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Preparation and characterization of ionic liquid intercalation compounds into layered zirconium phosphates

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Abstract In this work, immobilizing a series of ionic liquids (ILs) 1-alkyl-3-methylimidazolium chloride [C$_n$mim]Cl (n = 2, 4, 6, 8) on the layered zirconium phosphates were investigated. [C$_4$mim]Cl was used to explore in detail the factors affecting intercalation. By comparing several starting materials including α-zirconium phosphate (α-ZrP), γ-zirconium phosphate (γ-ZrP) and the corresponding alkylamine preintercalated composites, it was found that the α-ZrP · 2BA (i.e., preintercalated BA were arranged in a bilayer mode at the galleries of α-ZrP) was a suitable host for intercalating ILs. Intercalation was verified with X-ray diffraction (XRD), Raman, UV–Vis and other instrumental approaches. pH effect on immobilization was investigated. Other ionic liquids including [C$_n$mim]Cl (n = 2, 6, 8) intercalation compounds were prepared. Based on XRD data, the interlayer distances of the studied intercalation compounds were similar, suggesting that the ionic liquids were arranged in an approximately planar manner, as confirmed by molecular modeling.

Introduction

For the last few years, ionic liquids (ILs), a class of organic compounds with extraordinarily low melting temperatures, have received significant attention. In addition to being in the liquid phase at room temperature, ILs exhibit a negligible vapor pressure, remarkable solvation and coordination properties. There are one million binary ionic liquids and 10^{18} ternary ionic liquids available for various applications. Because ILs are considered as ‘‘green’’ or ‘‘designer’’ solvents, many studies have been done to explore potential industrial applications including synthesis media, catalysis reactions, and extraction [1–6]. Because industrial processes would use large quantities of ionic liquids, recycling to reduce cost would be desirable. And separation of catalyst from reactant and products is one important processing step. The technology named Supported Ionic Liquids Catalysis (SILT) has been investigated [7, 8] with one of the key steps being the effective immobilization of ionic liquids into suitable materials.

As proper hosts, layered inorganic materials such as clays, layered double hydroxides (LDHs) and group (IV) metal phosphates had unique features. The interlayer gallery of these layered matrices could be expanded and modified to accommodate almost any size entity from small ions to macromolecules. Zirconium phosphate (ZrP) has been one of the most extensively investigated layered materials. ZrP exhibits important characteristics for intercalation chemistry due to its reactivity, which arises from the high acidity in its protonic form and the weak interactions between the layers [9]. A number of guests in galleries of zirconium phosphate have been reported [10–13], but there has been no published work on immobilizing ILs into the gallery of zirconium phosphates.

In this study, we explored the intercalation behavior of a series of ionic liquids [C$_n$mim]Cl (n = 2, 4, 6, 8) (see Fig. 1) into layered zirconium phosphates. α and γ-ZrP, alkylamine pre-intercalated α and γ-ZrP were examined as starting materials for intercalation of ILs. Experimental results of XRD, Raman and UV–Vis spectroscopy

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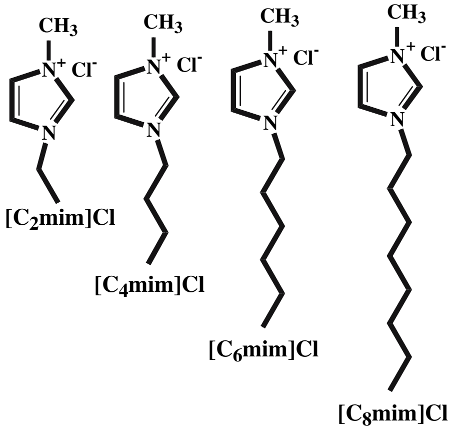

Fig. 1 Molecular structure of [$C_n$mim]Cl (n = 2, 4, 6, 8)

confirmed that α-ZrP · 2BA was the most appropriate host for intercalation. Orientation of intercalated guests in the galleries of the layered host was proposed based upon XRD results and molecular modeling calculation.

