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

WANG HAIYAN, HAN DAXIONG, LI NA* and LI KE-AN
College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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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 non linear 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 $Zr(O_3PO^-)_2 \cdot (C_4H_9NH_3^+)_2$, 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

* Author for correspondence. E-mail: Lina@pku.edu.cn

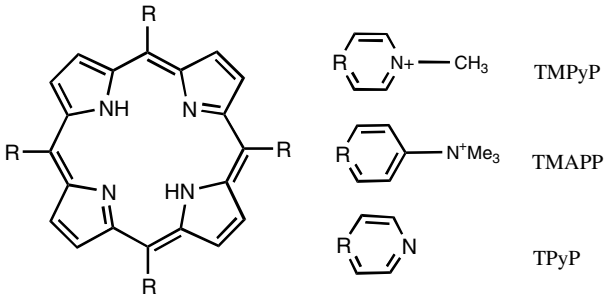

Figure 1. Structure of TMPyP, TMAPP and TpyP.

Kogyo Co. Ltd. 5,10,15,20-tetrakis (4-pyridyl) porphine (H_2TPyP) was purchased from Aldrich. The tosylate salt of 5,10,15,20-tetrakis (*N*,*N*,*N*-trimethyl-anilinium-4-yl) porphine (H_2TMAPP) 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 6Å 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

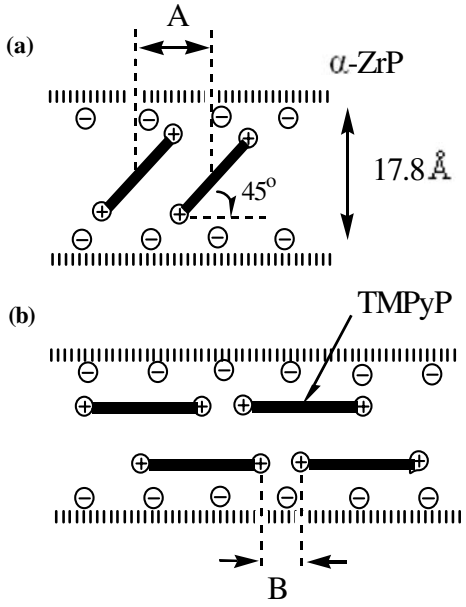

Figure 2. Stylized representations of (a) a canted TMPyP monolayer and (b) a planar TMPyP bilayer.

HyperChem 6.0 using default settings consistently (Assigning a dielectric of 1.0).

Results and discussion

Intercalation mechanism

TMPyP Interaction with α-ZrP · alkylamine

Figure 3 shows X-ray diffraction of BA intercalation compounds of α-ZrP prepared from different concentration level of BA. At 1.0 mmol BA added /g of α-ZrP, the phosphate layer remains the same as the original interlayer distance (7.6 Å). At 2.0 mmol BA added /g of α-ZrP, a new phase corresponding to an interlayer distance of 10.4 Å forms, indicating intercalation of BA into α-ZrP, in which BA forms a mobile monolayer (α-ZrP · BA). In this case, alkyl chains are oriented parallel to the layer plane with less than 30% of layer POH groups neutralized [16, 17]. Other new phases (16.4–18.9 Å) appear when more BA is added. These new peaks are related to the fact that BA forms a tilted bilayer in the interlayer region, i.e. α-ZrP · 2BA [16, 17]. In this case, all protons per mol α-ZrP are neutralized by BA. This reaction results in a more stable compound, in which BA is less movable than in α-ZrP · BA monolayer intercalation compound. This is also confirmed by molecular modeling: the lowest potential in the canted bilayer manner is much lower than that in the monolayer manner by 10.22 kcal/mol.

