Study on the Intercalation and Interlayer State of Porphyrins into α-Zirconium Phosphate

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Abstract

In this work, a new approach for TMPyP [5,10,15,20-tetrakis (1-methylpyridinium-4-yl) porphyrin] and TMAPP [5,10,15,20-tetrakis (N,N,N-trimethyl-anilinium-4-yl) porphyrin] intercalation into α-phase of zirconium hydrogen phosphate (α-ZrP) was described: porphyrins were inserted through exchanging pre-intercalated alkylamine. Pre-intercalated n-butylamine (BA) could form either a mobile monolayer or a stable bilayer in α-ZrP. The exchange speed between porphyrins and BA in mobile monolayer is obviously faster than that in stable bilayer. Therefore mobility of spacers is one important intercalation factor. In addition, we investigated the interlayer state of TMPyP by XRD, visible spectrum, fluorescence spectrum and molecular modeling. The results collectively revealed that the porphyrin was orderly arranged with their planes inclined to the host lamella and was presented as monomer instead of aggregation in the gallery of α-ZrP.

Introduction

Layered inorganic materials such as clays, layered double hydroxides (LDHs) and group (IV) metal phosphates have unique features. The interlayer gallery of these layered matrices can be expanded and tuned to incorporate guests of any size from ions to macromolecules. The host–guest interactions produce materials that can be employed as heterogeneous catalysts, devices for nonlinear optics, sensors, ionic conductors, molecular sieves, etc. [1–3]. Due to special oxygen-binding and catalytic activity as well as photoactive and conductive properties, the porphyrins and metalloporphyrins are interesting guests of layered matrices [4–6]. α-ZrP has been used for organization of a number of guests at the galleries [7–9]. However, limited investigation has been done on inserting porphyrins into zirconium hydrogen phosphate [10].

In the present study, we investigate intercalation of several porphyrins (see Figure 1) into α-ZrP to further study on the intercalation mechanism and intercalation state of porphyrins. As it is difficult for porphyrins to directly intercalate into the host, the use of spacer (i.e. material which can pre-intercalate into the host) to expand the zirconium phosphate interlayer region is but one practical approach. Thompson et al. used p-methoxyaniline (PMA) as the spacer [10]. However, the synthesis of α-ZrP·2PMA (i.e PMA is presented as a stable bilayer in α-ZrP) is considerably difficult and intercalation of porphyrins is time-consuming. We select n-butylamine (BA), one of alkylamines as a spacer because BA can easily react with α-ZrP via Brönsted acid–base reaction to yield an intercalation compound Zr(O_3PO_4)_2·(C_6H_5NH)_2, which has a larger interlayer distance than α-ZrP and is used to intercalate other guests with big dimension [11, 12]. Two cationic porphyrins of TMPyP and TMAPP are successfully intercalated by exchanging pre-intercalated BA in a much shorter period of time than via exchanging pre-intercalated PMA. We also find that α-ZrP·BA (where pre-intercalating BA forms a mobile monolayer) is a better precursor than α-ZrP·2BA (where BA is presented as a stable bilayer) because it is much easier for porphyrins to intercalate into the monolayer precursor. It is proposed that the mobility and flexibility of spacers should be another main factor affecting intercalation of porphyrins other than interlayer distance.

In addition, XRD data and molecular modeling results indicate a tilted arrangement of the TMPyP ring with respect to the host layer, and spectroscopic data (visible absorption and fluorescence) show that TMPyP is present as monomer instead of aggregation and free base without protonation in the gallery of α-ZrP. All these observations facilitate to better understand interlayer state of porphyrins into α-ZrP.

Experimental

Materials

α-ZrP was prepared according to Ref. [13]. The tosylate salt of 5,10,15,20-tetrakis (1-methylpyridinium-4-yl) porphine (H_2TMPyP) was purchased from Tokyo Kasei.

