

Gigantic Swelling of Inorganic Layered Materials: A Bridge to Molecularly Thin Two-Dimensional Nanosheets

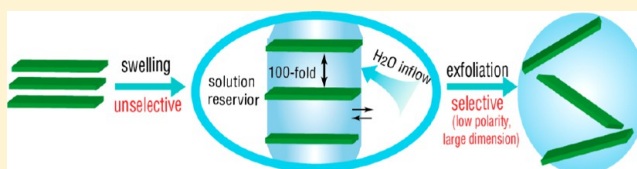
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S Supporting Information

ABSTRACT: Platy microcrystals of a typical layered material, protonated titanate, have been shown to undergo an enormous degree of swelling in aqueous solutions of various amines, including tertiary amines, quaternary ammonium hydroxides, and primary amines. Introducing these solutions expanded the crystal gallery height by up to ~100-fold. Through systematic analysis, we determined that ammonium ion intercalation is predominantly affected by the acid–base equilibrium and that the degree of swelling or inflow of H₂O is controlled by the osmotic pressure balance between the gallery and the solution environment, both of which are relatively independent of electrolyte identity but substantially dependent on molarity. In solutions of tertiary amines and quaternary ammonium hydroxides, the uptake of ammonium ions increases nearly linearly with increasing external concentration before reaching a saturation plateau, i.e., ~40% relative to the cation-exchange capacity of the crystals used. The only exception is tetrabutylammonium ions, which yield a lower saturation value, ~30%, owing to steric effects. The swelling behaviors in some primary amine solutions differ as a result of the effect of attractive forces between amine solute molecules on the solution osmotic pressure. Although the swelling is essentially colligative in nature, the stability of the resultant swollen structure is heavily dependent on the chemical nature of the guest ions. Intercalated ions of higher polarity and smaller size help stabilize the swollen structure, whereas ions of lower polarity and larger size lead readily to exfoliation. The insight gained from this study sheds new light on both the incorporation of guest molecules into a gallery of layered structures in general and the exfoliation of materials into elementary single-layer nanosheets.



INTRODUCTION

Inorganic materials with layered structures are of great interest because they can be separated or delaminated into unilamellar sheet units, i.e., nanosheets, which usually exhibit superior properties to their three-dimensional (3D) counterparts.^{1–5} In addition to the well-known inorganic material graphite, a variety of layered materials have been exfoliated, including clay,^{6,7} layered metal dichalcogenides,^{1,8} oxides,^{4,9} and hydroxides.^{3,10–13} The exfoliation arises from their unique structural characteristics: that is, strong covalent bonding in the layers but weaker layer-to-layer interactions, such as van der Waals or electrostatic attractions. This structural anisotropy allows the layered materials to incorporate ions and/or solvent species into the interlayer region, which induces layer-to-layer gallery expansion or *swelling*. Experimental and theoretical studies of this swelling behavior have been conducted on a wide variety of materials, including clays and some layered metal oxides, such as Cs_{0.7}Ti_{1.825}O₄,^{9,14} K_{0.45}MnO₂,^{15,16} and KCa₂Nb₃O₁₀.^{17–19} Two types of swelling have been documented: intracrystalline swelling and osmotic swelling. Intracrystalline swelling denotes an increase in the interlayer lattice dimension induced by the hydration of the gallery species, in which the entering H₂O

molecules are ordered at fixed positions.^{20–22} Montmorillonite, for example, shows gallery expansion from an original spacing of 1.0 nm stepwisely to 1.3, 1.6, and 1.9 nm, which corresponds to the successive hydration of three layers of H₂O molecules to the Na⁺ present in the gallery.²³ Osmotic swelling refers to the behavior resulting from the penetration of a significant volume of water, after which the material is generally considered to behave as a colloidal system.²⁴ A maximum of 30-fold macroscopic swelling was observed for vermiculite crystals in diluted butylammonium chloride solutions after the introduction of *n*-butylammonium ions into the interlayer region.²⁵ In general, concomitant with the high degree of swelling, mostly the 3D phase collapsed and was delaminated into nanosheets, as schematically illustrated in Figure 1, because of the weakening of the binding forces by the large gallery expansions.^{14,26} Thus the osmotic swelling process is highly important for the production of molecularly thin nanosheets, which are very difficult to prepare by other synthetic routes. However, a basic understanding of this important phenomenon

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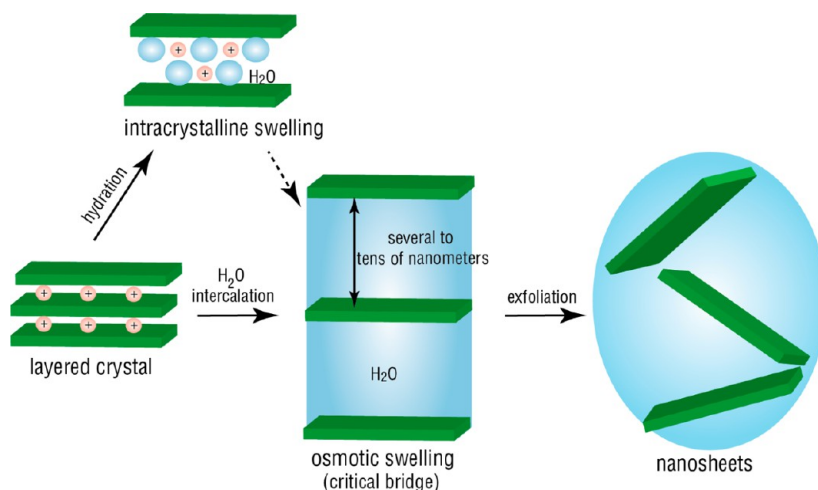


Figure 1. Schematic illustration of the swelling and exfoliation process.

Table 1. Reagents Used for Swelling Studies Classified According to the Length of the Main Chain and the Number of Alkyl Substitutions on Nitrogen^a

	Primary Amine	Tertiary Amine	Quaternary Ammonium Hydroxide
1C	$\text{H}_3\text{C}-\text{NH}_2$ Methylamine	$\text{H}_3\text{C}-\text{N}(\text{CH}_3)_3$ Trimethylamine	$\text{H}_3\text{C}-\text{N}^+(\text{CH}_3)_3 \text{OH}^-$ Tetramethylammonium hydroxide TMAOH
2C	$\text{H}_3\text{C}-\text{CH}_2-\text{NH}_2$ Ethylamine $\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ 2-Aminoethanol	$\text{H}_3\text{C}-\text{N}(\text{CH}_3)_2-\text{CH}_2-\text{CH}_3$ N,N-Dimethylethylamine DMA $\text{HO}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2$ 2-Dimethylaminoethanol DMAE	$\text{H}_3\text{C}-\text{N}^+(\text{CH}_3)_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}^-$ Diethyldimethylammonium hydroxide (DEDMAOH)
3C	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$ 3-Amino-1-propanol	$\text{H}_3\text{C}-\text{N}(\text{CH}_3)_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ N,N-Dimethylpropylamine (NA in Japan) $\text{HO}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2$ 3-Dimethylamino-1-propanol	
4C	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$ 4-amino-1-butanol	$\text{H}_3\text{C}-\text{N}(\text{CH}_3)_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ N,N-Dimethylbutylamine	$\text{H}_3\text{C}-\text{N}^+(\text{CH}_3)_3$ Tetrabutylammonium hydroxide TBAOH
Long			$\text{H}_3\text{C}-\text{N}^+(\text{CH}_3)_3$ Hexadecyltrimethylammonium hydroxide $\text{H}_3\text{C}-\text{N}^+(\text{CH}_3)_3$ Tetrakis(decyl)ammonium hydroxide

^aIdeally we would have used aminoethanol to perform systematic comparison studies, but in the tertiary amine category, most are available only in amine form. Within this series, the $-\text{OH}$ did not result in significant changes in swelling, as confirmed by a comparison of DMAE and *N,N*-dimethylethylamine (DMA); therefore, the corresponding amines were used except for *N,N*-dimethylpropylamine, which is not available (NA) in Japan.

remains limited; for example, the mechanism and reasons for this enormous swelling are still unclear.