Figure 4A shows XRD of TMPyP interaction with α-ZrP · nBA for 1-day exchange. As 1.0 mmol BA to 1 g α-ZrP could not expand interlayer spacing, TMPyP could not be intercalated in this situation. When TMPyP reacts with α-ZrP · BA, a new phase forms with an interlayer spacing of 17.8 Å, which is very similar to that of TMPyP reaction with α-ZrP · 2PMA reported in Ref. [10], and α-ZrP · BA peak disappears (see Figure 4A). This indicates complete conversion of α-ZrP·BA to the porphyrin-intercalated phase at a gallery height of 17.8 Å. However, in the case of α-ZrP·2BA, no intercalation of porphyrins is observed although interlayer distance (18.9 Å) is large enough to incorporate TMPyP. By prolonging interaction time to 6 days, same results are obtained with the formation of a new peak at 17.8 Å, indicating that TMPyP intercalates into the host by exchanging pre-intercalated bilamellar BA. Therefore

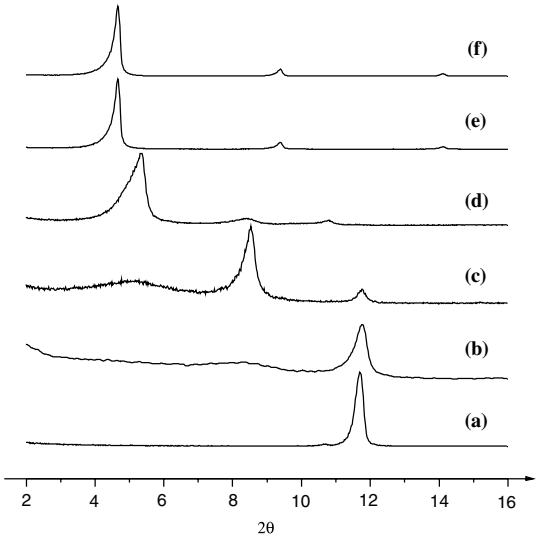

Figure 3. XRD patterns of (a, b) α-ZrP from 0, 1 mmol BA added/g α-ZrP, (c) α-ZrP · BA from 2mmol BA added/g α-ZrP and (d, e, f) α-ZrP.2BA from 4, 8, 10 mmol BA added/g α-ZrP (Temperature: 25 °C; time: 20 min).

