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Porphyrin intercalation into a layered niobate derived from $K_4Nb_6O_{17}$

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The incorporation of guest species into two-dimensional inorganic structures can lead to materials with interesting chemical, catalytic, electronic, optical or mechanical properties. Concerning porphyrins and metalloporphyrins intercalation compounds, nanostructured materials have been obtained and evaluated in studies about photoprocess and catalytic reactions in confined media. The intercalation of bulky species such porphyrins into layered niobates is not easy to perform due to their high layer charge densities when compared to other layered materials. In this work we describe a method for TMPyP [5,10,15, 20-tetrakis(1-methyl-4-pyridyl)-21*H*,23*H*-porphyrin] intercalation into a layered niobate derived from $K_4Nb_6O_{17}$. The potassium precursor was converted into the acidic-exchanged form and then intercalated with *n*-butylamine to produce an expanded material that was later used in the production of a dispersion containing exfoliated niobate sheets. The niobate dispersion was dropped into a porphyrin solution originating an organic-inorganic hybrid composite of formula $TMPyP_{0.35}H_{0.6}K_2Nb_6O_{17}\cdot 3H_2O$. XRD data suggest a tilted arrangement of the TMPyP ring with respect to the layers. Spectroscopic data (uv-visible absorption, fluorescence and resonance Raman) showed that TMPyP is intercalated in a non protonated form and that the interaction with the niobate layers surface is weak, corroborating with the proposed tilted orientation in the interlayer region. *© 2002 Kluwer Academic Publishers*

1. Introduction

Layered compounds have been extensively investigated with purposes of producing advanced materials through the intercalation of guests species into the two dimensional host interlayer region. The host-guest interactions produce materials that can be employed as heterogeneous catalysts, devices for non linear optics, sensors, ionic conductors, molecular sieves etc [1].

Photoprocesses [2] and catalytic reactions [3] in confined media have been explored in nanostructured materials obtained by intercalation of macrocycle molecules as porphyrins into two-dimensional inorganic matrices. Among the layered structures, the literature has reported studies about the porphyrin intercalation in smectite clays [4], layered double hydroxides [5], zirconium hydrogen phosphate [6], titanate [7] and niobate [8].

The intercalation of bulky species into layered niobate matrices is not easy to perform due to their high layer charge densities when compared to other layered materials as smectite clays. In a previous paper [8] we have shown, for the first time, the immobilization of a porphyrin between the layers of a niobate of formula KNb_3O_8 making use of a soft chemistry route. In the present work, we describe the intercalation of 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21*H*,23*H*-porphyrin (TMPyP) in the $K_4Nb_6O_{17}$ niobate phase through an improved method compared to that early reported.

The $K_4Nb_6O_{17}$ layers have a double ReO_3-type chain in which one $[NbO_6]$ octahedron out of two is missing in the second chain [9]. The unit cell of $K_4Nb_6O_{17}$ contains four layers along the *b*-axis and the interlayer region is occupied by potassium ions that maintain the charge balance. This layered material exhibits intracrystalline reactivity, i.e., the interlayer K^+ ions can be exchanged by protons [10], simple cationic ions [11, 12], organic ions as methylviologen dication [13] and alkylammonium [14, 15] and coordination compounds [15]. Recently, Abe *et al.* [16, 17] have reported the ion-exchange property of thin films made of $K_4Nb_6O_{17}$ and showed that it is similar to that observed for powdered samples. $K_4Nb_6O_{17}$ also shows semiconducting properties and some related compounds have been explored as photocatalysts for the water splitting [18–21].

As can be seen in Fig. 1, the $K_4Nb_6O_{17}$ puckered layers are oriented in two different ways originating two different interlayer regions, designated by I and II. These regions are crystallographically distinct and also show different intercalation properties. According to Kinomura *et al.* [11], the interlayer II cations are exchanged only by monovalent ions while those in interlayer I can be easily exchanged by other cationic species.