The conditions under which swelling occurs and the extent of swelling depend on many factors, such as layer charge density and gallery ion identity.^{20,21} For layered metal oxides with a relatively high layer charge density, swelling cannot proceed except by replacing the interlayer species with protons followed by reactions in basic solutions.²⁷ The acid–base intercalation properties of protonated titanate, $\text{H}_{0.7}\text{Ti}_{1.825}\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{H}_{1.07}\text{Ti}_{1.73}\text{O}_4 \cdot \text{H}_2\text{O}$, with both inorganic bases (LiOH, NaOH, and KOH) and organic *n*-alkylamines ($\text{C}_n\text{H}_{2n+1}\text{NH}_2$)

were studied, revealing that the compounds can take up hydrated alkali metal ions and organoammonium ions to form the crystalline swollen phases in which ion uptake quantity and hydration state vary depending on the cations incorporated.^{28,29} When quaternary ammonium hydroxides, such as tetrabutylammonium hydroxide (TBAOH) or tetramethylammonium hydroxide (TMAOH), were used as the electrolyte, extensive swelling with the penetration of a large amount of H_2O into the gallery space and ready exfoliation into individual sheets were observed.^{9,14,30}

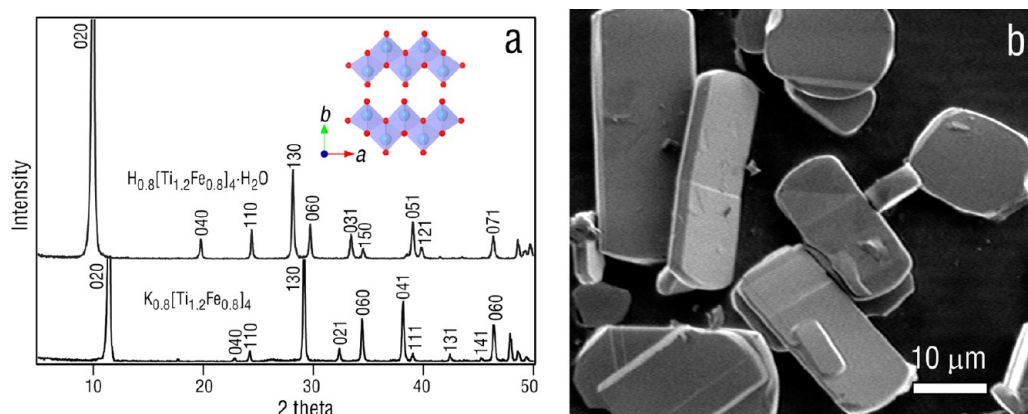


Figure 2. (a) A comparison of the PXRD patterns of the crystals before and after protonation, showing the clear shift in basal spacings. Inset: crystal structure illustrating the repeated stacking of the titania sheets. (b) SEM image of $K_{0.8}[Ti_{1.2}Fe_{0.8}]O_4$ parent crystals showing a typical rectangular shape with lateral sizes of $\sim 15 \mu m \times 35 \mu m$. The crystal thickness is $\sim 2\text{--}3 \mu m$, corresponding to stacks of ~ 3000 layers.

The highly swollen phase with layers widely separated by H_2O molecules is obviously a critical bridge from the layered phase to exfoliated nanosheets, and scrutiny of its structure and the swelling process is therefore necessary to elucidate exfoliation behaviors and to achieve controlled exfoliation. However, the swollen phases from extensive swelling are typically structurally unstable and prone to falling apart into individual nanosheets. It has been only recently that we achieved a stable swollen phase by swelling the crystals of a variety of protonated oxides in an aqueous solution of an amine, 2-(dimethylamino)ethanol (DMAE, $(CH_3)_2NC_2H_4OH$), resulting in an unusual monolithic ~ 100 -fold swelling with layer separations up to 90 nm ,³¹ which provided a basis for swelling studies. However, systematic knowledge about the swelling mechanism and a deeper understanding of the osmotic swelling phenomenon remain greatly underdeveloped. In this article, we performed swelling and stability studies with a typical layered material, $H_{0.8}[Ti_{1.2}Fe_{0.8}]O_4 \cdot H_2O$, in aqueous solutions of a series of amines and quaternary ammonium hydroxides. The insight we obtained is important to the understanding not only of the swelling but also of the exfoliation of inorganic layered materials in general, and our findings provide principles for the optimal selection of swelling or exfoliation reagents to produce high-quality nanosheets.

EXPERIMENTAL SECTION

Materials. The amines and quaternary ammonium hydroxides we employed for the swelling studies are listed in Table 1; the classification is based on the degree of substitution on the nitrogen. In a primary amine, one hydrogen atom on N is replaced by an alkyl group, while three alkyl groups are bonded to N in a tertiary amine. In the analogues of quaternary ammonium hydroxide, 4 groups are attached to the central N atom. Amines are weak bases because they deprotonate water to a small extent to form ammonium and hydroxide ions, whereas quaternary ammonium hydroxides are as strongly basic as NaOH or KOH. All chemicals were purchased from Sigma-Aldrich and were used as received without further treatment. Milli-Q water was used for all solutions.

Sample Synthesis. $K_{0.8}[Ti_{1.2}Fe_{0.8}]O_4$ parent crystals were grown through a flux-growth method. A reaction mixture containing the starting materials in a molar ratio of $TiO_2:Fe_2O_3:K_2CO_3:MoO_3 = 1.2:0.4:2.03:1.63$ was loaded in a Pt crucible with a tight-fitting lid. The mixture was preheated to $900 \text{ }^\circ\text{C}$ for decarbonation. After quenching, the powder was ground and then calcined at $1200 \text{ }^\circ\text{C}$ for 20 h. The crystals were collected from the flux matrix by dissolving the product

in water and isolating the crystals by filtration. Protonation was achieved by stirring the crystals in 0.5 mol dm^{-3} HCl solution at ambient temperature for 2 days. The acid was replaced after 24 h of reaction to ensure complete exchange. Finally, the $H_{0.8}[Ti_{1.2}Fe_{0.8}]O_4 \cdot H_2O$ crystals were separated by filtration, washed thoroughly with water, and dried before use.

