Chinese Chemical Letters Vol. 16, No. 4, pp 541-544, 2005
http://www.imm.ac.cn/journal/ccl.html

Study on the Intercalation of TMAPP into α-ZrP

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Abstract: In this paper, an intercalation compound of layered α-ZrP with TMAPP was firstly synthesized by using the α-ZrP-BA pre-intercalation compound as intermediate. And we systemically investigated the intercalation behavior of TMAPP into α-ZrP by XRD, visible spectrum and fluorescence spectrum.

Keywords: TMAPP, α-ZrP, intercalation, alkylamine.

For porphyrins and metalporphyrins, due to their particularly oxygen-binding and catalytic activity, as well as their photoactive and conductive properties, scientists have done tremendous investigations on intercalation of porphyrins into ordered materials such as clays and layered double hydroxides (LDHs)[1,2]. However, the intercalation of one cationic porphyrin tosylate of 5, 10, 15, 20-tetrakis(N, N, N-trimethylanilinium-4-yl) porphine (TMAPP) into layered host α-ZrP has been remained undiscovered, because TMAPP has considerable stereo hindrance. In this study, the porphyrin intercalation composite α-ZrP-TMAPP is prepared through an easy and practical approach and the factors affecting porphyrins intercalation into α-ZrP are explored.

Experimental

α-ZrP and TMAPP were synthesized based on the procedure described in literature[3,4]. Because TMAPP is a relative weak base and its molecular dimension is too big compared to the interlayer of α-ZrP, it cannot be directly intercalated into α-ZrP. Therefore a guest-exchange reaction was adopted, *i.e.* spacer molecules were pre-intercalated into α-ZrP to expand the interlayer spacing of the host. Due to the weak forces holding the molecules within the layers of zirconium phosphate and the high expanded interlayer spacing, the pre-intercalated compounds can be used successfully to intercalate other big molecules such as porphyrins. In this paper, we tested two alkylamine including N-butylamine (BA) and N-octylamine (OA) as spacers. The pre-intercalation composites were obtained by reactions of layered zirconium phosphate (0.25 g) with aqueous alkylamine solution at several concentration level (2, 8, 10 mmol BA and 8, 10 mmol OA were added to 1 g of layered materials respectively), and then the suspended

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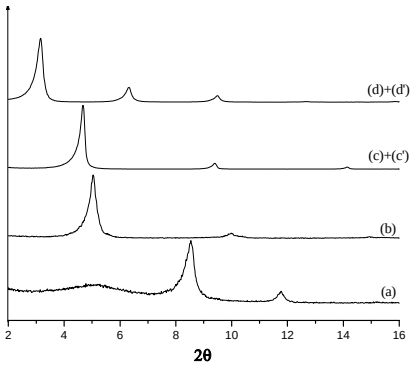
solutions were ultrasonically vibrated at room temperature for 20 min. The resulted composites were filtered, washed with distilled water, and air-dried. When pre-intercalated BA was presented as a monolayer, the intercalation composite was named as α-ZrP-BA. Similarly, the intercalation composite was named as α-ZrP-2BA when BA was arranged in bilayer in α-ZrP. The nomenclature for OA pre-intercalation composite is the same. TMAPP intercalation reaction involved addition of α-ZrP-alkylamine (30 mg) to an aqueous solution of 18 mg TMAPP. Then the suspension was stirred at 50 ºC in a temperature-controlled shaker for 24 hours. The resulted product was collected by centrifugation, washed with ethanol in order to remove the porphyrin from the external surface of material, and air-dried. Then the porphyrin intercalation composite was characterized by XRD (Rigaku Dmax 2000 diffractometer), visible spectrum (Hitachi U-3010 spectrophotometer) and fluorescence spectrum (Hitachi F4500 spectrometer). All calculations about molecular modeling were performed on a 2.4G PC utilizing MM+ force field in HyperChem 6.0.

Results and Discussion

Figure 1 shows X-Ray diffraction of α-ZrP-alkylamine and TMAPP processed α-ZrP-alkylamine. Obviously, α-ZrP-2OA has the largest interlayer distance (2.79 nm), while the interlayer height of α-ZrP-2BA is 1.89 nm and that of α-ZrP-BA is the smallest (1.04 nm) (**Table 1**)[5]. TMAPP interacts with the three compounds mentioned above. As a result, TMAPP can be easily intercalated into α-ZrP-BA by exchanging pre-intercalated monolayer BA. The formation of a new phase at 1.75 nm and the disappearance of α-ZrP-BA peak at 1.04 nm are evidence (see **Figure 1a, 1b** and **Table 1**). However, the spectra of TMAPP interaction with α-ZrP-2BA/OA remain unchangeable with α-ZrP-2alkylamine (see **Figure 1c, 1c′** and **1d, 1d′**), indicating that TMAPP cannot be intercalated into α-ZrP-2OA and α-ZrP-2BA although their interlayer