Experimental

Materials

Layered zirconium phosphates α-ZrP [14] and γ-ZrP [15], were prepared. Ionic liquids, 1-alkyl-3-methylimidazolium chloride, [$C_n$mim]Cl (n = 2, 4, 6, 8), were purchased from Aldrich. *N*-butylamine (BA), *N*-octylamine (OA) and other chemicals were analytical grade. Purified water was used throughout the study.

Instruments

X-ray diffraction (XRD) analyses were done with Rigaku Dmax 2000 diffractometer (Japan) with Ni-filtered Cu Kα radiation. The UV–Vis and Raman spectra were obtained with a Hitachi U-3010 spectrophotometer and Nicolet Raman 950. Dupont 1090B was used for thermogravimetric analysis (TGA). Immobilization was done under controlled temperature using Haerbin Dongliang HZQ-F160 incubator.

Synthesis of α-ZrP/γ-ZrP·alkylamine intercalation compounds

The pre-intercalated compounds were obtained by reaction of 0.25 g layered zirconium phosphate with 10 mL aqueous alkylamine solution with concentration in the final (expressed in ratio r) as 2 and 4 for BA and 8 for OA in mmol, respectively, to 1 g host. Then the suspended solutions were ultrasonically vibrated at room temperature for 20 min. The resulted compounds were filtered, washed with purified water, and air-dried.

Note: To simplify the expressions, materials corresponding to $r = 2$ (for BA to α-ZrP) were denoted α-ZrP · BA, $r = 4$ (for BA to α-ZrP/γ-ZrP) were denoted α-ZrP · 2BA or γ-ZrP · 2BA, and $r = 8$ (for OA to α-ZrP/γ-ZrP) were denoted α-ZrP · 2OA or γ-ZrP · 2OA [16].

Synthesis of [C_4mim]Cl intercalation compounds

The intercalation reactions were carried out by addition of 30 mg of different starting materials including α-ZrP, α-ZrP · BA, α-ZrP · 2BA, α-ZrP · 2OA, γ-ZrP, γ-ZrP · 2BA and γ-ZrP · 2OA to 20 mL aqueous solution of ILs (the molar ratio of starting materials and guests was about 1:4). After pH was adjusted to 7.5, the suspensions were shaken in HZQ-F160 incubator at 50 °C for 1 day. The resulted products were collected by centrifugation, washed with purified water and air-dried.

The effect of pH on intercalation of [C_4mim]Cl

Thirty milligrams of α-ZrP · 2BA was added to 20 mL aqueous solution of [C_4mim]Cl (the molar ratio of starting materials and guests was about 1:4) with pH adjusted from 5.5 to 10.0. Suspensions were shaken in HZQ-F160 incubator at 50 °C for 1 day. The resulted products collected by centrifugation were then washed with purified water until [C_4mim]Cl in supernatant was not detected by UV absorption at 210 nm. The intercalative amount of [C_4mim]Cl was calculated by subtracting [C_4mim]Cl remaining in the supernatant from the amount applied.

Preparation of [$C_n$mim]Cl (n = 2,6,8) intercalation compounds

Thirty milligrams of α-ZrP · 2BA was added to 20 mL aqueous solution of ILs (the molar ratio of starting materials and guests was about 1:4). After pH was adjusted to 7.5, suspensions were shaken in HZQ-F160 incubator at 50 °C for 1 day. The resulted products were collected by centrifugation, washed with purified water and air-dried.

Desorption of intercalation compound

Thirty milligrams of intercalation compound [C_4mim]Cl-α-ZrP was mixed with 20 mL hydrochloric acid solution (1:10 by volume ratio). Suspensions were shaken in HZQ-F160 incubator at 50 °C for 6 days. After centrifugation, the resulted solid products were collected and characterized using XRD. The UV–Vis spectra of supernatants were recorded to compare with that of 1 mol/L HCl and [C_4mim]Cl in 1 mol/L HCl aqueous solution.