Swelling. In a typical swelling experiment, 0.2 g of $H_{0.8}[Ti_{1.2}Fe_{0.8}]O_4 \cdot H_2O$ crystals were mixed with 100 cm^3 of an aqueous solution of amines or ammonium hydroxides. Throughout the text, the concentration of amines or of hydroxides is expressed as a ratio to the cation-exchange capacity (CEC) of the employed protonated titanate crystals ($0.8 \text{ mol per formula weight}$), N/H^+ . The mixture was stored for 1 day to permit equilibration. The swelling trends in solutions of tertiary amines and quaternary ammonium hydroxides were similar, and therefore, a detailed wide-range study was performed only for DMAE, $N/H^+ = 0.1, 0.15, 0.2, 0.25, 0.3, 0.5, 0.7, 1, 5,$ and 10 , while a representative region, $N/H^+ = 0.3, 0.5,$ and 0.7 , was selected for the other amines. $N/H^+ = 1$ corresponds to an absolute concentration of $0.00865 \text{ mol dm}^{-3}$. Because the swelling in the primary amine series was greatly affected by solute intermolecular forces, four swelling tests were performed for each primary amine, $N/H^+ = 0.5, 1, 5,$ and 10 , and the degree of swelling was compared.

Titration. The amount of amine or ammonium hydroxide in a solution was quantified by titration with standard HCl solutions. When performing titration for solutions after swelling, aliquot of the supernatant was taken out for analysis to avoid possible re-equilibration effect on the swollen crystals sedimented at the bottom. For each amine or ammonium hydroxide solution, a titration curve was constructed where the x - and y -coordinates corresponded to the volume of added HCl and the pH of the solution, respectively, and the equivalence point was determined by differentiation analysis. The quantity of intercalated ammonium ions in the gallery space was calculated by subtracting the equilibrated amount in the supernatant after swelling from the amount in the initial solution before swelling.

The concentrations in the gallery and environment solution were then determined, and their difference was studied. For calculating the interior concentration, the corresponding volume of H_2O inflow was obtained by multiplying sheet area of the crystals with expanded gallery spacing.

Stability Tests. The reaction mixtures were applied to mechanical shaking at a speed of 180 rpm overnight to study the relative stabilities.

Sample Characterizations. Phase purity of crystals before swelling was examined by powder X-ray diffraction (PXRD) using a Rigaku Rint ULTIMA+ diffractometer with a graphite monochromatized $Cu \text{ K}\alpha$ radiation ($\lambda = 0.15405 \text{ nm}$). Morphology of the crystals was characterized on a VE-8800 scanning electron microscope (SEM). Optical microscopy images of crystals after swelling were recorded on an Olympus BX51 using crossed polarizers with a 530 nm wave plate. Swollen crystals were dropped onto a glass substrate for observation.

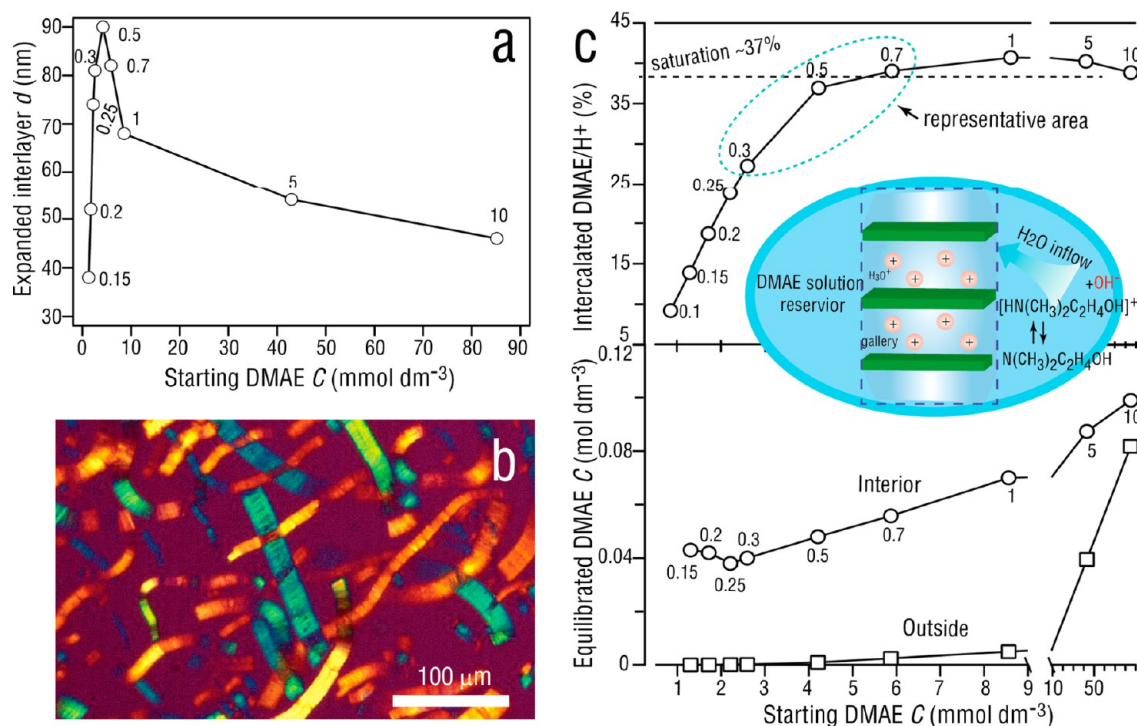


Figure 3. (a) The expanded interlayer distance as a function of the starting DMAE concentration. The maximum swelling was 100-fold at $N/H^+ = 0.5$, which yielded an interlayer spacing of 90 nm. (b) Optical microscopy image of maximum swelling. (c) Upper panel: the intercalated quantity of DMAE molecules increased linearly at low DMAE concentrations until a saturation value of 37% was reached at $N/H^+ = 0.5$. Lower panel: comparison of the DMAE concentrations in the gallery and external reservoir. Before reaching saturation, the interior concentration was almost constant at 0.04 mol dm^{-3} , whereas the concentration in the external solution was almost zero. Inset: illustration of the swelling process. Upon dissociation of DMAE in H_2O , OH^- is released and readily neutralizes the protons present in the gallery, which initiates the swelling.

The spacings after swelling were examined using small-angle X-ray scattering (SAXS) techniques. Two or three drops of the swollen crystals were packed in a cell with a depth of 2 mm and sealed with Kapton films to prevent solvent evaporation. SAXS data of typical samples swollen in tertiary amines and quaternary ammonium hydroxides were collected on beamline BL11 at the Kyushu Synchrotron Light Research Center using a fixed wavelength of 0.155 nm unless otherwise noted. SAXS data on other samples were collected on a Rigaku Nanoviewer employing $Cu K\alpha$ radiation. The obtained SAXS profiles were plotted in the product of the scattering intensity, I , and the inverse of the form factor for flat, thin sheets (q^2), I^*q^2 , as a function of the scattering vector, q . The expanded distances, d , between the sheets were calculated using Bragg's law, $d = 2\pi/q$. Tapping-mode atomic force microscopy (AFM; Seiko Instruments SPA400) with a silicon-tip cantilever (20 N m^{-1}) was used to characterize the lateral size and thickness of exfoliated nanosheets deposited on a silicon substrate.

