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ORIGINAL PAPER

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Molecular modeling of the intercalation of porphyrins into a-zirconium phosphate

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Abstract In this work, *n*-alkylamines (number of carbon atoms ranging from 3 to 10) were investigated in detail by molecular modeling as spacers for intercalating porphyrins into α-zirconium phosphate (α-ZrP). Pre-intercalated *n*-alkylamines can form either a flat monolayer or a canted bilayer in the gallery of α-ZrP. Based on the interlayer state and intercalative potential of the two modes in α-ZrP, it is suggested that the flat monolayer is a better spacer than the bilayer and that *n*-propylamine (PA) and *n*-butylamine (BA) in mobile monolayers are the best spacers among the *n*-alkylamines studied, as is also found experimentally. The intercalation behavior of TMPyP [5,10,15,20-tetrakis (1-methylpyridinium-4-yl) porphyrin] and several other porphyrins was investigated by calculating the intercalative potential. The calculated results showed that the porphyrins were densely packed in a canted monolayer model, and an increase of polarity of the substituent would facilitate the intercalation of the porphyrins.

Keywords α-Zirconium phosphate · *n*-Alkylamine · Porphyrins · Intercalation

Introduction

Porphyrins have been studied extensively during the past decades because of their unique physical and chemical properties [1–7]. Hence, the intercalation of porphyrins into layered materials such as clays, layered double hydroxides (LDH) and niobates has been widely studied in an effort to control the attractive properties of these molecules better [8–10]. α-Zirconium phosphate (α-ZrP) is a class of layered inorganic materials with a combination of swelling, intercalation and ion-exchange properties. This material has a natural ability to adsorb organic or inorganic cationic guests (and even neutral molecules) from solution. The "storage" feature gives unique properties to such minerals, which can be used as catalysts, proton conductors, or components in optical devices [11–13]. The intercalation of porphyrins into α-ZrP as materials interesting for a variety of purposes, has been explored by the experimental methods including X-ray diffraction (XRD), EPR, absorption spectroscopy, fluorescence spectroscopy, etc. [14, 15]. However, it is very difficult to elucidate the nature of the microenvironment between the host and the guest and interlayer state of the guest molecule by current experimental techniques. For such systems, molecular simulation is but one possible approach to providing valuable information.

In this work, the intercalation of *n*-alkylamines (with between 3 and 10 carbon atoms) as spacers and porphyrins as guests into the layered host of α-ZrP was studied by molecular modeling. The simulation results reveal that the pre-intercalated *n*-alkylamine in a flat monolayer mode is a better spacer for intercalating porphyrins into α-ZrP than the amines in bilayer mode and among the amines studied, α-ZrP·PA and α-ZrP·BA [i.e. *n*-propylamine (PA) and *n*-butylamine (BA) are arranged in a planar monolayer in the matrix of α-ZrP] are the most suitable for exchanging with porphyrins. Moreover, to elucidate the interlayer state of porphyrins, TMPyP was taken as the model molecule to explore the intercalation orientation and the optimum space of adjacent porphyrin. The intercalative potentials of several other porphyrins investigated experimentally in our lab and in the literature [14, 15] are also calculated to explore the contribution of porphyrin substituents on intercalation behavior further. The calculated results suggest that the porphyrins are densely packed in a canted monolayer model, and the polarity and dimension of the porphyrin substituents are two factors that influence intercalation behavior of the porphyrins. There are reasonably good correlations between the simula-

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tions and experimental results, indicating that our molecular modeling methods are feasible.

Modeling methods

Construction of α-ZrP

The structural parameters of the layered host were adopted from Ref. [16]. The valence model was used to reproduce the layer geometries of α-ZrP. The two layers of α-ZrP forming one interlayer set to 28 × 140 Å were constructed with the help of the *HyperChem* program package [17]. The parameters for Zirconium were from the *CS Chem3D* program. The partial charges of the layers were transferred from a repeated octahedron unit. The Zirconium metal center is coordinated by six oxygen atoms from six PO_4 groups. All partial charges in the octahedron unit were obtained by a semi empirical calculation using the PM3 Hamiltonian.