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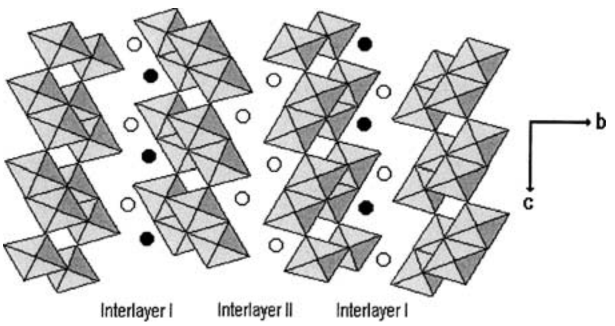


Figure 1 Schematic representation of the structure of layered niobate $K_4Nb_6O_{17}$ (the distortions in the $[NbO_6]$ octahedral units are not shown).

The results obtained in the present work have pointed out the porphyrin intercalation only at region I and through the restacking or reassembly of the exfoliated niobate sheets. The hybrid material textural characterization and also the spectroscopic data have been considered to propose an orientation to the porphyrin molecules between the niobate layers.

2. Experimental details

$K_4Nb_6O_{17}$ was prepared heating a stoichiometric mixture of Nb_2O_5 (CBMM – Companhia Brasileira de Metalurgia e Mineração) and K_2CO_3 (Merck) in a platinum crucible at 1100°C for 10 h [13]. The H^+-exchanged form was prepared suspending the $K_4Nb_6O_{17}$ in a 6 mol/L HNO_3 solution for 3 days under heating. *n*-Butylamine (Merck) was intercalated into the proton exchanged niobate through an acid-base reaction of 0.5 g of the niobate and 20 mL of the amine water solution (10% v/v). This suspension was maintained under refluxing at 80°C for 20 days. After this step, the suspension was transferred into dialysis tube to eliminate the butylamine excess. Subsequently the intercalated compound was let under stirring in deionized water for one week at room temperature. The solid niobate fraction maintained in suspension, after keeping the system without stirring for one day, was separated from the deposited solid and then dropped in 50 mL of a 3×10^{-3} mol/L aqueous solution of TMPyP (chloride salt from Midcentury). The porphyrin-niobate suspension was kept under continuously stirring at 60°C. After two days the solid was centrifuged, washed with deionized water and dried under vacuum in a desiccator with silica gel.

X-ray diffraction (XRD) patterns of oriented films were recorded on a Philips diffractometer mod. PW1710 using Cu K_α radiation. Thermogravimetric analysis (TGA) were made in a Shimadzu thermogravimetric analyzer mod. TGA-50 under synthetic air (flow rate = 50 mL/min) using a heating rate of 20°C/min up to 900°C. Uv-visible absorption spectrum of the niobate suspension was recorded in a Shimadzu spectrophotometer mod. UV-2401PC equipped with an integration sphere. Resonance Raman spectra were recorded in a Renishaw Raman Microscope mod. 3000, with laser power around 0.2 mW and excitation line at 457.9 nm (air cooled Ar^+ laser, Omnichrone). The scanning electron micrographs (SEM) of gold coated samples were recorded using a Leica microscope model Stereoscan 440 with Li detector (secondary electrons). The emission spectrum of the powdered sample was performed in a SPEX Fluorolog-2 spectrofluorimeter, model FL212, consisting in double grating SPEX 1680 monochromators; the excitation source was a 450 W Xenon lamp and the spectra were obtained using the front face mode. This apparatus is fully controlled by a DM3000F spectroscopic computer.

3. Results and discussion

XRD pattern recorded for $K_4Nb_6O_{17}$ (Fig. 2a) indicates that the compound was obtained in a single crystallographic phase and that particles have different hydration degrees. Some studies carried out about $K_4Nb_6O_{17}$ structure [22, 23] showed that the anhydrous phase ($d_{040} = 8.08$ Å) absorbs water readily and two hydrates can be formed: one with three water molecules ($d_{040} = 9.48$ Å) and a second one with 4.5 water molecules ($d_{040} = 10.27$ Å); in both of them the interlayer II is not hydrated. As judged by XRD 0*k*0 peak intensities (Fig. 2a), the anhydrous phase is present at very low level and the hydrated forms are predominant.