RESULTS AND DISCUSSION

The $K_{0.8}[Ti_{1.2}Fe_{0.8}]O_4$ parent structure consists of regularly stacked, negatively charged slabs of $[Ti_{1.2}Fe_{0.8}]O_4^{0.8-}$ with K^+ residing in the gallery to neutralize the charges. As determined by PXRD and shown in Figure 2a, accompanying the replacement of K^+ by hydrated H^+ through proton exchange, the gallery distance increased from 0.78 to 0.89 nm, which was consistent with the values reported in the literature.^{32,33} Figure 2b shows a representative SEM image of the $K_{0.8}[Ti_{1.2}Fe_{0.8}]O_4$ crystals, which had a typical rectangular shape with lateral sizes of $\sim 15 \mu\text{m} \times 35 \mu\text{m}$. The thickness was $\sim 2\text{--}3 \mu\text{m}$, which roughly corresponds to ~ 3000 stacked layers.

Swelling Behaviors. When the protonated $H_{0.8}[Ti_{1.2}Fe_{0.8}]O_4 \cdot H_2O$ crystals were dispersed in DMAE solutions, an increase in the sample volume or crystal swelling was immediately

observed, the extent of which was strongly associated with the solution concentration. The macroscopic crystal swelling was based on the expansion of interlayer spacing measured by SAXS, which reached maximum of 90 nm at $N/H^+ = 0.5$ (Figure 3a). The interlayer spacing of the original crystals was 0.89 nm; thus, the maximum expansion was as large as 100-fold. Figure 3b shows a typical optical microscopy image obtained at the maximum swelling and illustrates the anisotropic swelling of the crystals perpendicular to the planes of the host layers. The crystals comprising a stack of ~ 3000 layers swelled from their original thickness of $\sim 2\text{--}3 \mu\text{m}$ to an average swollen length of $250 \mu\text{m}$. In dilute solutions, the degree of swelling increased nearly linearly with the increasing DMAE concentration. However, homogeneous swelling could not be achieved at very low concentrations, for example, $N/H^+ = 0.1$. At this concentration, swollen crystals with iridescent colors were observed by optical microscopy, and weak and diffuse diffraction was detected by SAXS (Figure S1, Supporting Information). In solutions beyond the maximum stage, the degree of swelling first decreased sharply from 90 nm at $N/H^+ = 0.5$ to 68 nm at $N/H^+ = 1$, after which the swelling decreased more gradually. In extremely concentrated solutions, the change in the degree of swelling was almost negligible: 46, 42, and 40 nm for $N/H^+ = 10, 20,$ and 100 , respectively. The inset in Figure 3c schematically illustrates the swelling process. Driven by acid–base reactions between protons in the gallery and OH^- dissociated from DMAE in the external reservoir solution, protonated DMAE penetrates between the layers along with H_2O , yielding a unidimensional lattice increase along the interlayer direction. Therefore the system can be conceptually divided into two regions: the interior DMAE

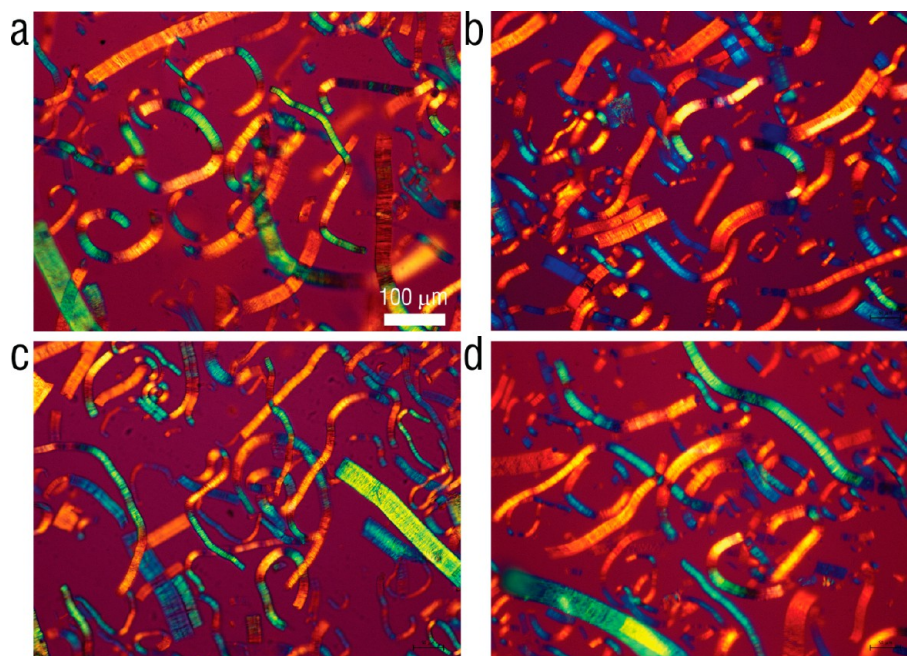


Figure 4. Optical microscopy images of crystals swollen in (a) trimethylamine, (b) 2-dimethylethylamine, (c) 3-dimethylamino-1-propanol, and (d) *N,N*-dimethylbutylamine solutions at the maximum swelling, i.e., $N/H^+ = 0.5$. The swollen lengths of the crystals are similar, $\sim 250 \mu\text{m}$.

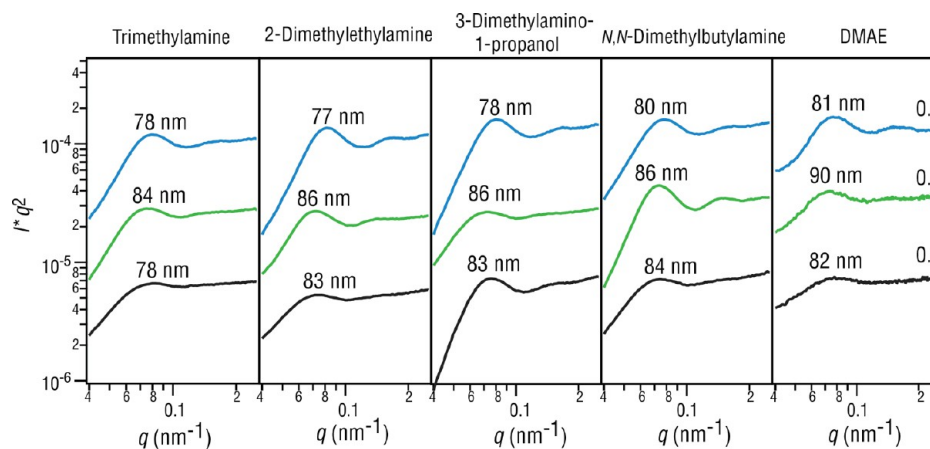


Figure 5. SAXS profiles of crystals swollen in solutions of the tertiary amines, trimethylamine, 2-dimethylethylamine, 3-dimethylamino-1-propanol, and *N,N*-dimethylbutylamine at $N/H^+ = 0.3, 0.5$, and 0.7 . The patterns for DMAE are also shown for reference. For the purpose of clarity, the curves are shifted vertically. The swollen spacings are roughly independent of the amine type. The values for the largely expanded spacings may contain certain deviations, especially at low concentrations, because of the intrinsic nature of relatively wide spacing distribution and difficulty in locating the maxima from the broad hump-like peak signal.