Modeling methods

Construction of [C$_4$mim]Cl intercalation compounds

The two layers of α-ZrP forming one interlayer (24 × 100 Å) were constructed with the help of the *HyperChem* program package [17]. The interlayer distance was defined as 17.9 Å according to the XRD data of [C$_4$mim]Cl-α-ZrP. Fifty six [C$_4$mim]Cl molecules were positioned in the way of 4 × 14 into the galleries of α-ZrP (Fig. 2). In order to identify orientation of intercalated [C$_4$mim]Cl, eight possible modes (Fig. 3) were designed based on the following aspects: (1) for ionic liquid intercalation compounds, the net interlayer spacing was 11.6 Å because the thickness of one α-ZrP layer (6.3 Å) was subtracted. Based on XRD data and the dimension of ILs, guests in the gallery should be either a monolayer tilted to the host layer or a bilayer roughly parallel to the host sheets. Then the angle between the imidazole ring of [C$_4$mim]Cl and the zirconium phosphate sheets was assigned to three typical geometrical occurrences including planar (mode *a*, *b*, *c* and *d*), 45° (*e* and *f*), and 90° (*g* and *h*); (2) for adjacent [C$_4$mim]Cl molecules in the planar mode in host, there were two possible modes. The head-tail mode (mode *a* and *b*) resulted in high density of the guests intercalated, and the head-head mode (mode *c* and *d*) resulted in the lower density compared to head-tail mode; (3) configuration difference of [C$_4$mim]Cl dictated a difference between mode *a* and *b*, *c* and *d*, *e* and *f*, as well as *g* and *h*. Based on potential minimum perspective, there existed two optimum configurations for [C$_4$mim]Cl with very close potentials at 30.26 and 30.22 kcal/mol, corresponding to *trans* and *gauche* configuration, respectively. The *trans* configuration showed that the angle between N1-C1-C2 and C1-C2-C3 was 180° (as shown in mode *a*, *c*, *e* and *g*). The *gauche* configuration showed that the angle between N1-C1-C2 and C1-C2-C3 was 60° (as shown in mode *b*, *d*, *f* and *h*).

Computational procedure

For free [C$_4$mim]Cl, the structure was obtained by energy minimization in MM+ force field without any restraints. The structure of α-ZrP layers was optimized in a similar way. The interlayer distance was manually adjusted to 17.9 Å and fixed. The optimized [C$_4$mim]Cl was then manually assembled into the galleries of α-ZrP. In the intercalation procedure, there was no bond breaking or formation. The intercalative potential was then approximately equal to the difference between the potential of the assembled system ([C$_4$mim]Cl-α-ZrP), and the collective value from both free host (α-ZrP) and free guests ([C$_4$mim]Cl). Since α-ZrP layers were fixed only to provide a specified intercalative circumstance for guests [C$_4$mim]Cl, the potential values of α-ZrP layers were kept unchanged pre and post intercalation. Therefore, the intercalative potential was simply equal to the potential difference of the intercalated [C$_4$mim]Cl with and without α-ZrP layers. In this study, potential values were derived from energy minimization with a conjugate-gradient optimizer at a convergence criterion of 0.5 kcal mol^{-1} Å^{-1}. All calculations were performed on a 2.4G PC utilizing MM+ force field in *HyperChem 6.0* using default settings consistently (Assigning a dielectric constant of 1.0).