Figure 1 XRD patterns of α-ZrP-alkylamine and TMAPP intercalation compound



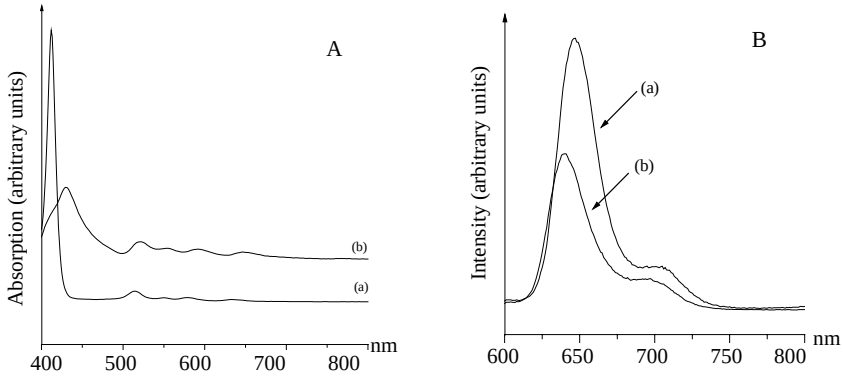
(a) α-ZrP-BA prepared from 2 mmol BA added/g α-ZrP; (b) TMAPP interaction with α-ZrP-BA; (c) α-ZrP-2BA prepared from 8,10 mmol BA added/g α-ZrP; (c′)TMAPP interaction with α-ZrP-2BA; (d) α-ZrP-2OA prepared from 8,10 mmol OA added/g α-ZrP; (d′) TMAPP interaction with α-ZrP-2OA

distances are much larger than that of α-ZrP-BA. Based on XRD results, the following conclusions are drawn: (1) spacer is necessary to enlarge the interlayer distance of hosts, otherwise porphyrins cannot overcome the energyic barrier upon intercalation; 2) porphyrins can be intercalated into the host through exchanging the pre-intercalated spacer, so the leaving ability of spacer is an important intercalation factor. For α-ZrP-2OA and α-ZrP-2BA, their interlayer heights are much larger than that of α-ZrP-BA and it would be easier to incorporate TMAPP than α-ZrP-BA. On the contrary, TMAPP easily intercalates into α-ZrP-BA with small interlayer spacing, but not α-ZrP-2OA/BA with large interlayer distances. It could be that α-ZrP-BA is more mobile than α-ZrP-2alkylamine due to their monolayer arrangement, which is also confirmed by molecular modeling: the lowest energy of α-ZrP-2alkyamine is much lower than that of α-ZrP-BA (see **Table 1**), which means α-ZrP-2alkylamine is much more stable than α-ZrP-BA. Therefore, it is suggested that the suitable spacer not only could expand the interlayer spacing of hosts but also should be mobile so as to be easily removed and exchange with the porphyrins.

The result of XRD shows that the interlayer distance of the porphyrins composite is 1.75 nm, which is very close to that of α-ZrP-*p*-H_2TAPP reported in Ref [6]. These two porphyrins could adopt similar orientation in the interlayer of α-ZrP: as a canted monolayer.

In addition, we investigated the spectrum behavior of α-ZrP-TMAPP as shown in **Figure 2**. The Soret band of TMAPP in α-ZrP shifts to 430 nm while at 412 nm in aqueous solution in **Figure 2A**. We suggest that the obvious bathochromic shift should be ascribed to the close packing of TMAPP in α-ZrP, which can be confirmed by molecular modeling results. Modeling graphics (see **Figure 3**) show that the arrangement of TMAPP is in high density in the interlayer of α-ZrP. Close stacking of porphyrins enhances the coplanar between the porphin ring and the peripheral substitute group, thus, a big π-stacking produces and leads to the observed red shift. Moreover, similar fluorescence spectra of TMAPP between in aqueous solution and in α-ZrP (**Figure 2B)** show that intercalated TMAPP still can emit considerable fluorescence.

Figure 2 Visible absorption (A) and fluorescence spectra (B) of TMAPP

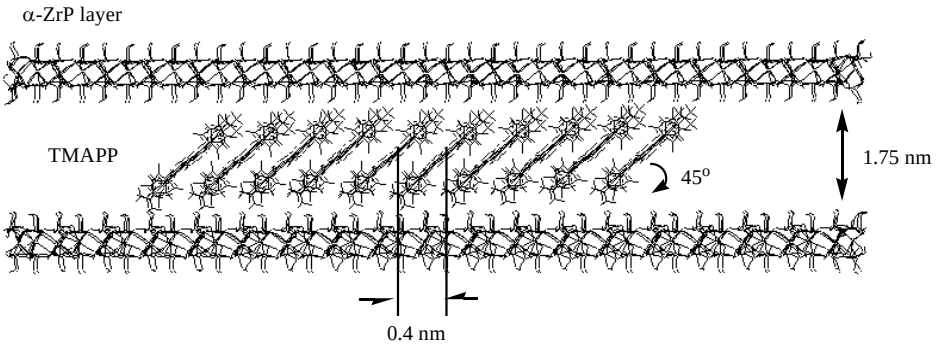


(a) in water (1.2×10^{-6} mol/L); (b) in the interlayer of α-ZrP.
The fluorescence spectra were obtained by excitation at 420 nm.

Table 1 X-Ray powder diffraction data and calculated system potentials

Compound	Interlayer distance(d/nm)		Potential (kcal/mol)
	Preintercalated α-ZrP	TMAPP processed α-ZrP	
α-ZrP	0.76	0.76	
α-ZrP-BA	1.04	**1.75**	-11.6
α-ZrP-2BA	1.89	1.87	-880.99
α-ZrP-2OA	2.79	2.85	-897.58

Figure 3 Molecular modeling graphic of TMAPP into α-ZrP



The lowest potential occurs when the distance of adjacent TMAPP is 0.4 nm corresponding to the normal C-C nonbond distance, suggesting that intercalated porphyrins are densely stacked.

We take an easy and practical method to synthesize α-ZrP-TMAPP in which TMAPP adopts an inclined orientation and packs closely in the interlay of α-ZrP. Comparing porphyins intercalation behavior in α-ZrP-BA with in α-ZrP-2BA and α-ZrP-2OA, we find that the mobility and flexibility of pre-intercalated spacer is a very important factor upon intercalation.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 20271074)

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Received 2 April, 2004