solution in the expanded gallery region and the external DMAE solution reservoir. The upper and lower panels of Figure 3c depict the quantity of DMAE intercalated into the gallery space and the resultant difference in concentration between the interior and external regions, respectively. At low concentrations in which $N/H^+ < 0.5$, most of the DMAE molecules in the external reservoir enter the gallery accompanied by proportional intercalation of H_2O , resulting in a linear increase in the degree of swelling; the concentration of DMAE remains approximately constant in the gallery (0.04 mol dm^{-3}) but is almost zero in the external solution reservoir. Beyond $N/H^+ = 0.5$, increasing the starting DMAE concentration does not result in further DMAE intercalation, which remains at approximately 37%, but H_2O inflow decreases, as indicated by the observed reduction in swelling, which results in a rapid increase in the gallery concentration of DMAE. At $N/H^+ = 10$,

the concentrations in the inside gallery and external reservoir become similar; at higher N/H^+ values, the degree of swelling or H_2O inflow remains roughly constant (vide ante).³¹

To examine the effect of varying the electrolytes, swelling was investigated in solutions of several other tertiary amines, including trimethylamine, *N,N*-dimethylethylamine, 3-dimethylamino-1-propanol, and *N,N*-dimethylbutylamine. The swelling trend was the same as that for swelling in DMAE solutions: a linear increase in the degree of swelling at low concentrations before reaching a maximum value at $N/H^+ = 0.5$ and reduced swelling in concentrated solutions. Thus, three representative points near the maximum swelling were used for detailed studies, corresponding to concentrations of $N/H^+ = 0.3, 0.5$, and 0.7 . Figure 4 shows optical microscope images of the crystals at the maximum swelling; the images for the other concentrations are provided in Figure S2, Supporting

Information. Interestingly, swelling was independent of electrolyte identity, and the swollen crystals were of similar lengths in all the tertiary amine solutions at the same concentrations. The most extensive swelling occurred at $N/H^+ = 0.5$, which gave an average length as large as $\sim 250 \mu\text{m}$. The corresponding SAXS profiles are presented in Figure 5; the SAXS profiles of crystals swollen in DMAE solutions are shown as a reference. In this concentration range, $N/H^+ = 0.3, 0.5$, and 0.7 , the patterns displayed a well-resolved first-order reflection, which confirms the presence of mesostructural order arising from the regular stacking of the layers. The broadening of the diffraction signals for $N/H^+ = 0.3$ indicates a relatively wide distribution of repeated layer distances at low concentrations. Notably, all tertiary amines brought the achievement of the enormous ~ 100 -fold swelling, with the swollen spacings at $N/H^+ = 0.5$ narrowly ranging from 84 to 90 nm. In solutions of the other concentrations, the interlamellar distances were also comparable for all amines at the same concentrations: 78–84 nm and 77–81 nm for $N/H^+ = 0.3$ and 0.7 , respectively.

The quaternary ammonium hydroxides TMAOH, diethyldimethylammonium hydroxide (DEDMAOH), and TBAOH possess different sizes and molecular geometries, particularly DEDMAOH, whose arms are asymmetrical. However, for all of these quaternary ammonium hydroxides, the swollen crystals displayed comparable spacings at the same concentrations as observed by SAXS (Figure 6). Furthermore, the maximum

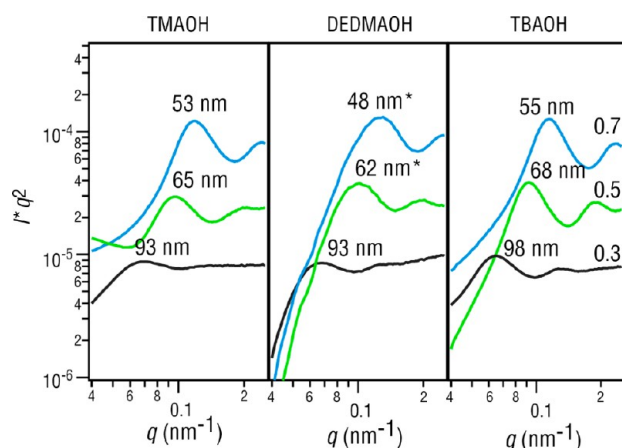


Figure 6. SAXS profiles for crystals swollen in aqueous solutions of quaternary ammonium hydroxides, including TMAOH, DEDMAOH, and TBAOH. Numbers marked with * indicate the spacings from lab SAXS measurements employing Cu $K\alpha$ radiation. The maximum swelling at $N/H^+ = 0.3$, ~ 90 nm, is comparable to the maximum swelling for samples swollen in tertiary amines at $N/H^+ = 0.5$.

spacings are of the same order as those for tertiary amines, ~ 90 nm. However, in contrast to the crystals in the tertiary amine solutions, which exhibited maximum swelling at $N/H^+ = 0.5$, the crystals in the quaternary ammonium hydroxide solutions swelled most at a lower concentration, $N/H^+ = 0.3$. The shift to lower concentrations for quaternary ammonium hydroxides is likely due to the higher osmotic pressure of the starting solutions compared with the tertiary amine solutions of equal concentrations. The osmotic pressure of a dilute solution is directly proportional to the summed concentrations of all solute substances in the solution, either molecules or ions. Aqueous quaternary ammonium hydroxides are strong electrolytes with completely dissociated ions, which increases the solute molarity and doubles the osmotic pressure compared

with tertiary amine solutions, which are only 5% dissociated on the basis of a typical pK_b of 3–5.

Optical microscopy images of the maximum swelling at $N/H^+ = 0.3$ are shown in Figure 7. Although the degree of expansion in the different quaternary ammonium hydroxide solutions was similar, as indicated by SAXS, the lengths of the swollen crystals in TBAOH were apparently much shorter, with an average length of $\sim 50 \mu\text{m}$, in sharp contrast to ~ 150 and $200 \mu\text{m}$ for TMAOH and DEDMAOH and $\sim 250 \mu\text{m}$ for the tertiary amines. The shorter swollen lengths are likely due to partial fragmentation; crystals swollen in TBAOH have been shown to fall apart easily and exfoliate naturally.^{3,14,34}

Figure 8 depicts the obtained intercalated quantity (as a percentage of the CEC) with increasing starting concentration, on the basis of three concentrations of the tested amines and quaternary ammonium hydroxides ($N/H^+ = 0.3, 0.5$, and 0.7) and a wider concentration range over $N/H^+ = 0.1$ – 5 for DMAE as a reference. The lines for the tertiary amines and quaternary ammonium hydroxides, with the exception of TBAOH, are nearly superimposed on each other, reflecting the unselective nature of the swelling behavior. The saturation with respect to the CEC of the crystals ranged narrowly from 0.35 to 0.39. Similar to DMAE, most of the amines are taken into the gallery at lower concentrations, for example, ~ 0.28 for $N/H^+ = 0.3$, with little increase in the uptake of amine ions beyond $N/H^+ = 0.5$. The intercalation values at all concentrations are given in Table S1, Supporting Information. The comparable intercalation quantity and expanded spacings at the same concentrations suggest that the swelling behavior is colligative in nature and is essentially related to the molarity of the solution and independent of the ion type present in the solutions. TBAOH is an exception, in which a lower degree of intercalation was observed. Even at a concentration of $N/H^+ = 0.7$, at which oversaturation occurs, the ammonium fraction in the swollen crystals is 0.3 relative to the CEC of the crystals (0.8 exchangeable protons per cell), and accordingly only 0.24 TBA ions are incorporated. The lower intercalation of TBAOH, we believe, is attributable to steric reasons. In osmotically swollen crystals, it is generally thought that the ions in the widely expanded gallery form a diffuse double layer, in which we suppose the ion distribution in the in-plane projection tends to be close-packed or interdigitated for electrostatic reasons. TBA ions have a near-spherical shape with a cationic size of ~ 0.8 nm,³⁵ and close-packing on an area for sheet surface of 0.114 nm^2 ($0.38 \times 0.30 \text{ nm}^2$) yielded 0.20 TBA⁺ (Figure S4, Supporting Information), similar to our experimental value.