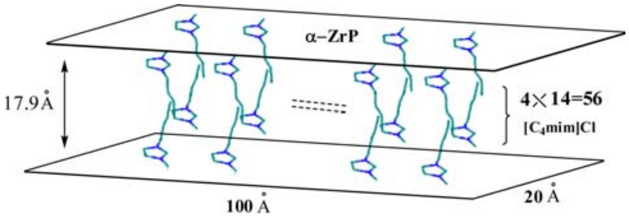

Fig. 2 Stylized representation of [C$_4$mim]Cl into α-ZrP

Results and discussion

Preparation of [C$_4$mim]Cl intercalation compounds

Selection of suitable hosts

In the technology SILT, one of the key steps is to identify a suitable host to efficiently accommodate ILs. Zirconium phosphates and alkylamine pre-intercalated compounds including α-ZrP, α-ZrP · BA, α-ZrP · 2BA, α-ZrP · 2OA, γ-ZrP, γ-ZrP · 2BA, and γ-ZrP · 2OA were examined as starting materials for intercalating [C$_4$mim]Cl. Table 1 gives the interlayer distances of the studied materials before and after interaction with [C$_4$mim]Cl. Amongst the host materials investigated, it was clear that α-ZrP · 2BA was one suitable host because the interlayer distance changed from 16.4 to 17.9 Å, resulting from [C$_4$mim]Cl intercalation. Other hosts did not show the intercalation effect for the guests because XRD patterns showed that interlayer distances of hosts were substantially unchanged after reaction. By comparing intercalation behavior of different materials listed in Table 1, it could be suggested that: (1) direct intercalation into layered zirconium phosphates was not successful, therefore spacer (such as alkylamines) was necessary to pre-expand the original small *d*-spacing in order to incorporate guests. This indirect intercalation route has been confirmed and adopted in many studies [10–13, 18, 19]; (2) interlayer distance was not the main intercalation factor because starting materials with larger *d*-spacing such as α-ZrP · 2OA (d = 27.9 Å) and γ-ZrP · 2OA (d = 25.3 Å) could not incorporate