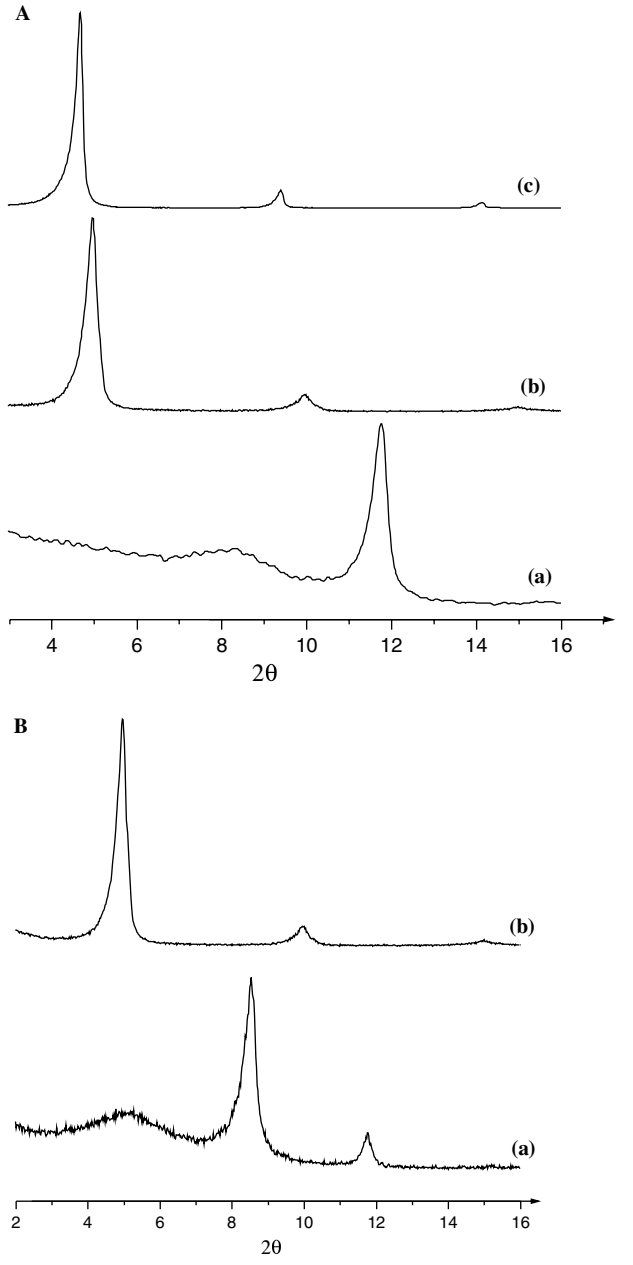

Figure 4. (*A*): XRD patterns of TMPyP interaction with (a) α-ZrP prepared from 1 mmol BA added/g α-ZrP, (b) α-ZrP·BA prepared from 2 mmol BA added/g α-ZrP, and (c) α-ZrP · 2BA prepared from 8,10 mmol BA added/g α-ZrP. (Temperature: 50 °C; time: 1day) (B): XRD patterns of (a) α-ZrP · BA and (b) TMPyP interaction with α-ZrP · BA.

the following conclusions could be drawn: (1) when the amount of added BA is not enough to expand phosphate interlayer spacing, the small interlayer distance in α-ZrP (7.6 Å) poses a kinetic barrier to open the layers and incorporate the porphyrins. Therefore interlayer spacing is one predominant factor in porphyrins intercalation; (2) when the extended interlayer distance is large enough, it is possible for porphyrins to intercalate. But it does not mean that larger distance is more favorable for porphyrins insertion. We have found that TMPyP intercalates into α-ZrP·BA much faster than into α-ZrP·2BA although the interlayer spacing of the former (10.4 Å) is much smaller than that of the latter (18.9 Å). The monolayer BA pre-intercalated into α-ZrP is at higher energy level than bilayer by 10.22 kcal/mol and is more readily to exchange with porphyrins. Therefore mobility and arrangement of spacers in the interlayer might be another important factor affecting intercalation speed of big molecules.

To further illustrate the opinion mentioned above, we also select OA as a spacer (pre-intercalated OA is presented as a canted bilayer like BA, $d = 27.9$ Å). After interaction with α-ZrP · 2OA for 6-day-exchange, the intercalation of TMPyP is observed. This is proved by the formation of a new peak at interlayer distance of 17.9 Å and the disappearance of α-ZrP · 2OA peak corresponding to gallery height of 27.9 Å. Although the interlayer distance of α-ZrP · 2OA is much larger than that of both α-ZrP · BA and α-ZrP · 2BA, the exchange speed is not any faster because pre-intercalated OA forms a stable bilayer. This again confirms that mobility and flexibility of spacers is an important factor, which affects the exchange speed between porphyrins and spacers. We propose that α-ZrP · BA could be a better precursor for intercalating porphyrins than α-ZrP·2BA/2OA with large interlayer height, nevertheless α-ZrP · 2alkylamine have always been used as precursor before [11, 12].

Other porphyrins interaction with α-ZrP · BA

We also try to intercalate other porphyrins into α-ZrP·BA. For cationic TMAPP, the new peak corresponding to the interlay height of 17.5 Å suggests that TMAPP adopts similar orientation with TMPyP after exchanging with α-ZrP · BA. However, neutral TPyP cannot be inserted under the same conditions due to the lack of both hydrogen bonding and electrostatic interaction between the host and the guest.

Interlayer state

Molecular modeling of porphyrins intercalation orientation

For porphyrins intercalation compounds, the interlayer spacing at about 18 Å is equivalent of 11.7 Å (the thickness of an α-ZrP layer is 6.3 Å). Considering the XRD data and the dimension of TMPyP (see Figure 5), porphine planes in the gallery should be either a monolayer tilted to the host layer or a bilayer roughly parallel to the host sheets (see Figure 2). Thompson inferred the intercalation model of aminophenyl and pyridinium-substituted porphyrins by studying the orientation of metal porphyrins through EPR [10]. Here, we will directly explore porphyrins orientation by molecular modeling and try to obtain more information.