Although the swelling was mostly independent of ion identity, no osmotic swelling was detected for hydroxides in which the hydrophobic segment was too long, including both nonpolar and polar ions, such as tetrakis(decyl)ammonium hydroxide or hexadecyltrimethylammonium hydroxide, and the resultant interlayer spacings corresponded to a monolayer intercalation of the organic molecules (Figure S5, Supporting Information). The result is not surprising, as long-chain fatty molecules usually help bind repeated layers and the hydrophobic interactions between the polymer tails prevent the penetration of water.

Effect of Intermolecular Forces. When the primary amine 2-aminoethanol is adopted as the electrolyte, a higher concentration is required to produce extensive swelling, even though its base dissociation constant (pK_b) is similar to that of tertiary amines.³⁶ At a concentration of $N/H^+ = 0.5$, at which the maximum swelling occurs for tertiary systems, optical

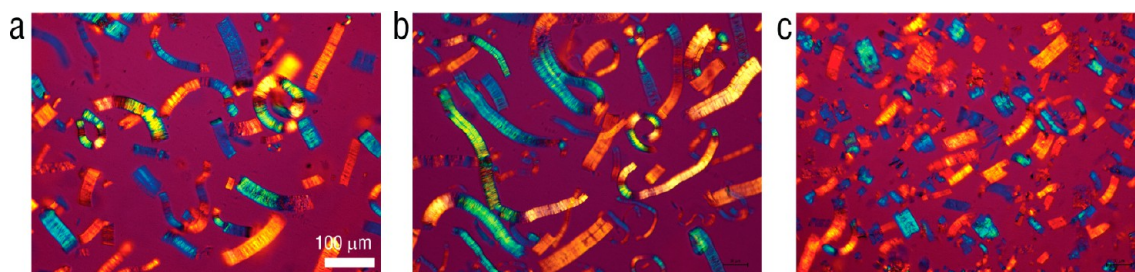


Figure 7. Optical microscopy images of crystals at the maximum swelling in (a) TMAOH, (b) DEDMAOH, and (c) TBAOH solutions at a concentration of $N/H^+ = 0.3$. The crystals in the TMAOH and DEDMAOH solutions exhibited an extended swollen length of ~ 150 and $200 \mu\text{m}$, whereas most of the crystals in the TBAOH solution were very short, $\sim 50 \mu\text{m}$, most likely because of fragmentation. Images for other concentrations are given in Figure S3, Supporting Information.

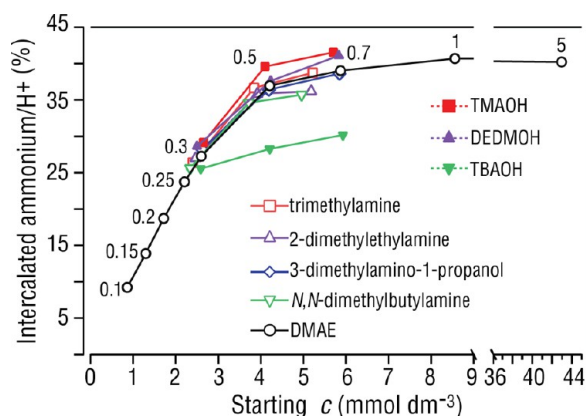


Figure 8. Quantity of intercalated ammonium for tertiary amines and quaternary ammonium hydroxides as a percentage ratio of the CEC of the titanate crystals. The open symbols represent tertiary amines, while the filled symbols represent quaternary ammonium hydroxides. The numbers in the panel are the ratios of the starting amine or ammonium hydroxide to the CEC of the crystals. All lines except the one for TBAOH overlap, suggesting that these tertiary amines and quaternary ammonium hydroxides have similar affinities for the crystals. The lower intercalation of TBAOH is likely due to steric effects.

microscopy revealed that the swollen length was limited to tens of micrometers; in addition, the heterogeneous nature of the swelling was indicated by the appearance of an iridescence color. Homogeneous and extensive swelling to a spacing of 56 nm could be obtained by increasing the concentration to $N/H^+ = 1$. Further increasing the solution concentration to $N/H^+ = 5$ and 10 produced suppression, in which the swollen spacings decreased to 48 and 39 nm, respectively (Figure 9a and Figure S6, Supporting Information). We believe that the deviation of maximum swelling to high concentrations is due to a decrease in the osmotic pressure of the starting solutions from the hydrogen bonding forces among the primary amine molecules. For ideal solutions containing no intermolecular forces between the solutes, the osmotic pressure is proportional to the molarity of the solutes; however, deviation occurs when solute–solute interactions have to be taken into account. A positive contribution is expected for repulsive interactions, and a negative contribution is expected for attractive interactions. The interactions among the amine molecules or ammonium ions are predominantly dipole–dipole interactions due to the polar C–N and N–H bonds, which can be neglected except when hydrogen bonding is involved. While all amines have a lone pair of electrons on N functioning as a proton acceptor in hydrogen bonding, only primary amines can participate in intermolecular

hydrogen bonding because tertiary amines³⁷ and quaternary ammonium ions contain no N–H bonds to function as hydrogen donors.³⁸ Because the conditions in solution are complex and it is difficult to quantify the related forces, for comparison purposes, 4 swelling tests were conducted for each amine of this category, at $N/H^+ = 0.5, 1, 5,$ and 10. When employing the solutions in which the hydrogen bonding is relatively weak, high concentration was no longer required to achieve extensive swelling. For example, 3-amino-1-propanol and 4-amino-1-butanol with increased molecular size or carbon chain length, extensive swellings could be readily obtained at $N/H^+ = 0.5$, with suppression occurring in more concentrated solutions (Figure 9b and Figure S6, Supporting Information). Meanwhile, as removing the polar O–H bond may weaken the hydrogen bonding network, ethylamine ($\text{H}_3\text{C}-\text{CH}_2-\text{NH}_2$), which is structurally similar to 2-aminoethanol ($\text{HO}-(\text{CH}_2)_2-\text{NH}_2$) but contains no –OH substitution on the end carbon, also readily yielded extensive swelling at $N/H^+ = 0.5$ (Figure 9c). However, the structurally similar but smaller amine methylamine ($\text{H}_3\text{C}-\text{NH}_2$) could only yield crystalline swelling with monolayer ammonium ion intercalation (Figure S7, Supporting Information), as will be explained in the section discussing the mechanism.