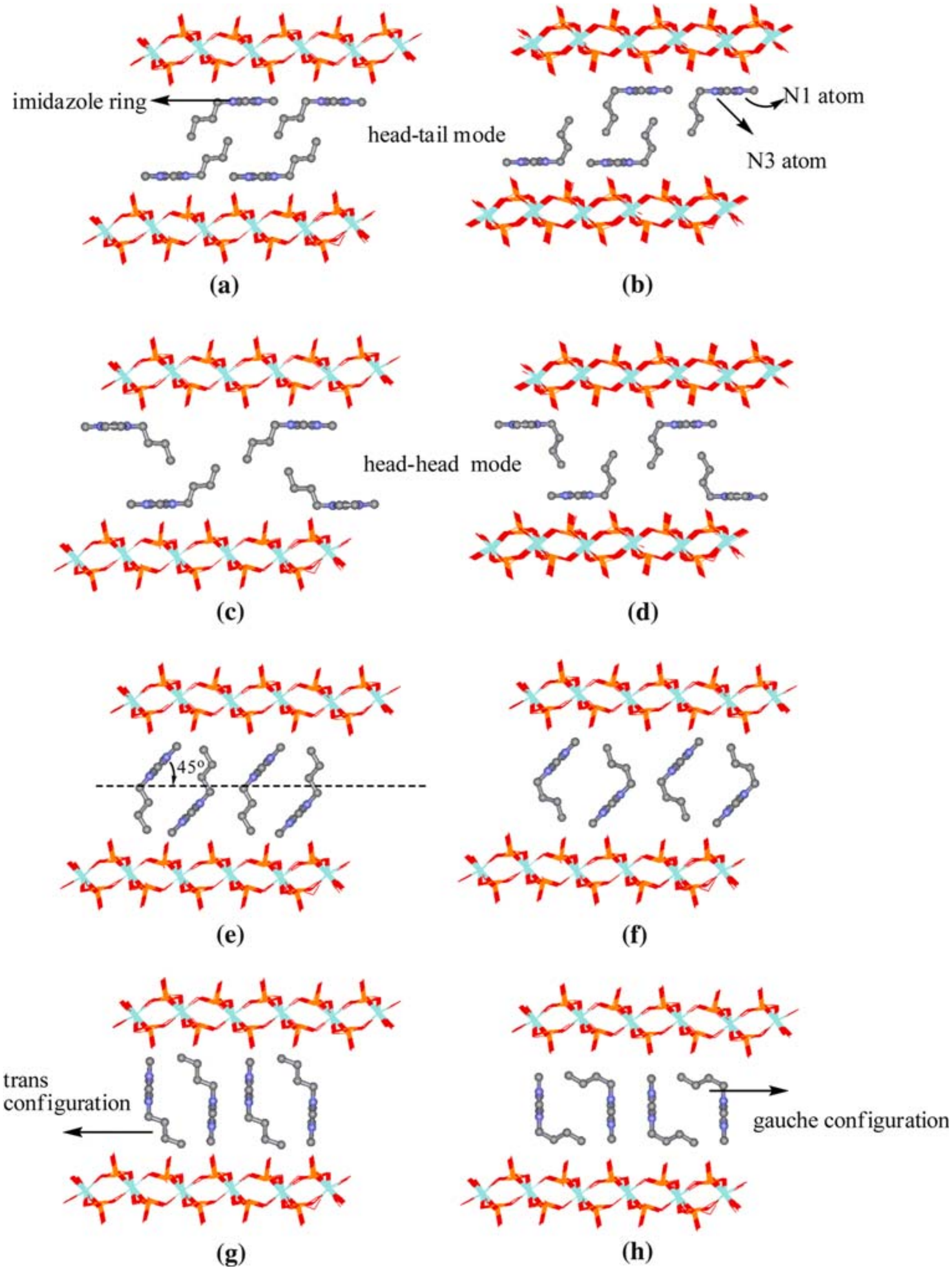

Fig. 3 Hypothetical modes of intercalated [C_4mim]Cl into α-ZrP

Table 1 Interlayer distances of starting materials and [C_4mim]Cl intercalation compounds

Zirconium phosphates	Interlayer distances (Å)	
	Before interaction	After interaction
α-ZrP	7.6	7.7
γ-ZrP	12.0	12.1
α-ZrP · 2OA	27.9	28.5
α-ZrP · BA	10.4	10.7
α-ZrP · 2BA	*16.4*	*17.9*
γ-ZrP · 2BA	18.3	18.0
γ-ZrP · 2OA	25.3	25.6

[C_4mim]Cl. Long alkyl chain formed stable hydrophobic area in the gallery of the host, which made it difficult to exchange with hydrophilic ILs. Therefore, a suitable spacer should be able to not only expand the interlayer distance but also be easily exchanged with guests.

pH dependency of [C_4mim]Cl intercalation

Figure 4 shows the effect of pH on the intercalative content of [C_4mim]Cl into α-ZrP. The intercalative content of [C_4mim]Cl remained constant from acid pH (5.5) to basic pH (9.50), thus pH had little effect on the intercalative

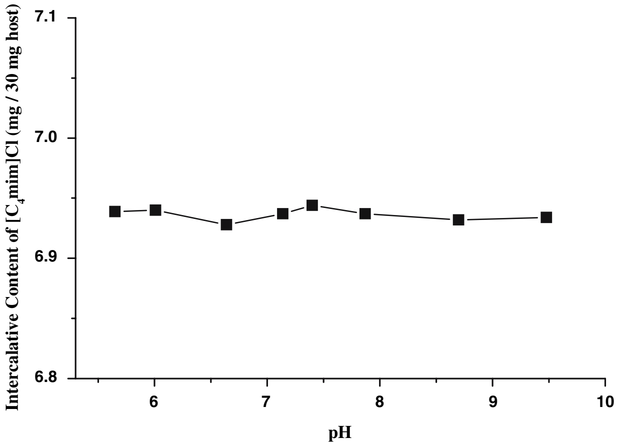

Fig. 4 The effect of pH on intercalative content of [C_4mim]Cl into α-ZrP

content. In subsequent study, pH 7.5 was adopted to intercalate [C_4mim]Cl.

Characterization of [C_4mim]Cl intercalation compounds

XRD characterization

Figure 5 shows typical X-ray powder patterns of the starting materials (α-ZrP and α-ZrP · 2BA) and the produced ILs intercalated material. XRD pattern recorded for α-ZrP (Curve a) indicated that the compound was obtained in a single crystallographic phase corresponding to interlayer distance at 7.6 Å. α-ZrP · 2BA showed a new peak at *d* = 16.4 Å (Curve b) indicating that a double amine layer formed with alkyl chains roughly inclined at 60° to the plane of the host layer [16]. The new peak at *d* = 17.9 Å (Curve c) and simultaneous disappearing of *d* = 16.4 Å proved the complete conversion from starting material α-ZrP · 2BA to ILs-intercalated phase. It was proposed that [C_4mim]Cl was intercalated by exchanging with pre-intercalated BA bilayer. Sharp and narrow peak suggested that guests were orderly arranged between the sheets of layered phosphate.