The TGA curve shown in Fig. 3a indicates that $K_4Nb_6O_{17}$ loses all water molecules up to approximately 330°C (using a heating rate of 20°C/min). We have performed TGA experiments with some samples

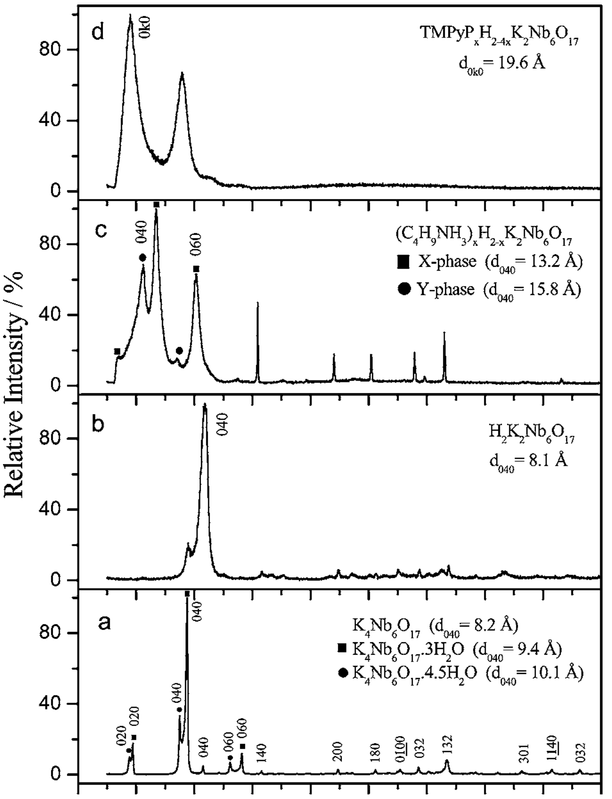


Figure 2 XRD patterns of (a) $K_4Nb_6O_{17}$, (b) $H_2K_2Nb_6O_{17}$, (c) $(C_4H_9NH_3)_xH_{2-x}K_2Nb_6O_{17}$ (circles represent the peaks of *Y*-phase while squares represent the peaks of *X*-phase) and (d) $TMPyP_xH_{2-4x}K_2Nb_6O_{17}$.

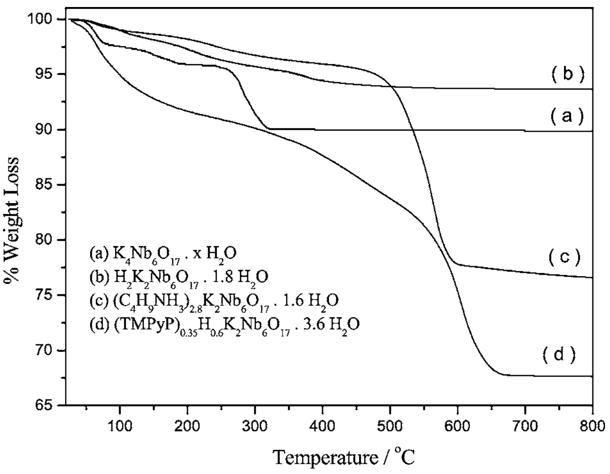


Figure 3 TGA curves of (a) $K_4Nb_6O_{17}$, (b) $H_2K_2Nb_6O_{17}$, (c) $(C_4H_9NH_3)_xH_{2-x}K_2Nb_6O_{17}$ and (d) $TMPyP_xH_{2-4x}K_2Nb_6O_{17}$ (heat rate of 20°C/min under synthetic air) .

of $K_4Nb_6O_{17}$ and have observed the dehydration process occurring mainly in three steps (temperature ranges 25–100°C, 100–220°C and 220–330°C). However, the amount of water released in each step depends on the ambient conditions due to the $K_4Nb_6O_{17}$ sensitivity to the atmospheric humidity. The samples kept in a desiccator with silica gel under vacuum rehydrate readily during sample manipulation in air.

