the XRD data and visible absorption spectra, the intercalated $FePc^+$ is monomeric and arranged with the molecular axis parallel to the layers.

Photoinduced electron transfer

The photoinduced electron transfer from $FePc^+$ to $Ti_{2-x/4}\square_{x/4}O_4$ for the sample of FePc–$Ti_{2-x/4}\square_{x/4}O_4$ was examined using fluorescence measurements. The suspensions of the samples used were the same as those used to obtain the visible absorption spectra. The spectrum of FePc–TSM exhibits an intense emission at 679 nm [Fig. 7(a)]. On the other hand, the spectrum of the suspension of FePc–$Ti_{2-x/4}\square_{x/4}O_4$ exhibits a remarkably reduced emission peak at around 680 nm [Fig. 7(b)]. In spite of the similar freqencies at which the emissions of these two samples are observed, the significant quenching observed for FePc–$Ti_{2-x/4}\square_{x/4}O_4$ strongly suggests

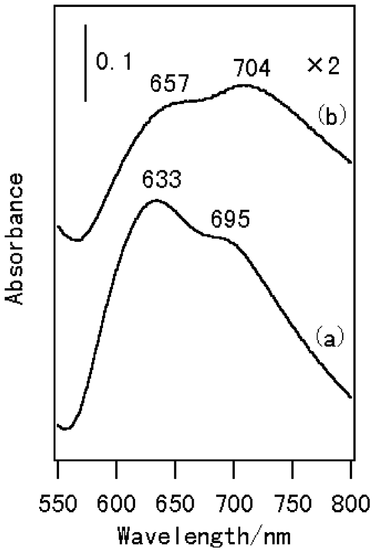


Fig. 4 Visible spectra of (a) ABpy–$Ti_{2-x/4}\square_{x/4}O_4$ and (b) the product of thermal treatment *in vacuo*.

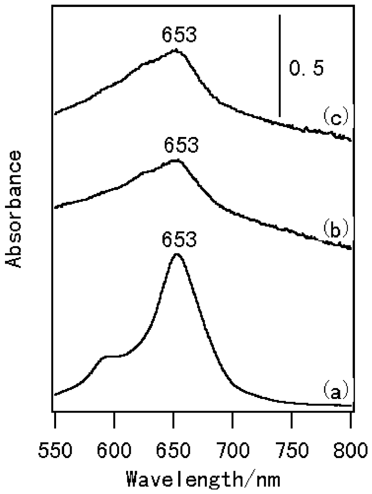


Fig. 6 Visible spectra of (a) a 1×10^{-5}M $FePc^+$ DMSO solution and suspensions of (b) FePc–TSM and (c) FePc–$Ti_{2-x/4}\square_{x/4}O_4$.

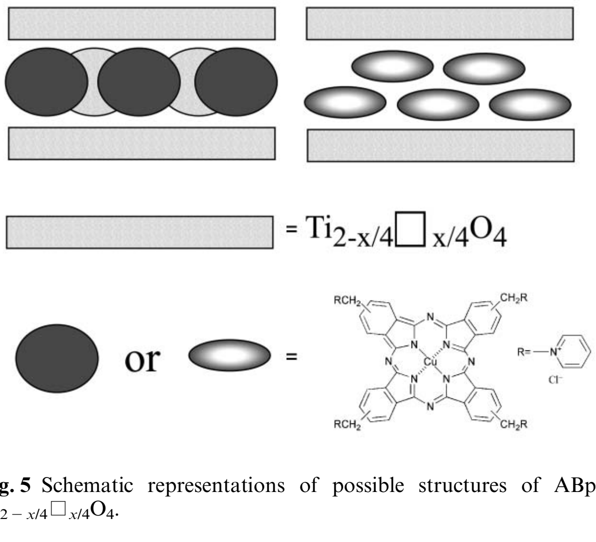


Fig. 5 Schematic representations of possible structures of ABpy–$Ti_{2-x/4}\square_{x/4}O_4$.

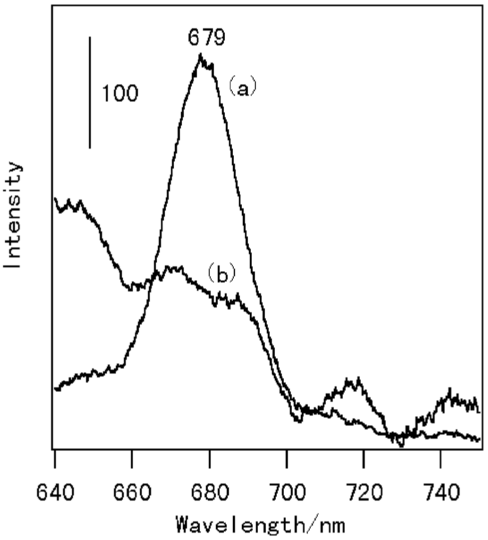


Fig. 7 Emission spectra of suspensions of (a) FePc–TSM and (b) FePc–$Ti_{2-x/4}\square_{x/4}O_4$ (λ_{ex} = 600 nm).

electron transfer from FePc to $Ti_{2-x/4}\square_{x/4}O_4$. Photoexcited $FePc^+$ in FePc–TSM emits photons and returns to the ground state, whereas in the layered titanate, photoexcited electrons are transferred from $FePc^+$ to the conduction band of $Ti_{2-x/4}\square_{x/4}O_4$ and the emission is quenched. By comparing the emission intensities of FePc–TSM and FePc–$Ti_{2-x/4}\square_{x/4}O_4$, the electron transfer efficiency was estimated to be *ca.* 60%. Peaks at 664, 667, 717, and 742 nm were observed for a suspension of $H_xTi_{2-x/4}\square_{x/4}O_4\cdot H_2O$ under the same measurement conditions. Therefore, the peaks found only in the spectrum of the suspension of FePc–$Ti_{2-x/4}\square_{x/4}O_4$ and not that of $H_xTi_{2-x/4}\square_{x/4}O_4\cdot H_2O$ must be due to $FePc^+$.

Conclusions

The layer charge densities of layered titanates greatly affect the intercalation of bulky cationic species like phthalocyanines. Propylammonium-exchanged titanates (PA–$Ti_{2-x/4}\square_{x/4}O_4$ and PA–Ti_3O_7) were used as intermediates for displacement reactions with Pc. When PA–$Ti_{2-x/4}\square_{x/4}O_4$ was used, Pc cations were co-intercalated in the presence of PA. On the other hand, when PA–Ti_3O_7 was used, segregated states formed where intercalated phases and remaining PA-containing phases were present. By incorporating further $ABpy^{4+}$ into ABpy–$Ti_{2-x/4}\square_{x/4}O_4$ and by thermal treatment, it is possible to form higher agglomerated phases in the interlayer space. The fluorescence intensity of FePc–$Ti_{2-x/4}\square_{x/4}O_4$ was remarkably reduced in comparison to that of FePc–TSM, suggesting photoinduced electron transfer from $FePc^+$ to $Ti_{2-x/4}\square_{x/4}O_4$.

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