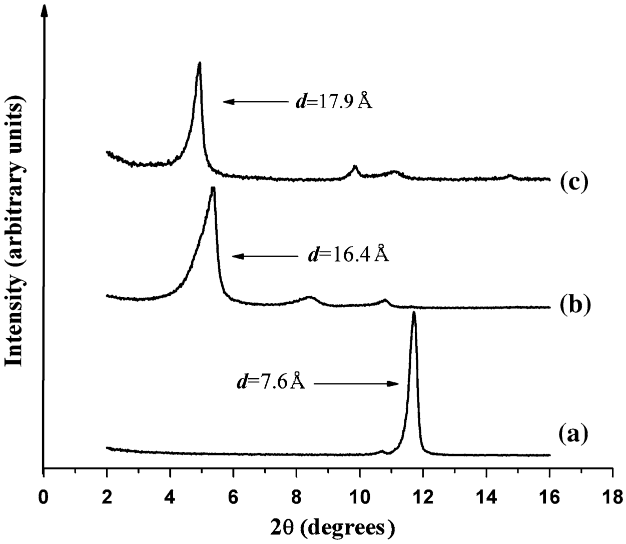

Fig. 5 The XRD patterns of α-ZrP (**a**), α-ZrP · 2BA (**b**), and intercalation compound of [C_4mim]Cl-α-ZrP (**c**)

Raman spectra characterization

Raman spectra of host α-ZrP, guest [C_4mim]Cl and intercalation compound [C_4mim]Cl-α-ZrP are shown in Fig. 6. α-ZrP showed peaks at 287 and 1051 nm. [C_4mim]Cl showed two peaks at 1413 and 2964 nm. The peaks of [C_4mim]Cl-α-ZrP combined peaks of both the host and guest, indicating occurrence of the intercalation. The maintenance of the characteristic peaks of α-ZrP illustrated that α-ZrP layers were rigid during intercalation. Comparing with the peaks of the host and guest in their free forms, the bands of the assembled system [C_4mim]Cl-α-ZrP shifted slightly, indicating interactions between the host and guest.

TGA characterization

TGA curve of [C_4mim]Cl-α-ZrP is shown in Fig. 7, provided supporting information about intercalation of [C_4mim]Cl. There was a 20.96% weight loss process from 200 °C to 400 °C. The weight loss was close to the content of intercalated [C_4mim]Cl (intercalative content of [C_4mim]Cl per 30 mg host = 6.95 mg/30 mg = 23.00% with 6.95 mg obtained from Fig. 4). It was inferred that [C_4mim]Cl intercalated into α-ZrP was thermally degraded during TGA scanning. The weak loss peak around 100 °C should be attributed to the loss of interlayer water.