The XRD pattern of the proton exchanged material (Fig. 2b) presents a decrease in the basal spacing value ($d_{040} = 8.1$ Å) and the absence of the 020 diffraction peak when compared to the potassium hydrated phases. Lagaly and Beneke [14] also observed a basal spacing of 8 Å to the acidic $K_4Nb_6O_{17}$phase. Comparing the TGA curves of K^+ and H^+ phases (Fig. 3a and b, respectively) it is possible to observed that the last one has a lower thermal stability than the potassium phase. Studies about the thermal stability of acidic KNb_3O_8 phase [24], which has a structure similar to the $K_4Nb_6O_{17}$, and layered perovskite niobates [25] showed that these materials undergo a dehydroxylation reaction at temperatures above 250°C and 350°C, respectively. Based on these data, we are attributing the weight loss observed above 330°C (ca. 1.8%) in the TGA curve of the acidic $K_4Nb_6O_{17}$ (Fig. 3b) as a water release due to the condensation of terminal –OH groups. The amount of water released above 330°C corresponds to one water molecule per formula, evidencing that the proton exchange occurred only in interlayer I. Other authors have also observed the partial exchange (ca. 50%) of potassium ions by H^+ [26, 27]. Hence considering the proton exchange occurring only in region I and the release of intercalated water in the range of 100–330°C (ca. 3.6%), the calculated formula for our acidic layered niobate is $H_2K_2Nb_6O_{17}\cdot 1.8H_2O$.

As described in the experimental section, the acidic niobate was intercalated with n-butylamine and two fractions were isolated (after the removal of the organic molecules excess and after keeping the system resting for one week): a fraction containing the particles deposited and another having the particles kept in suspension. As can be observed in the XRD pattern (Fig. 2c), the deposited fraction is a mixture of two phases containing *n*-butylamine intercalated between the niobate layers. Nakato *et al.* [15] also observed the formation of two phases, designated by X and Y phases, when conducting studies about the amine intercalation into $K_4Nb_6O_{17}$ (we have used the same phases designation in Fig. 2c for comparison purposes). Suspending $K_4Nb_6O_{17}$ in a solution containing an excess of n-butylammonium chloride, these authors observed that under mild conditions (room temperature, 30 min.), X-phase ($d_{040} = 12$ Å) is the major one while under higher temperature and reaction time the Y-phase ($d_{040} = 17$ Å) predominates; the formation of pure Y-phase seems not to be possible [15]. According to Nakato *et al.*, X-phase contains *n*-butylammonium intercalated only in interlayer I and Y-phase contains the organic ion in both interlayer regions. Lagaly and Beneke [14] also performed the *n*-butylammonium intercalation into $K_4Nb_6O_{17}$ and reported the isolation of a compound of composition $(C_4H_9NH_3)_{1.74}K_{2.26}Nb_6O_{17}$. Taking into account that in our work the amine was intercalated in the acidic precursor $H_2K_2Nb_6O_{17}\cdot 1.8H_2O$, we can propose that in X- or Y-phases, the organic guest is present only at interlayer I.

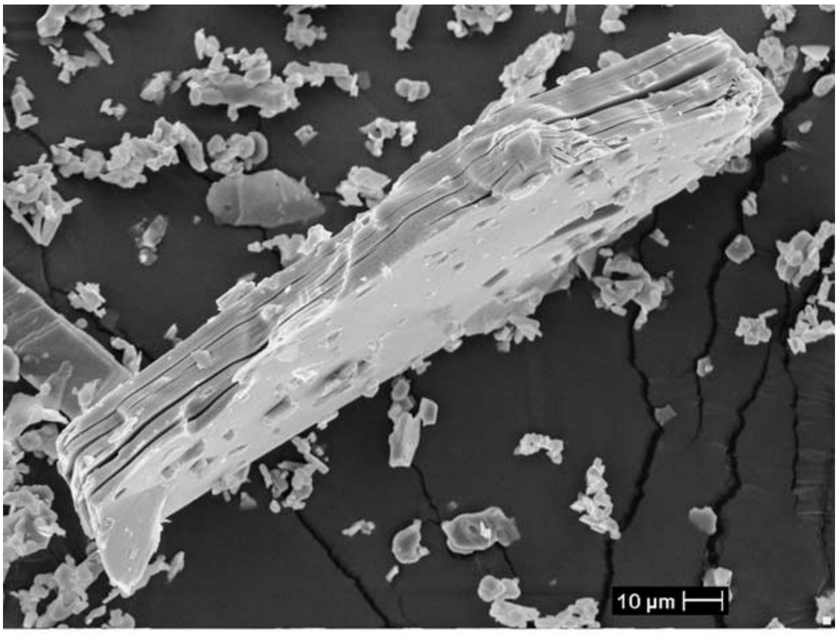
According to the following formula: $d = [(n–1).1.26 + 1.25 + 1.50 + 2.00]$ Å (n = number of carbon atoms), that gives the dimension of the *trans*-configuration of primary monoalkylamines [28], *n*-butylamine has a length of about 8.5 Å. Considering the basal spacing value of the X-($d_{040} = 13.2$ Å) and Y-phases ($d_{040} = 15.8$ Å) and the b_o value of the anhydrous $K_4Nb_6O_{17}$ unit cell ($d_{040} = 8.1$ Å), we can say that the *n*-butylamine intercalation caused an unit cell expansion of 20.5 Å and 30.8 Å in X and Y- phases, respectively. Bearing in mind the *n*-butylamine dimension (8.5 Å) and its insertion only into interlayer I, we suggest an amine perpendicular arrangement as a monolayer in X-phase and as a bilayer in Y-phase. In the last phase, the lower value of the basal spacing compared to that expected for a perpendicular bilayer can be due to an inter-penetration of carbon chains of adjacent organic layers.