Construction of *n*-alkylamine intercalated compounds

Sufficient amounts of *n*-alkylamine were projected to be intercalated in the galleries of α-ZrP by three intercalation modes including a planar monolayer, a canted monolayer and an inclined bilayer, as shown in Fig. 1. In the flat monolayer manner, the interlayer distances (*d*) of all *n*-alkylaimne/α-ZrP compounds were assigned to be 10.4 Å, according to the experimental results of PA and BA intercalation compounds [18]. The interlayer distance is denoted as the distance between Zr atoms of two adjacent layers. In the canted monolayer and bilayer intercalation orientations, the amine group of *n*-alkylamine is placed among three P-OH groups to form (P)-HO–HNH–OH-(P) hydrogen bonds (H-bond). From other viewpoint, the proton H is transferred from a (P)-OH group to $-NH_2$ so as to form an ionic-type structure with one $-NH_3^+$ in the middle of three (P)-O^- groups. The C–C chains of the *n*-alkylamine are tilted 60° toward the host sheets (see Fig. 1b) [18]. The theoretical interlayer distances are calculated accordingly; in the bilayer intercalation mode, $d_{bi} = L \times \sin 60° + 6.3$ Å (*L* represents the length of *n*-alkylamine, 6.3 Å represents the thickness of one α-ZrP layer); in monolayer mode, $d_{mo} = L \times \sin 60°/2 + 6.3$ Å. In order to obtain the optimum interlayer distance, a series of intercalative potentials of the *n*-alkylamine/α-ZrP compounds were calculated by changing the theoretical interlayer distances stepwise until the potential minimum was reached.

Construction of TMPyP intercalated compounds

Eight TMPyP molecules were positioned into the α-ZrP layers in two possible orientations, a flat bilayer arrangement and an inclined monolayer orientation, as shown in Fig. 2. The interlayer distance was set to 17.8 Å according to our previous study [15]. In order to obtain the optimum space corresponding to the potential minimum, the intercalative potentials of TMPyPs in α-ZrP were calculated by changing the space from 12.0 to 4.8 Å. Here, the space is defined as the straight distance between hydrogen atoms on adjacent porphine rings (see Fig. 2a).

Construction of other porphyrin intercalated compounds

Porphyrins, including TMAPP [5,10,15,20-tetrakis (*N*,*N*, *N*-trimethylanilinium-4-yl) porphyrin], *p*-TAPP [5,10,15,20-tetrakis (anilinium-4-yl) porphyrin] and TPyP [5,10,15,20-tetrakis (pyridinium-4-yl) porphyrin] (see Fig. 3) were positioned into the host layers in the same canted mode as TMPyP. The interlayer distances were set to 17.0 Å for *p*-TAPP and 17.5 Å for TMAPP, respectively, according to the experimental results [14, 15]. As TPyP could not be intercalated into the galleries of α-ZrP in our experiments, the interlayer distance was set to 16.1 Å based on its molecular dimensions. The space of adjacent porphyrins was altered stepwise from 6.5 to 7.3 Å to evaluate the intercalative potential.

Computational procedure

The partial charges of *n*-alkylamines and porphyrins were obtained from a semi empirical calculation using the PM3 Hamiltonian, and then *n*-alkylamines and porphyrins were minimized using the MM + force field without any restraints. After the interlayer distances of α-ZrP were changed manually based on the bulks of the intercalated molecules, the optimized *n*-alkylamines or porphyrins were docked manually into the galleries of α-ZrP. Thus, the intercalation compounds were constructed individually and then optimized to obtain the potential value of the interaction system consisting of the intercalated species and α-ZrP layers. In this procedure, the α-ZrP layers were fixed so as to maintain the assigned interlayer distances. Finally, without breaking or formation of a bond in the modeling processes, the intercalative potential is equal to the difference between the potentials of the isolated host and guest and the potential of the assembled system. Here, the main effect of the α-ZrP layers is to provide a specific intercalative environment for guests while the intercalated system were minimized, i.e. the potential value of α-ZrP layers remains unchanged before and after reaction. Therefore, the intercalative potential is simply equal to the potential difference of the intercalated species between the constraining environment with and without α-ZrP layers. The system potential was calculated by 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 2.4 GHz PC using the MM +