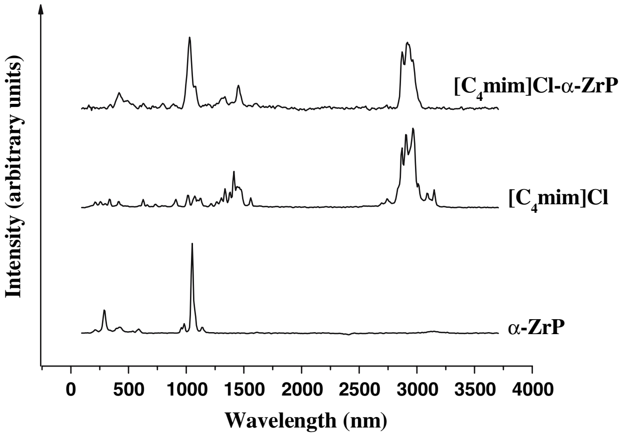

Fig. 6 The Raman spectra of α-ZrP, [C_4mim]Cl and [C_4mim]Cl-α-ZrP

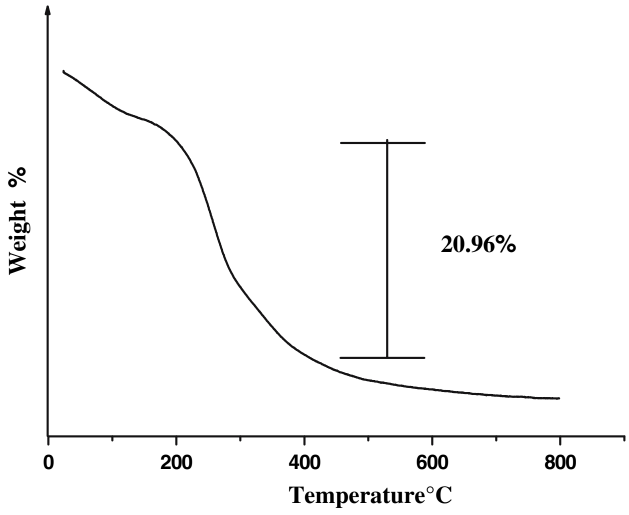

Fig. 7 Thermogravimetric analysis (TGA) diagram of [C_4mim]Cl-α-ZrP

Desorption characterization

Based on the fact that guests can be exchanged with H^+ due to the exchangeable and swelling properties of α-ZrP [20], the desorption experiment was designed to clarify further that [C_4mim]Cl was intercalated into α-ZrP. Produced material [C_4mim]Cl-α-ZrP was washed until there was no [C_4mim]Cl in the supernatant observed (Fig. 8, Curve a), thus there were little ILs on the surface of intercalation compounds. Curve b shows the absorption peak of hydrochloric acid at 202 nm. Curve c shows the absorption peak of 202 and 210 nm of hydrochloric acid and [C_4mim]Cl, respectively. Similar to Curve c, there were two peaks at 202 and 210 nm in Curve d, demonstrating that the supernatant of desorption study contained both excess hydrochloric acid and de-intercalated [C_4mim]Cl previously presented in the gallery of α-ZrP. After the desorption in hydrochloric acid, the XRD pattern (Figure not shown) showed that the peak corresponding to [C_4mim]Cl-α-ZrP (d = 17.9 Å) disappeared, while a single phase corresponding to α-ZrP (d = 7.6 Å) appeared, indicating decomposition.

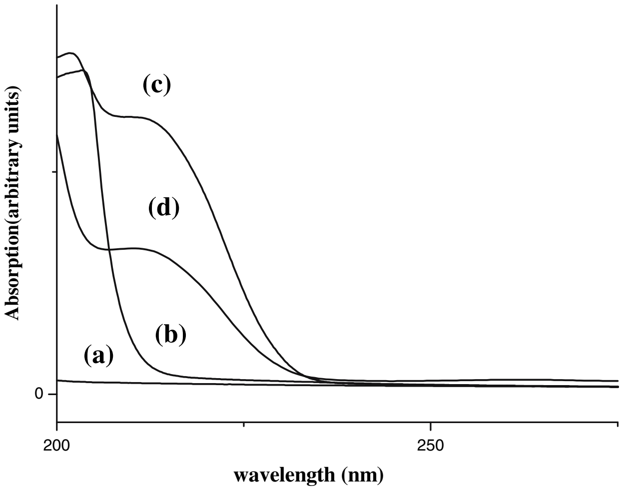

Fig. 8 The UV spectra obtained in desorption experiment. (**a**) spectrum for supernatant after intercalation; (**b**) spectrum for HCl (1 mol/L) solution; (**c**) spectrum for [C_4mim]Cl in HCl (1 mol/L); and (**d**) spectrum for desorption solution

Other ILs intercalation compounds

In order to clarify the relationship between the intercalation behavior and structural characteristics of ionic liquids, a series of ionic liquids [$C_n$mim]Cl (n = 2, 4, 6, 8) with varied alkyl chain length were interacted with α-ZrP · 2BA as exchange intermediate. Table 2 presents the interlayer distances of α-ZrP · 2BA before and after interaction with ionic liquids. The interlayer distances of the host changed after interaction, indicating that all of the studied ILs could exchange with the pre-intercalated BA and be intercalated into the gallery. Moreover, the interlayer distances of the series of ionic liquid intercalation compounds were almost identical (d = 18.0 Å), suggesting that the interlayer distances of intercalation compounds were irrelevant to the length of the alkyl-substituent of ILs and guests should be roughly parallel with host sheets. The orientation of intercalated guests was explored in detail as follows.