Considering the intercalated water release (ca. 2.6% in the range 100–330°C) and the decomposition of the intercalated amine (about 19.8% above 330°C; the amount of water released by dehydroxylation was discounted), the calculated composition based on TGA experiment (Fig. 3c) for the butylamine-niobate composite is $(C_4H_9NH_3)_{2.8}K_2Nb_6O_{17}\cdot 1.6H_2O$. The isolated material contains an excess of the organic guest ion that was not removed in the washing step.

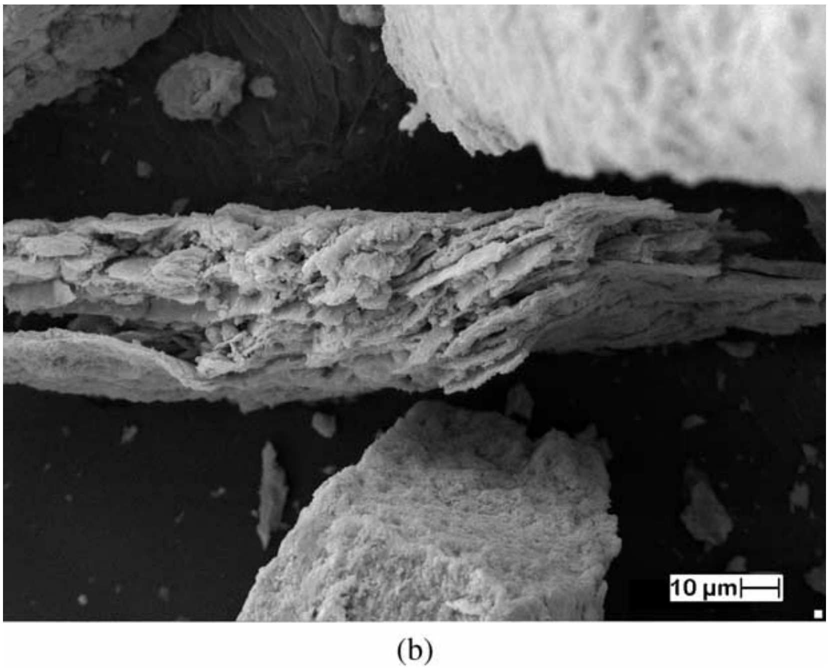
The amine-niobate fraction containing the particles kept in aqueous suspension was used to perform the porphyrin intercalation. The XRD pattern of the TMPyP-niobate material (Fig. 2d) shows an increase in the basal spacing ($d = 19.6$ Å) compared to the other intermediate compounds. It is possible to observe the presence of broad diffraction peaks related only to 0*k*0 planes. This fact, added to some experimental details that will be described ahead, suggests the occurrence of an exfoliation process during the formation of the amine-niobate suspension. In fact, the formation of a stable suspension during the dialysis can be noticed by eye. As the n-butylamine concentration decreases inside the dialysis tube, the supernatant become translucent indicating the formation of a dispersion of exfoliated niobate sheets. In this process, the continuous hydration of the interlayer I might promote the separation of the crystal layers originating particles of colloidal dimensions containing two niobate sheets sandwiching a layer of K^+. The $K_2Nb_6O_{17}$ exfoliation process was previously observed using tetra-n-butylammonium ion [26, 27, 29]. The high electrical attractive force between the positive TMPyP ion and the negative niobate exfoliated sheets is probably promoting the layers restacking or reassembly as soon as the niobate dispersion is added to the TMPyP solution.