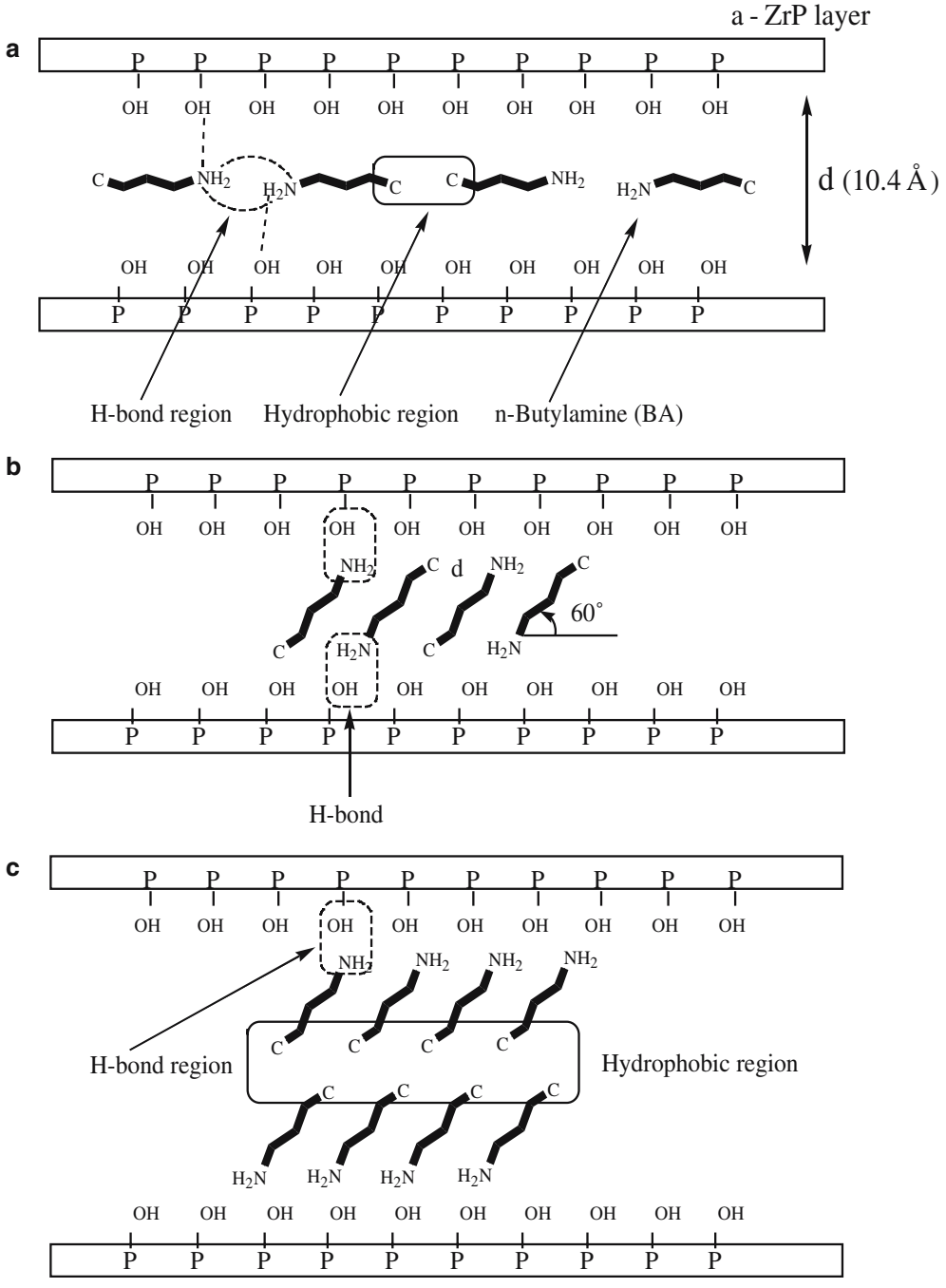

Fig. 1 Three intercalation orientations of *n*-alkylamine into α-ZrP: **a** a flat monolayer; **b** a canted bilayer; **c** a canted bilayer (taking *n*-butylamine as an example)

force field in *HyperChem 6.0* using the default settings consistently (assigning a dielectric of 1.0).