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Kogyo Co. Ltd. 5,10,15,20-tetrakis (4-pyridyl) porphine (H$_2$TPyP) was purchased from Aldrich. The tosylate salt of 5,10,15,20-tetrakis (N,N,N-trimethyl-anilinium-4-yl) porphine (H$_2$TMAPP) was prepared according to the Ref. [14]. N-butylamine (BA), N-octylamine (OA) and other chemicals were of analytical grade. Doubly deionized water was used.

**Characterization**

X-ray diffraction (XRD) analysis of the samples was carried out with Rigaku Dmax 2000 diffractometer (Japan) using Ni-filtered CuKα radiation. The visible and fluorescence spectra were recorded by a Hitachi U-3010 spectrophotometer and a Hitachi F4500 fluorimeter, respectively. The suspensions for measurement were prepared by mixing the porphyrin intercalation compound with water.

**Synthesis of α-ZrP/alkylamine**

As direct intercalation of porphyrins into layered phosphate was not successful, a guest-exchange reaction was adopted, i.e. prior to the intercalation of porphyrins, α-ZrP/alkylamine were prepared. The pre-intercalated compounds were obtained by reactions of layered zirconium phosphate (1 g) with 20 ml aqueous alkylamine solution at several concentration level (1,2,4,8,10 mmol BA and 8 mmol OA were added to 1 g of layered materials respectively), and then the suspended solutions were ultrasonically vibrated at room temperature for 20 min. The resulted compounds were filtered, washed with distilled water, and air-dried.

**Reaction of α-ZrP/alkylamine with porphyrins**

The intercalation reactions were carried out by addition of α-ZrP/alkylamine (30 mg) to 20 ml aqueous solution of TMPyP (18 mg, 0.013 mmol). Then the suspensions were stirred at 50 °C for 1–6 days (α-ZrP/BA for 1 day, while α-ZrP/2BA for 6 days). The resulted products were collected by centrifugation, washed with ethanol in order to remove the porphyrin from the external surface of material, and air-dried.

Compared with TMPyP, a solution of other porphyrins at 18 mg in 20 ml appropriate solvents (TMAPP (0.012 mmol) was in water and TPyP (0.029 mmol) was in CHCl$_3$) reacted with α-ZrP/BA (30 mg) for 1–6 days (TMAPP for 1 day and the others for 6 days). The following procedures were performed in the same way as described above.

**Molecular modeling**

The two layers of α-ZrP forming one interlayer set as 24 Å by 100 Å were constructed with the help of the HyperChem program package [15]. The interlayer distance was defined as 10.4, 18.9 and 17.8 Å corresponding to α-ZrP/BA, α-ZrP/2BA and TMPyP intercalation compound respectively. Sufficient amounts of BA were arranged in the galleries of α-ZrP by the flat monolayer or inclined bilayer intercalation modes. The amine group of BA is placed midway among three adjacent P-OH groups and held in place by hydrogen bonds [16]. Ten TMPyP molecules were positioned into the α-ZrP interlayers based on the two possible orientations, a flat bilayer arrangement and an inclined monolayer orientation as shown in Figure 2. Simultaneously, the distance of adjacent porphyrin (A in monolayer manner and B in bilayer manner) was altered to evaluate energy level at each distance: A value was assigned to 3, 4, 5 and 6 Å while B value was assigned to 0, 1, 2, 3 and 4 Å. While the α-ZrP layers were fixed in a way of taking into account the van der Waals and electric interaction between layer atoms and adjacent guest atoms, intercalated molecules were performed using a conjugate-gradient optimizer with a convergence criterion of 0.5 kcal mol$^{-1}$ Å$^{-1}$. All calculations are performed on a 2.4G PC utilizing MM+ force field in

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**Figure 1.** Structure of TMPyP, TMAPP and TpyP.

**Figure 2.** Stylized representations of (a) a canted TMPyP monolayer and (b) a planar TMPyP bilayer.