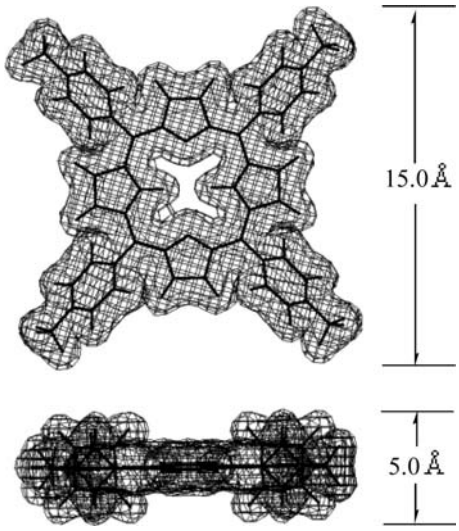

Figure 5. Space-filling model of TMPyP.

For TMPyP intercalation compound, the calculation results show that the lowest potential in the canted monolayer manner is lower than that in parallel bilayer manner by 7.92 kcal/mol. Therefore, it can be deduced that porphyrins, such as TMPyP and TMAPP, adopt an inclined orientation. This conclusion is consistent with that drawn by Thompson. Our modeling results could well explain why porphyrins adopt canted orientation. In a canted arrangement, the modeling graphics show that the free area per cationic pyridinium group is 0.23 nm^2, which is almost identical with that of α-ZrP layer (the free area per phosphate OH is 0.24 nm^2), thus porphyrins can optimize electrostatic interaction; whereas parallel porphyrins are not able to counter charges on host layers because the free area per cationic pyridinium group ($1.5 \times 1.5/4 = 0.56$ nm^2) are much higher than that of α-ZrP layer (0.24 nm^2). In addition, the calculation results show that for the inclined monolayer orientation, the lowest potential occurs when the distance of adjacent porphyrin is 4 Å corresponding to the normal C—C nonbond distance, suggesting that intercalated porphyrins are densely stacked.

Absorption spectra

Figure 6 shows the visible spectra of an aqueous solution of TMPyP and the suspension of porphyrin intercalation compound. Intercalated into the galleries of α-ZrP, the Soret band of TMPyP shifts from 422 nm

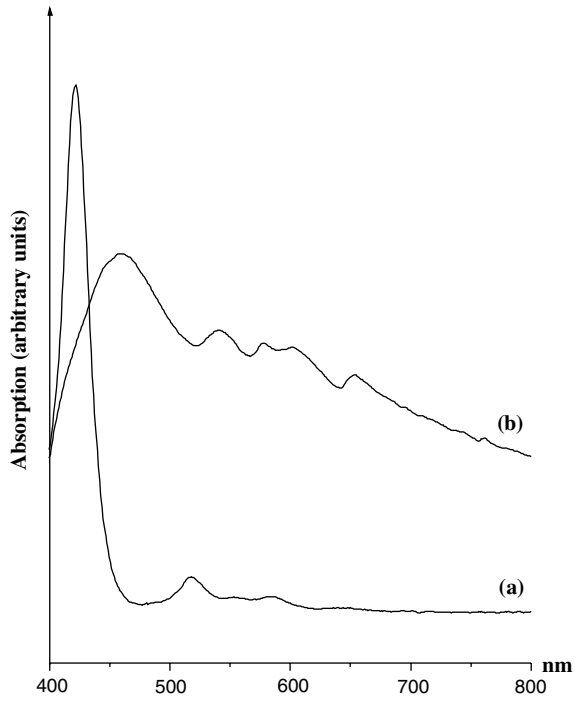

Figure 6. Visible absorption spectra of TMPyP (a) in water (1.32×10^{-6} mol/dm^3) and (b) in the interlayer of α-ZrP.

to 462 nm. In similar work on the TMPyP-smectite clay compound, the red shift was interpreted as diprotonation of TMPyP, i.e. the formation of the $H_2TMPyP^{4+}2H^+$ [18]. In the case of diacids $H_2TMPyP^{4+}2H^+$, there will be only two transitions including Q(0,0) and Q(1,0) in addition to the Soret band because the four hydrogen atoms are arranged in a square (D_{4h} symmetry). However there are four Q transitions presented in the visible spectrum of porphyrin intercalation compound as shown in Figure 6b (542, 579, 603 and 654 nm, respectively). This illustrates that TMPyP is present as the free base without diprotonation. We suggest that the obvious bathochromic shift should be ascribed to the close packing of TMPyP in α-ZrP, which can be confirmed by molecular modeling results. Modeling graphics show that close stacking of porphyrins makes TMPy groups (i.e. the four cationic methylpyridiniumyl moieties, which are originally tilted to the plane of the porphine) twist and roughly parallel to porphyrin ring in the minimized geometries corresponding to the optimum distance (4 Å) of adjacent TMPyP molecules. The torsion of TMPy groups enhances the coplanar between the porphyrin ring and the pyridine ring of TMPy, thus, a big π-stacking produces and leads to the observed red shift.