Results and discussion

N-alkylamine/α-ZrP intercalation compounds

One of the main features of α-ZrP is that the layers can be expanded and this facilitates binding of small molecules and ions in the galleries. However, the small interlayer distance in α-ZrP (7.6 Å) poses a kinetic barrier to opening the layers in order to incorporate large molecules such as porphyrins. In this case, *n*-alkylamines are introduced into the interlayers as spacers so that porphyrins can then be intercalated by exchanging the pre-trapped spacers. Thus, it is interesting to explore *n*-alkylamine/α-ZrP intercalation compounds before having an insight into the porphyrin/α-ZrP compounds.

Pre-intercalated *n*-alkylamines can either form a monolayer or a bilayer in the α-ZrP gallery. At low amine content, amines form a monolayer; at high content, a double layer forms with alkyl chains roughly inclined at 60° to the plane of the host layer. For the

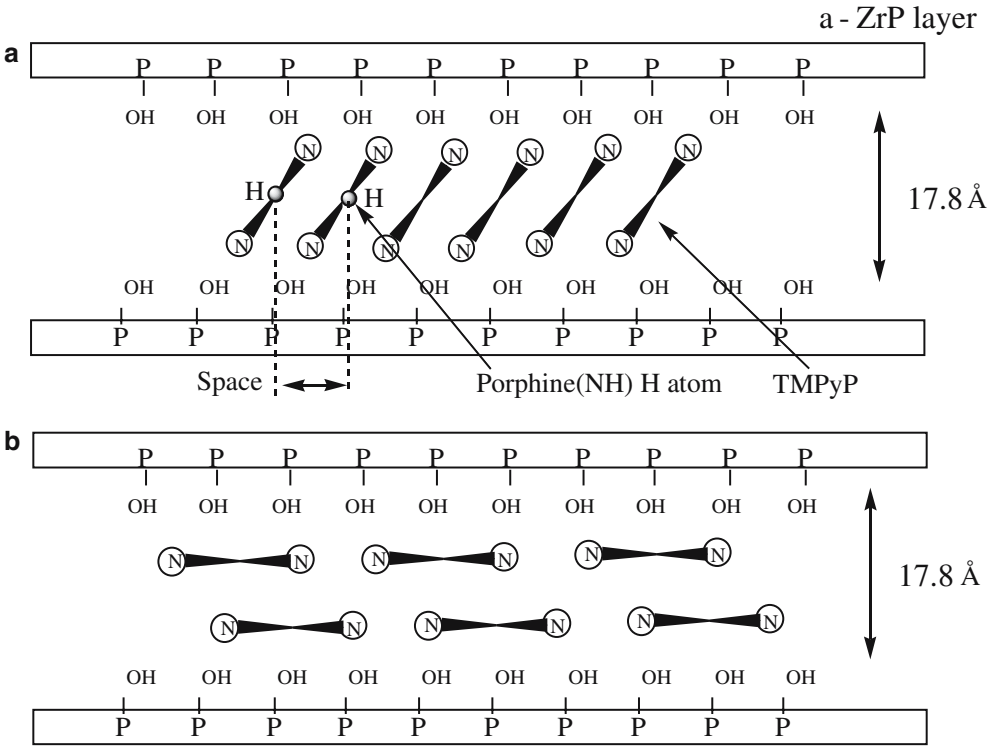

Fig. 2 Stylized representation of **a** a canted TMPyP monolayer, **b** a planar TMPyP bilayer