SEM images of $K_4Nb_6O_{17}$ (Fig. 4a) and the porphyrin intercalated compound (Fig. 4b) also illustrate the exfoliation process above discussed. The $K_4Nb_6O_{17}$ micrograph shows a well-built crystal where is easy to see the fractures planes along the layers direction, a characteristic behavior of layered compounds. It is possible to observe in the TMPyP-niobate composite micrograph the presence of sheets staked "face to face" along the vertical direction but with very low organization when compared to the potassium phase. The SEM images seem to be in agreement with the XRD data (Fig. 2d): the presence of broad $0k0$ peaks are related to the low crystallinity of the material. As judged by experimental (formation of stable niobate dispersion) and instrumental (XRD and SEM) data, the porphyrin intercalation reported in this study can not be classified as a topochemical reaction.

Considering that porphyrin decomposition occurs above 330°C [8], the calculated formula for the TMPyP



(a)



(b)

Figure 4 SEM images of (a) $K_4Nb_6O_{17}$, (b) $TMPyP_xH_{2-4x}K_2Nb_6O_{17}$.

intercalated material is $TMPyP_{0.35}H_{0.6}K_2Nb_6O_{17}\cdot 3.6H_2O$. The amount of water released by OH terminal condensation (ca. 1.8%) was discounted from the weight loss observed above 330°C (21.9%). The elemental analysis data (C = 15.34%, N = 3.44%, H = 2.31%) also are in agreement with the proposed formula and the experimental C/N molar ratio of 5.2 is very close to the expected value of 5.5, which indicates that there is no n-butylamine co-intercalated.

We try to infer an orientation for the TMPyP between the layers considering its dimension, charge and also the XRD and TGA data. $[Nb_6O_{17}]^{4-}$ layer has a charge density of 12.6 Å^2 per negative charge [30] and TMPyP has dimensions of about 17.5 Å x 17.5 Å and a thickness of about 4 Å [7, 31]. Hence if the porphyrin intercalation occurred only at the two interlayers I (present in each unit cell) and in a flat monolayer arrangement, the amount of TMPyP should be 0.08 mol per $[K_2Nb_6O_{17}]^{2-}$. On the other hand, in a perpendicular arrangement the amount of TMPyP must be 0.36 mol per $[K_2Nb_6O_{17}]^{2-}$. The experimental $TMPyP^{4+}/[K_2Nb_6O_{17}]^{2-}$ molar ratio of 0.35 is in agreement with a perpendicular or tilted arrangement of the porphyrin ring relative to the host layers. The basal spacing value ($d = 19.6$ Å) observed in the TMPyP-niobate composite is higher than the porphyrin length (17.5 Å), but is no possible to ascertain how tilted the porphyrin is between the layers owing to the fact that we can not estimate the $[K_2Nb_6O_{17}]^{2-}$thickness. Based on the data available we can assure that the TMPyP is not flat with respect the niobate layers.

The TMPyP intercalated niobate has a brown color and an electronic absorption spectrum (Fig. 5a) similar to that recorded to the free base macrocycle (spectrum not showed). The Soret and Q bands do not show significant shifts when compared to the TMPyP absorption bands in water (422, 518, 551, 585 and 641 nm) or even in the solid state (424, 522, 559, 600 and 661 nm) [32]. This result indicates that the porphyrin is not intercalated as a protonated species (H_2TMPyP^{6+}). The protonated porphyrin has green color and due to a symmetry change from D_{2h} to D_{4h}, the electronic spectrum shows only two Q bands [33, 34]. The small red shift of the Soret band observed for the intercalated material is caused by a small interaction between the macrocycle and the host surfaces which is in agreement with XRD data interpretation (tilted orientation).