Swelling Mechanism. On the basis of the above results, we summarize a general swelling process. For layered metal oxides, because the swelling is initiated by an acid–base reaction between the protons in the gallery and OH^- in the external reservoir, the swelling does not occur or is heterogeneous in very dilute basic solutions. Ion intercalation is strongly dependent on the available bases in the solution environment and typically increases with increasing external base concentration before reaching a saturation value of $\sim 40\%$. The saturation plateau may be due to reaching acid–base equilibrium. Before saturation, almost all base molecules in the solution enter the gallery and neutralize the protons, resulting in a very small ammonium fraction in the solution reservoir. Meanwhile, H_2O inflow or the degree of swelling is governed by the equilibrium in osmotic pressure between the gallery region and the external solution. As a consequence, before reaching acid–base equilibrium, the H_2O inflow is typically proportional to the ammonium ion intercalation, resulting in a constant gallery concentration of ammonium ions, which was experimentally determined to be $\sim 0.04 \text{ mol dm}^{-3}$, and an external concentration of approximately zero. Notably, the osmotic pressure of the amine solution in the gallery at this concentration is approximately the same as the atmospheric pressure [$P_{\text{osmotic}} = cRT = 0.04 \text{ mol dm}^{-3} \times 0.0821 \text{ dm}^3 \text{ atm}/(\text{K mol}) \times 298 \text{ K} = 0.98 \text{ atm}$]. Considering the concentration in

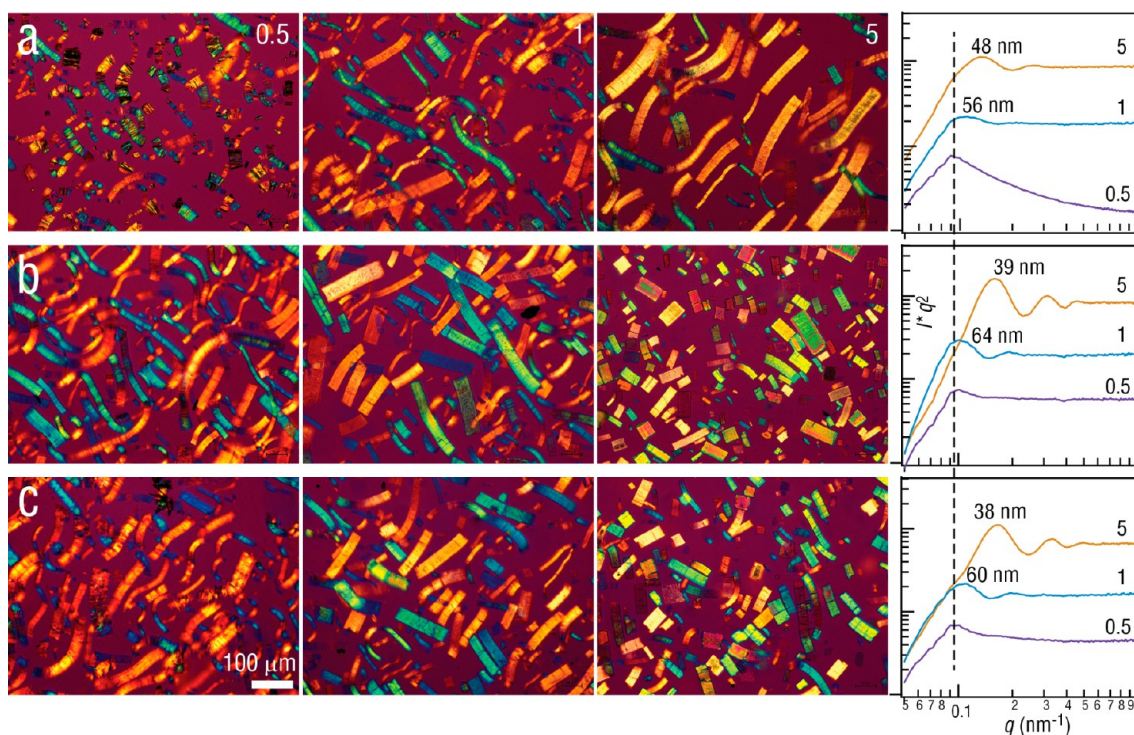


Figure 9. Optical microscope images and corresponding SAXS profiles of crystals swollen in primary amine solutions at $N/H^+ = 0.5, 1,$ and 5 : (a) 2-aminoethanol, (b) 3-amino-1-propanol, and (c) ethylamine. The dotted line in the SAXS panels indicates the position of the stopper, which is used to block the direct beam, and thus only signals with larger q values are truly scattered from the measured samples. The decay in intensity at high q -values for swelling in 2-aminoethanol ($N/H^+ = 0.5$) is due to heterogeneous swelling. The massive swelling in the 3-amino-1-propanol and ethylamine solutions at $N/H^+ = 0.5$ produces gallery expansion beyond the measurement range. Data for other primary amines and for $N/H^+ = 10$ are provided in Figure S6, Supporting Information.

the external reservoir is essentially zero with negligible generation of osmotic pressure, the pressure in the gallery perfectly balances the normal atmospheric pressure, suggesting that the osmotic pressure in the gallery is probably equilibrated with the sum effect of external solution and atmosphere. Beyond the saturation point, while there are no apparent changes in ammonium ion intercalation, the osmotic pressure of the environmental solution increases with increasing external solution concentrations, resulting in the expulsion of H_2O molecules from the gallery to maintain the osmotic pressure in equilibrium with the environment, with a consequent reduction in swelling. For reference, a table listing the osmotic pressure change in the gallery and reservoir at different concentrations is provided in Table S2, Supporting Information. As the acid–base reaction is a relatively unselective process and osmotic pressure is mainly related to the molarity of the solution, ideally the swelling is essentially independent of the ion identity, and comparable swellings can thus be induced in any solution of the same solute concentration. However, only ions of intermediate size are suitable for this purpose. Small molecules tend to be keyed at fixed positions, which favors the binding between layers and ions and therefore inhibits the intercalation of water. For example, the reactions stop at the intracrystalline swelling stage for bases such as $LiOH$, $NaOH$, and KOH .^{28,29} In addition, although ethylamine easily induces osmotic swelling, the structurally similar but smaller methylamine can only yield crystalline swelling with monolayer intercalation (*vide ante*). In other words, to induce osmotic swelling or substantial penetration of H_2O molecules, a threshold may exist, and the electrostatic attraction forces between layers and guest molecules must be attenuated or overcome by gallery

expansion. The same requirement also applies to other layer systems. For swelling with hydration of the interlayer ions in montmorillonite crystals, if a less-hydrating ion such as K^+ is present in the gallery, the layers still bind strongly after hydration by one layer of H_2O , and consequently the swelling ceases at 1.3 nm. However, macroscopic swelling can be achieved by first expanding the layers with heavily hydrated Na^+ followed by immersion in KCl solutions.²³ Similarly, the introduction of *n*-butylammonium ions into the interlayer region of vermiculite crystals efficiently weakens the binding forces between the layers, and the subsequent reaction in dilute butylammonium chloride solutions results in swellings of tens of fold;²⁵ macroscopic swelling, however, cannot be attained using smaller methyl or ethylammonium ions.³⁹