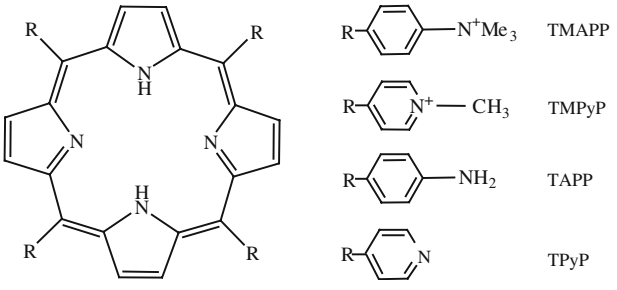

Fig. 3 Structure of porphyrins

monolayer, there are two possible modes, a flat and a canted configuration, in which the alkyl chain is similarly inclined to the host sheets at an angle of 60°. Based on the fact that PA/BA intercalation compounds have the same interlayer distance of 10.4 Å, Clearfield and Tindwa [18] proposed a flat monolayer mode. However, there is no direct evidence for a flat monolayer arrangement for other *n*-alkylamines, so it is desirable to clarify the interlayer state of the monolayer *n*-alkylamine by molecular modeling. Our calculation results (Table 1) show that between the two monolayer intercalated modes the intercalative potential of *n*-alkylamines at a flat orientation is more negative than that of a canted orientation, indicating that the flat orientation with the interlayer distance of 10.4 Å, independent of the amine chain length, is a preferable intercalation mode at low amine content. This can be explained by Fig. 1 (a) In the flat orientation, additionally to the H-bonds between *n*-alkylamines and the host sheet similar to the canted orientation, there are also H-bonds between adjacent *n*-alkylamine molecules; (b) adjacent nonpolar C-terminals of the alkyl chain form a stable hydrophobic region.

The *n*-alkylamine/α-ZrP compounds with amines in both the monolayer and bilayer orientation can all be synthesized in experiments. To identify which mode would be more feasible for intercalating guest porphyrins, the exchanging capability of spacers should be considered. Our experimental results show that the exchange speed between porphyrins and planar monolayer *n*-alkylamines is obviously much faster than that between porphyrins and amines in a canted bilayer. For example, the exchange time is one day for α-ZrP·BA, while it is 6 days for α-ZrP·2BA [15]. The results can be interpreted better by the following aspects. For *n*-alkylamines in the planar monolayer arrangement, a hydrophilic and hydrophobic region of *n*-alkylamines adjoining the interface of α-ZrP layer is formed, by polar N-terminal and nonpolar C-terminal of *n*-alkylamines, respectively (see Fig. 4a). Porphyins not only contain polar substituent groups and a nonpolar porphine ring, but also in the canted mode maintain the amphiphilic distribution collectively similar to flat *n*-alkylamines (see Fig. 4b). However, for *n*-alkylamines in a canted bilayer mode, only the polar terminal of amine faces one side of α-ZrP surface (see Fig. 4c). As the distribution of hydrophobic and hydrophilic regions of flat *n*-alkylamines is similar to inclined porphyrins, the former is relatively easy to exchange with the latter. On the other hand, with respect to the potential of the *n*-alkylamine/α-ZrP systems, the more negative the intercalative potentials, the more stable the intercalation compounds,

Table 1 The intercalative potential of *n*-alkylamine incorporated into α-ZrP in a flat monolayer, a canted monolayer and a canted bilayer[a]

C atom number	Flat monolayer		Canted monolayer		Canted bilayer	
	d (Å)	Potential (kcal mol^{-1})	d (Å)	Potential (kcal mol^{-1})	d (Å)	Potential (kcal mol^{-1})
3(PA)	10.4	−8.37	12.1	−8.23	17.0	−5.30
4(BA)	10.4	−9.24	12.5	−6.51	18.4	−4.24
5(PeA)	10.4	−10.37	13.3	−6.86	20.7	−2.81
6(EsA)	10.4	−12.88	14.8	−7.13	21.4	−4.30
7(EpA)	10.4	−10.98	16.1	−5.40	23.9	−3.87
8(OA)	10.4	−12.05	16.7	−5.57	24.8	−5.20
9(NA)	10.4	−13.72	17.3	−7.88	26.1	−5.29
10(DA)	10.4	−16.24	17.9	−7.85	29.0	−6.62

[a] The intercalative potential minimum per *n*-alkylamine molecule

and the more difficult it is for intercalated amines to exchange with porphyrins. It is confirmed that the amine in the bilayer mode is more stable than that in the monolayer mode. For example, the same α-ZrP gallery may accommodate eight BA molecules in the flat monolayer mode and 10 × 2 BA in the bilayer mode (see Fig. 4a, c). Thus, the potential of the latter [−4.24 × 10 × 2 = −84.8 kcal mol^{-1}, −4.24 (BA) from Table 1] is more negative than that of the former [−9.24 × 8 = −73.9 kcal mol^{-1}, −9.24 (BA) from Table 1]. Other *n*-alkylamines display the same character.