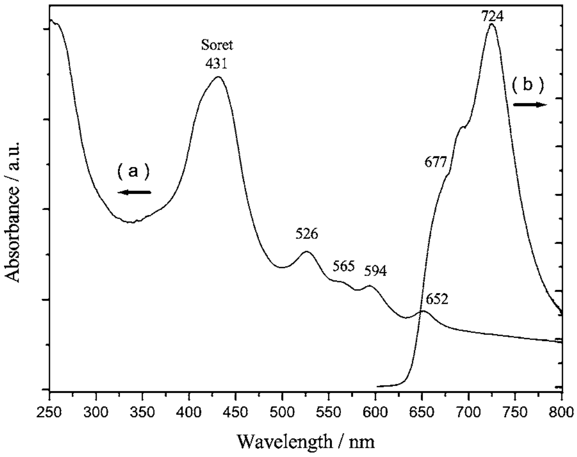


Figure 5 (a) Electronic absorption spectrum of TMPyP-niobate in water suspension and (b) emission spectrum of $TMPyP_xH_{2-4x}K_2Nb_6O_{17}$ solid sample ($\lambda_{exc.} = 430$ nm, $T = 298$ K).

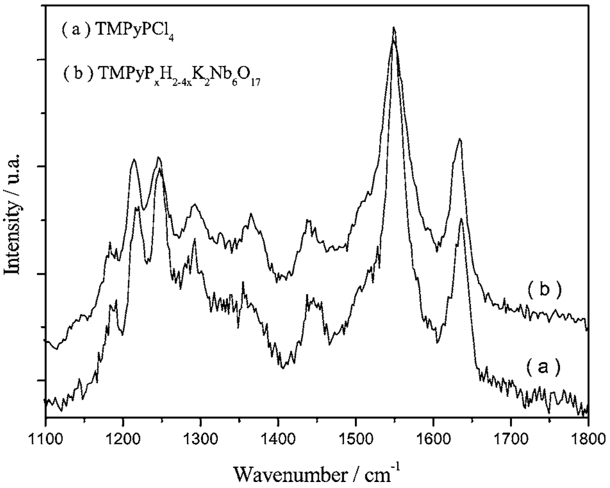


Figure 6 Resonance Raman spectra of the solid samples (a) $[TMPyP]Cl_4$ and (b) $TMPyP_xH_{2-4x}K_2Nb_6O_{17}$($\lambda_{exc} = 457.9$ nm).

The emission spectrum of the intercalated compound excited at the Soret band (Fig. 5b) is similar to that recorded for the TMPyP in the solid state (spectra not shown) or to those in aqueous solution reported in the literature [34–36]. The emission data presented in this work seem to indicate a small host-guest interaction, which corroborate with the proposed tilted arrangement of the TMPyP in the interlayer region of the niobate matrix.

The resonance Raman spectrum of the porphyrin intercalated material also evidences the macrocycle insertion as a free base in the niobate gallery. We have performed spectroscopic studies on the TMPyP interaction with cationic clays and observed that the vibrational mode more sensitive to protonation is that at 1556 cm^{-1} [32]. In the diprotonated porphyrin spectrum this band is shifted to ca. 1540 cm^{-1}. When a comparison between the free porphyrin (Fig. 6a) and the intercalated (Fig. 6b) is made this change is not observed. Intercalation affects the relative intensity of some bands in the 1150–1350 cm^{-1} and 1500–1700 cm^{-1} regions. The former region is dominated by pyridyl vibrations whereas the 1550 cm^{-1} and 1642 cm^{-1} peaks are assigned to C-C stretching (porphyrin and pyridyl, respectively). The reason for such change in relative intensities is not straightforward due to the large number of factors that contribute to Raman intensity. The lack of significant shifts in peak position in the uv-visible and resonance Raman spectra suggests that the matrix environment is playing the major role.

The interpretation of the experimental data reported in this work is consistent with a TMPyP intercalation in a non protonated form, with a tilted arrangement relative to the layers.

4. Conclusions

This study describes a method to intercalate TMPyP macrocycle ion into $K_4Nb_6O_{17}$ using an aqueous media of exfoliated particles, a promising route to intercalate bulky species in high charged layered materials. The porphyrin intercalation produces an expanded material with a tilted arrangement of guest species relative to the sheets. Porphyrin is intercalated in a non protonated form with a small interaction with the host matrix.

Acknowledgments

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