Fluorescence spectra

The fluorescence spectra of TMPyP and porphyrin intercalation compound are shown in Figure 7. The spectrum of the intercalation compound shows two bands at 654 nm and 688 nm, while that of free TMPyP has only one broad peak at 660 nm. According to the similar results of porphyrins into layered host $H_2Ti_4O_9$

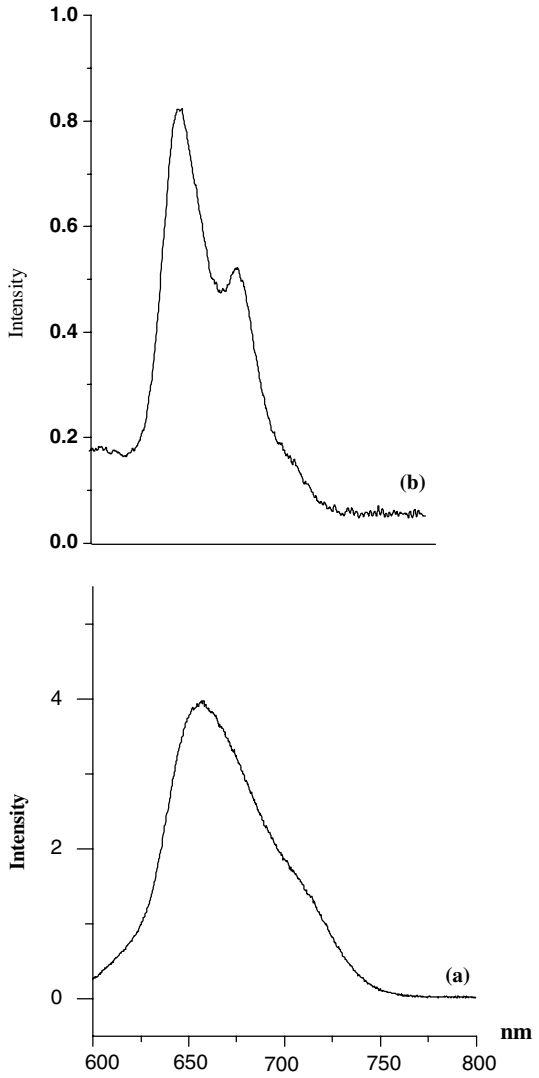

Figure 7. Fluorescence spectra of TMPyP (a) in water (1.32×10^{-6} mol/dm^3) and (b) in the interlayer of α-ZrP.

obtained by Nakato et al. [19], we infer that TMPyP is presented as monomer although it is densely packed with an inclined arrangement. Similarly, Robins regards that ZnTPPC in Li/AL LDH is in the monomeric form although the porphyrin intercalates with its plane perpendicular to the metal hydroxide layer [20]. It is clear that high packing density does not mean aggregation. And this indicates the importance of α-ZrP as an excellent layered host to retain porphyrins in monomeric state, which is very important to immobilize metalloporphyrins as highly efficient catalysts.

Conclusions

Three pre-intercalated α-ZrP: α-ZrP · BA with interlayer height at 10.4 Å, α-ZrP · 2BA with interlayer height at 18.9 Å, and α-ZrP · 2OA with interlayer height at 27.9 Å, are prepared to further intercalate cationic porphyrins TMPyP and TMAPP. The exchange of porphyrins with α-ZrP · BA is most effective in terms of intercalation speed. These results reveal that mobility and flexibility of

spacer is another important factor affecting intercalation other than interlayer height. The experimental results combining with molecular modeling reveal that TMPyP adopts an inclined orientation to α-ZrP sheet and remains as monomer instead of aggregation in α-ZrP.

Acknowledgement

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