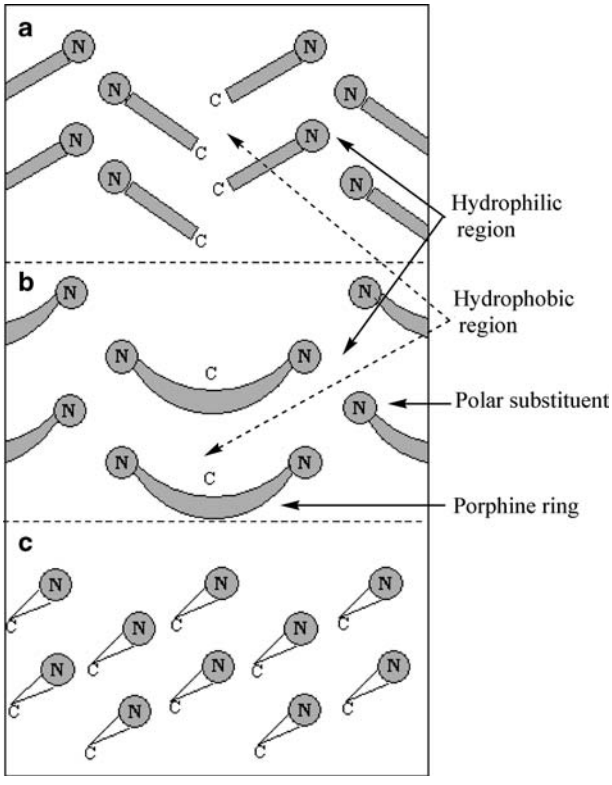

Fig. 4 Schematic representation of platform of intercalated spacers and guests taking *n*-butylamine and TMPyP as an example, respectively: **a** a flat monolayer of *n*-bultylamine in α-ZrP; **b** a canted monolayer of TMPyP in α-ZrP; **c** the top layer of the canted bilayer *n*-bultylamine in α-ZrP (the *gray area* indicates the amphiphilic distribution on the interface between α-ZrP layers and *n*-alkylamine/porphyrin)

For the *n*-alkylamines in flat monolayer mode, basically the intercalative potentials become more negative as the length of alkyl chain increases, from PA (−8.37 kcal mol^{-1}) to decylamine (hearafter DA, −16.24 kcal mol^{-1}). Therefore, α-ZrP·PA and α-ZrP·BA should be the most appropriate candidates as spacers among the *n*-alkylamines studied. The α-ZrP·DA is not considered to be a good intermediate for exchanging with porphyrins, because its potential is very favorable, implying that pre-intercalated compounds will be too stable to exchange. That is the reason that PA and BA are widely used as spacers in intercalation experiments [10, 15, 19]. The good correlation between simulation data and experimental observations confirm the feasibility of our modeling methods.

TMPyP intercalation compounds

The XRD patterns of α-ZrP, α-ZrP·BA and TMPyP-exchanged α-ZrP·BA are shown in Fig. 5. The spectrum of the intercalated host (Fig. 5c) shows that TMPyP has been successfully intercalated into α-ZrP, as well as a high crystallinity and ordered arrangement of the guests. For TMPyP intercalation compounds, the interlayer distance at 17.8 Å (from our XRD data) is equivalent to a gallery height of 11.5 Å (the thickness of one α-ZrP layer is 6.3 Å). Considering the XRD data and the dimensions of TMPyP (15.0 × 15.0 × 5.0 Å), porphine planes in the gallery may either be a monolayer tilted to the host layer or a bilayer roughly parallel to the host sheets (see Fig. 2). Assuming the TMPyP molecules are densely stacked, i.e. the atoms of adjacent TMPyPs are in reasonable van der Waals contact the intercalative potentials of TMPyPs in the two intercalation modes were calculated. The results show that the potential in the canted monolayer mode is lower than that in the parallel bilayer mode by 9.90 kcal mol^{-1}. In addition, the modeling graphics show that the surface area per cationic pyridinium group of TMPyP is 22.5 $Å^2$ in a canted arrangement (the TMPyP length × the space of adjacent TMPyPs/the charge number of the assigned area = 15.0 × 6.0/4 = 22.5 $Å^2$) is very close to that of the α-ZrP layer (the free area per phosphate OH is 24.0 $Å^2$ [14]), thus the canted monolayer mode adopted by