Stabilities. The swollen protonated titanate crystals in aqueous solutions of DMAE were much more stable than crystals swollen in TBAOH solutions, although the spacing was as large as ~ 90 nm. First-principle calculations attributed the high stability to the ordering of H_2O molecules surrounding DMAE, which may arise from the smaller size and higher polarity of the DMAE molecules and the resultant stronger DMAE– H_2O interactions.³¹ To elucidate the effects of size and polarity on the stabilities of the swollen crystals, we performed stability comparisons of swollen crystals in aqueous solutions of two series of similarly constituted compounds. One series was DMA and *N,N*-dimethylbutylamine, which differ only in chain length. The other series was DMA and ethylamine, which have similar sizes; however, the nitrogen portion of DMA possesses a higher inherent polarity because of the presence of two methyl substitutions. After one night of mechanical shaking, the solutions of crystals swollen with the larger reagent, *N,N*-

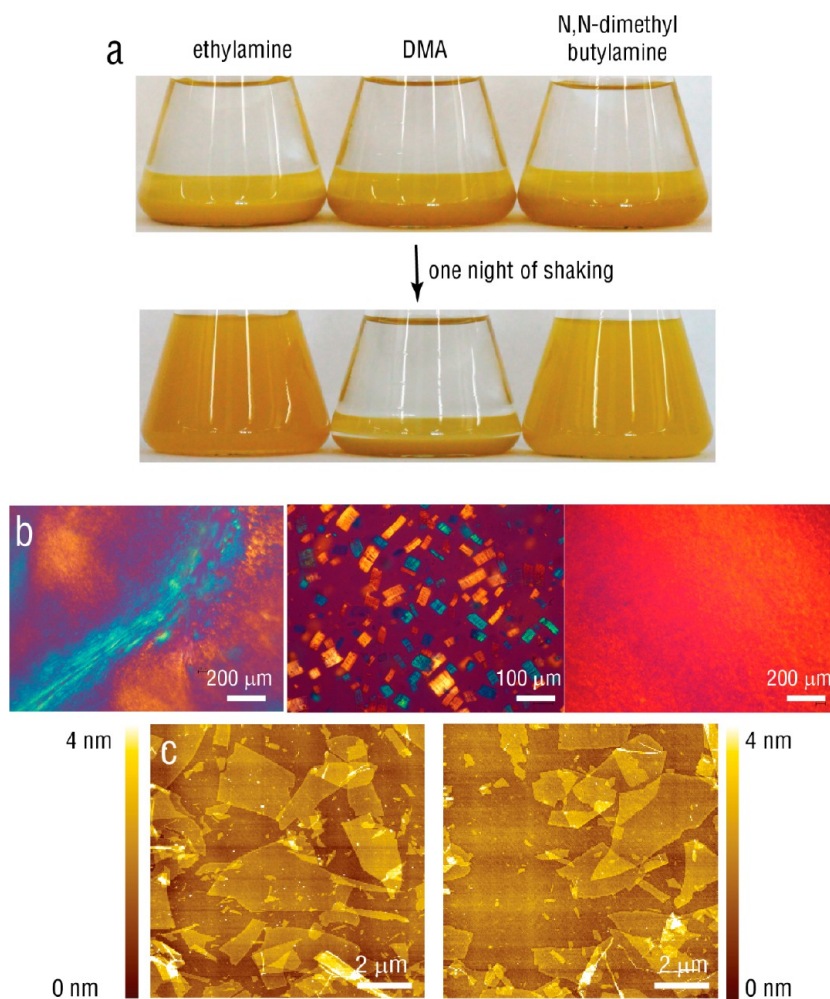


Figure 10. (a) Optical photographs of the crystals swollen with ethylamine, DMA, and *N,N*-dimethylbutylamine before and after overnight mechanical shaking. (b) Optical microscopy images of solutions after overnight shaking. Left: ethylamine, middle: DMA, and right: *N,N*-dimethylbutylamine. (c) AFM images of delaminated nanosheets in ethylamine and *N,N*-dimethylbutylamine.

dimethylbutylamine, and the low-polarity reagent, ethylamine, became colloidal, while the crystals in the small and highly polar DMA solutions remained sedimented at the bottom (Figure 10a). Examination by optical microscopy revealed broken fragments in the precipitates, while the colloids displayed strong or weak stripes due to the birefringent nature of the liquid-crystal phase, suggesting complete delamination into nanosheets (Figure 10b). Total delamination was confirmed by AFM analysis, which revealed unilamellar nanosheets with a thickness of ~ 1 nm (Figure 10c). To delaminate the crystals swollen with DMA, extended shaking for weeks was required. In combination of our previous first-principle calculation studies,³¹ in which ordering of H_2O molecules was found in the confined gallery of crystals swollen with smaller and polar electrolyte solutions, such as DMAE, it is therefore reasoned that smaller size and polarity tend to induce ordering of the surrounding H_2O molecules and bring ordered hydrogen bond network, which in turn helps connect the expanded layers and stabilize the swollen structure, and vice versa.

CONCLUSIONS

In summary, we explored the swelling behavior of inorganic layered materials using protonated titanate crystals in solutions

of various organic bases, including primary amines, tertiary amines, and quaternary ammonium hydroxides. The swelling is initiated by acid–base reactions, and in basic solutions of tertiary amines and quaternary ammonium hydroxides the intercalated amount of protonated amines or ammonium ions increases with increasing initial concentration until saturation is achieved, i.e., $\sim 40\%$ for all cases (as a percentage to the CEC of the crystals), which is mostly determined by the acid–base equilibrium. The only exception is the swelling that occurs in TBAOH solution. The TBAOH intercalation is restricted by steric effects, resulting in a lower saturation value of $\sim 30\%$. The amount of H_2O that enters the gallery or the swollen spacing is mainly governed by the equilibrium of osmotic pressure between the gallery and external reservoir, which is essentially molarity dependent. Therefore, crystals swollen in solutions of the same concentration manifest comparable interplanar spacings. However, the concentration required for the maximum swelling in quaternary ammonium hydroxides is lower than the concentration required for the maximum in tertiary amine solutions due to the increased osmotic pressure resulting from the complete dissociation of the quaternary ammonium hydroxides. Conversely, the attractive interaction between primary amine molecules leads to a reduction in osmotic pressure; therefore, more concentrated solutions are required to produce comparable swellings. Although the

swelling is independent of the identity of the ion, the stability of the swollen crystals is substantially affected by the nature of the incorporated ammonium ions. The crystals are typically more stable when the ammonium ions are smaller or more polar, which may help induce ordering of the surrounding H₂O. Our results therefore shed light on the mechanism by which inorganic layered materials swell and how the intercalated ions affect crystal stability. This knowledge will be useful for controlling the exfoliation of various layered materials into molecularly thin 2D nanosheets.

■ ASSOCIATED CONTENT

● Supporting Information

More optical microscope images, intercalated quantity of amines and hydroxides obtained by titration, calculation details for TBA⁺ close-packing, PXRD patterns for intercalation phases in tetrakis(decyl)ammonium hydroxide and hexadecyltrimethylammonium hydroxide solutions, SAXS profiles for crystals swollen in primary amine solutions, PXRD pattern for the intracrystalline swelling in methylamine solution. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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