Orientation of intercalated ionic liquids

To date, it has been very difficult to clarify orientation of intercalated guests by currently available experimental techniques. In this situation, molecular modeling was but one possible approach to provide valuable information. To elucidate the interlayer state of studied ILs, orientation of intercalated [C_4mim]Cl was explored by molecular modeling.

Figure 3 presents eight hypothetical assembly modes of [C_4mim]Cl in the matrix. The intercalative potential values were listed in Table 3. The potential level corresponding to planar mode *a* was the lowest. Based on the arrangements of intercalated [C_4mim]Cl, it was deduced that the other ILs studied including [C_2mim]Cl, [C_6mim] and [C_8mim]Cl adopted an approximately planar mode, which was consistent with the experimental results that the basal spacing was almost identical (Table 2). The orientation adopted by ILs could be that: (1) the planar arrangement adopted by intercalated ILs was mainly attributed to the molecular structure of ILs themselves, especially the distribution of charge. For the studied ILs, the positive charges were distributed over imidazole ring. In this situation, only in bilayer planar manner could the charges of zirconium phosphate layers be sufficiently countered by ionic liquids.

Table 2 Interlayer distances of ionic liquid intercalation compounds

Intercalation compounds	α-ZrP · 2BA	$[C_2mim]Cl$-α-ZrP	$[C_4mim]Cl$-α-ZrP	$[C_6mim]Cl$-α-ZrP	$[C_8mim]Cl$-α-ZrP
Interlayer distances (Å)	16.4	18.0	17.9	18.1	18.0

Table 3 Intercalative potentials of $[C_4mim]Cl$ in assigned intercalation modes

Intercalation modes	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*
Potentials (kcal/mol)	*–21.32*	–18.04	–16.64	–15.53	–20.88	–17.65	–19.45	–19.64

Thus, it was inferred that the structural character of intercalated guests was an important factor affecting their mode of assembly. This was also confirmed by intercalation of cationic porphyrins into α-ZrP. Cationic porphyrins such as 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] were arranged with their planes inclined to the host lamella [16, 18]. In porphyrins, cationic groups were on substituents of the porphyrin ring, thus the canted porphyrins could optimize electrostatic interaction, whereas parallel porphyrins were not able to counter charges on host layers. This also indicated that the electrostatic interaction was the primary interaction between hosts and guests; (2) in optimal mode, adjacent molecules adopted the head-tail mode. This resulted in higher charge density compared with other modes, so that charges on the zirconium phosphate layers could be ultimately balanced by the guests.

The potential of free $[C_4mim]Cl$ molecule with *gauche* configuration and that with *trans* configuration were almost the same (30.26 and 30.22 kcal/mol, respectively), deducing that similar configurations in bilayer planar mode, mode *a* (*trans*) and mode *b* (*gauche*),mode *c* and *d*, as well as mode *e* and *f*, should be equally stable. However, our modeling results showed that the modes with molecules assembled in *trans* configuration (mode *a*, *c* and *e*) were distinctively more stable than those in *gauche* configuration (mode *b*, *d* and *f*). It may be that the restriction of α-ZrP layers cause the interaction between $[C_4mim]Cl$ molecules, which lead to steric interference. In this case, *trans* configuration favored the close stack of $[C_4mim]Cl$ molecules more than the *gauche* configuration.

Conclusions

This paper reported a new route for immobilizing ILs, 1-alkyl-3- methylimidazolium chloride $[C_nmim]Cl$ ($n = 2, 4, 6, 8$) into layered materials. A series of intercalation compounds were synthesized using an easy-to-prepare and environment friendly host, α-ZrP · 2BA. It is our hope that this work would provide a practical and easy approach for immobilization of ILs and application in the green technology SILT. Moreover, both molecular modeling and experimental results showed that ILs took an approximately planar mode in the galleries of α-ZrP. The results obtained would be helpful for understanding the ILs intercalation compounds.

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