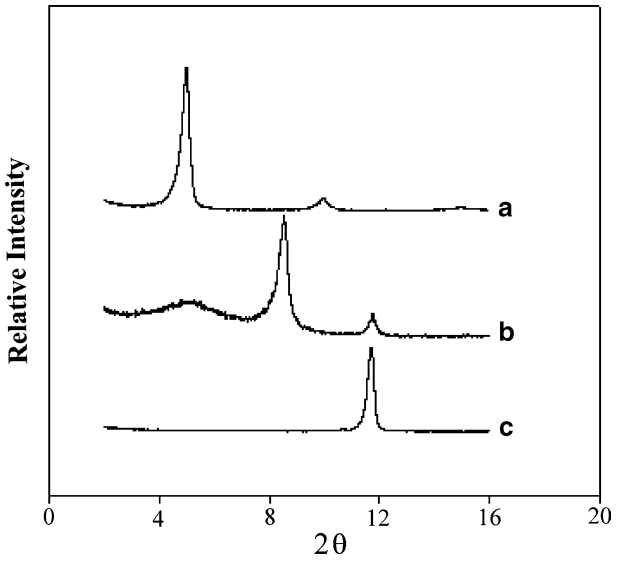

Fig. 5 The XRD patterns of **a** α-ZrP, **b** α-ZrP·BA, **c** TMPyP interaction with α-ZrP·BA

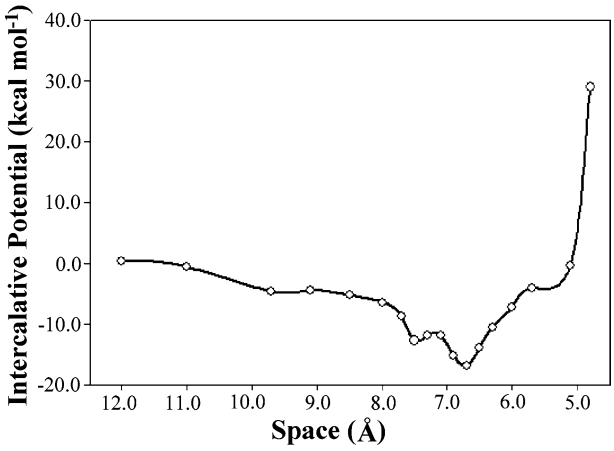

Fig. 6 A plot of potential versus space of adjacent TMPyP

TMPyP can optimize electrostatic interaction. However, TMPyPs in the parallel mode are not able to counter host surface charges sufficiently because the surface area per cationic pyridinium group (the TMPyP length × the space of adjacent TMPyPs/the charge number of the assigned area = $15.0 \times 15.0/4 = 56.3$ Å^2) is much higher than that of the α-ZrP layer (24.0 Å^2). Based on the considerations above, it is reasonable to consider that TMPyPs should adopt an inclined orientation. Additionally, it is reported that TMPyP molecules tend to stack spontaneously in aqueous solution to form dimers [20]. Modeling graphics show that the planar bilayer arrangement of porphyrins is the most rational mode for forming dimers in the gallery of α-ZrP; whereas the canted monolayer arrangement is suitable for monomers (see Fig. 2). Considering the monolayer arrangement of porphyrins in the host layers concluded from our modeling results, it is proposed that the intercalated TMPyP should be present as monomers in the matrix of α-ZrP. This is supported by our experiments [15].

The optimum space of adjacent TMPyPs is explored to understand the thermodynamic state of porphyrins in the galleries of α-ZrP better. The intercalative potentials of TMPyP with space varied from 12.0 to 4.8 Å were calculated. The potential curve is shown in Fig. 6. The potential drops initially owing to van der Waals and π–π overlap interactions between adjacent molecules stabilizing the compound system. As the distance continues reducing, the excessive stacking of TMPyPs causes the system potential to increase dramatically. The potential minimum occurs at 6.7 Å, a distance corresponding to the normal C–C nonbond distance (4.0 Å) of adjacent substituent groups, suggesting that the intercalated porphyrins are densely stacked.

Other porphyrin intercalation compounds

Besides TMPyP, other porphyrins such as TMAPP and aminophenyl substituted porphyrins *p*-H_2TAPP have been reported to be intercalated successfully into α-ZrP [14, 15]. However, H_2TPyP cannot be intercalated into α-ZrP [15]. In order to obtain a correlation between structure character and intercalation behavior of porphyrins from point of view of the potential, several porphyrin intercalation compounds were constructed and the system potentials were calculated. The intercalative potentials of several porphyrins in α-ZrP with varied spaces from 6.5 to 7.3 Å are shown in Table 2. It is obvious that the potential minimum of the intercalated porphyrins is negative (−16.97, −13.21 and −13.14 kcal mol^{-1} for TMPyP, TMAPP, and *p*-TAPP, respectively), while the non-intercalated porphyrin TPyP has a positive value (32.48 kcal mol^{-1}). The order of the intercalative

Table 2 The intercalative potential of several porphyrins intercalated into α-ZrP with space varied[a]

Space (Å)	*p*-TAPP (kcal mol^{-1})	TMAPP (kcal mol^{-1})	TMPyP (kcal mol^{-1})	TPyP (kcal mol^{-1})
6.5	−2.08	−8.69	−13.94	74.20
6.7	−13.14	−10.49	−16.97	32.48
6.9	−12.57	−13.21	−15.19	33.71
7.1	−11.60	−8.66	−11.99	55.89
7.3	−6.62	−7.99	−11.90	64.12

[a] The intercalative potential per porphyrins molecule; *bold* text represents the minimum

potential is generally consistent with the order of polarity of substituents of the porphyrins studied (*N*,*N*, *N*-trimethylanilinium-yl of TMAPP > methylpyridinium-yl of TMPyP > anilinium-yl of *p*-TAPP > pyridinium-yl of TPyP). Therefore, it is suggested that the polarity of the substituents is one important intercalation factor. The order of the potentials of the former two does not obey with the order of polarity. This maybe attributed to a higher stereo-barrier produced by the larger dimensions of the TMAPP substituent groups upon intercalation. In addition, larger substituents lead to the fact that the optimum space of TMAPP (6.9 Å, bold text in Table 2) is larger than that for TMPyP (6.7 Å). For *p* -TAPP, the optimum space (6.7 Å) is the same as TMPyP because the dimensions of the two substituents are close to each other. The data show that the intercalation behavior of these porphyrins is mostly dictated by the dimensions and polarity of the substituent group, which could be used to predict the intercalation behavior of other symmetrical porphyrins. Looking at the intercalative potential between *n*-alkylamines in the flat mode and porphyrins (see Tables 1, 2), the potential differences between α-ZrP·PA/α-ZrP·BA and porphyrin intercalation compounds are the largest amongst the alkylamines studied, suggesting that the exchange reaction between them is more apt to occur. This again illustrates that PA and BA should be the most appropriate spacers.

Conclusions

Through the use of molecular modeling, this work has characterized structural details of intercalated *n*-alkylamines and porphyrins into α-ZrP. First, the intercalative potential was calculated for *n*-alkylamine/α-ZrP to investigate the ease of pre-intercalated amine as precursor for porphyrins intercalation. Amongst the *n*-alkylamines studied, BA and PA are found to be the most appropriate spacers. Second, TMPyP is found to be ordered in a canted monolayer mode and densely stacked based on the computer simulation. More importantly, we have further illustrated that the characters of porphyrin substituents lead to profound influences in intercalation behavior and interlayer state upon intercalation. This modeling work will enhance the understanding of the nature of intercalation of *n*-alkylamines and porphyrins into the host. It will be important in helping with the selection of spacers and predicting of the intercalation behavior of other porphyrins.

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