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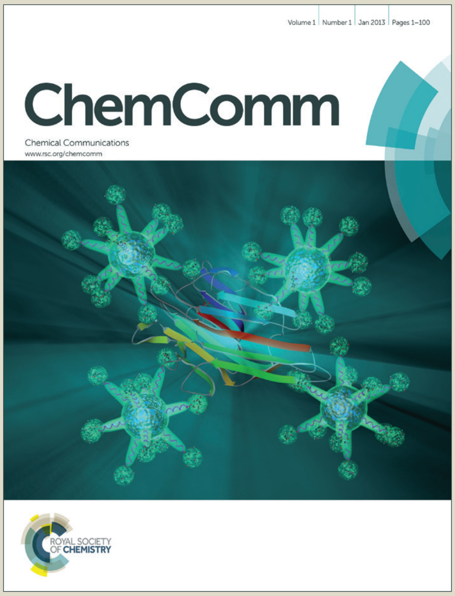

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Accordion-like swelling of layered perovskite crystals via massive permeation of aqueous solutions into 2D oxide galleries

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Platelet crystals of a layered perovskite showed massive accordion-like swelling in tetrabutylammonium hydroxide solutions. The permeation of the solution induced the huge expansion of the interlayer spacing as well as the crystal shape up to 50-fold, leading to a very high water content of >90 wt%.

Recently, we found that platelet crystals of a layered titanate underwent enormous swelling in aqueous solutions of various amines.[1,2] A huge amount of water penetrated into the interlayer galleries of the layered crystals, greatly expanding their thickness up to ~100-fold while keeping thousands of oxide layers stacked in a crystalline manner. The platelet crystals elongated in a columnar shape as a result of the enormous hydration. The greatly expanded crystal consists primarily of water, and thus is seemingly comparable to the lyotropic liquid crystalline state of exfoliated nanosheet suspensions because both show the lamellar stacking of 2D oxide layers on the mesoscale;[3,4] however, the elongated columnar-shaped crystal holds the regular lateral positional order of oxide layers, which is distinct from the liquid crystals of nanosheets, which lack such regularity. This structural feature of the elongated crystal allows the initial platelet morphology to be virtually reverted by applying acid solutions or alcohols. The shrunken crystals could repeatedly swell upon contact with amine solutions.[1] This reversible swelling/shrinking behavior evidently indicated that the elongated crystal is an unprecedented type of crystal whose layer components are tightly bound together even when largely separated by an aqueous medium.

Due to these rare and unique features, the highly swollen crystals may be utilized as a base to develop novel applications such as anisotropic functional hydrogels. Furthermore, the exploration of the expanded crystals is important because the infinite swelling of layered compounds will lead to the production of molecularly thin nanosheets in high yield. Several routes exist to derive 2D materials from bulk layered crystals. Repeated peeling with Scotch tape and the application of ultrasonic waves in proper polar solvents are typical and popular procedures.[5] However, it is rather difficult to obtain large quantities of single-layer sheets with these techniques. Another important method is exfoliation via swelling; the considerable expansion of the interlayer distance significantly weakens the attractive forces between the layers. Consequently, an external shearing force such as mechanical shaking can effectively promote the homogeneous exfoliation of swollen crystals into unilamellar nanosheets in high yield.[6]

The hydration swelling and subsequent exfoliation in electrolyte solutions have been examined for clay and layered transition metal oxides.[7-10] However, in these previous studies, powder samples of layered compounds were mostly used, and swelling to more than 10-fold of the initial size was seldom observed because such a highly swollen state of rather small crystallites became unstable to collapse. Such significant swelling was observed only with a single crystal sample of the layered titanate[1] and vermiculite.[11] Therefore, further study on the highly swollen crystals is of crucial importance to understand the fundamental aspects of hydration-driven swelling as the key stage of exfoliation. Massive swelling behavior is expected to depend on the layer architecture, composition, and charge density of the host material, and it would be interesting to examine the hydration swelling of layered materials other than the titanate.[1,2]

In this communication, we employ the most typical member of the Dion-Jacobson-type layered perovskite niobates, $KCa_2Nb_3O_{10}$, as the host material. Layered perovskite oxides are characterized by their rich pool of functionalities and thus have been investigated from diverse viewpoints. In addition, a wide variety of functional nanosheets have been produced from them via exfoliation. Perovskite-type oxide nanosheets, *e.g.*, $Ca_2Nb_3O_{10}^-$, have attracted significant attention due to their fascinating properties such as dielectric, photocatalytic, and fluorescent properties;[12-15] such nanosheets have also been used as seed layers for epitaxial growth.[16] For these reasons, it is very important to study the swelling behaviors of the layered perovskite niobate and

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† Electronic Supplementary Information (ESI) available: The SEM images, XRD data, chemical analysis data of precursor crystals, SEM images of perovskite nanosheet, and a video concerning reversible swelling/shrinking of perovskite niobate crystals. See DOI: 10.1039/x0xx00000x

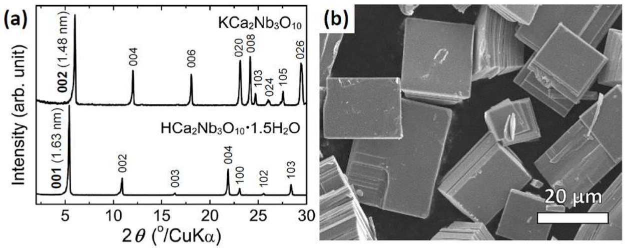

Fig. 1 Powder XRD data before and after the acid treatment (Fig. S-2b in ESI for the fully indexed XRD profiles up to 2θ = 60°).† (b) SEM image of $HCa_2Nb_3O_{10}\cdot1.5H_2O$ showing the platelet shape with sharp edges. The thickness of 5–20 μm corresponds to stacks of 3000–12000 layers.

characterize the resulting swollen crystal. In this work, we synthesized platelet single crystals of $KCa_2Nb_3O_{10}$, converted them into the acid-exchanged form, and examined swelling behaviors in aqueous solutions containing organoammonium ions. As a result, we successfully obtained a highly expanded structure of the crystals, which are composed of a large volume of water exceeding 90 wt%.

We explored the optimum synthetic conditions for growing single crystals of the parent layered perovskite, $KCa_2Nb_3O_{10}$, with size several tens of microns; such crystals are suitable for swelling experiments. Parent platelet crystals of $KCa_2Nb_3O_{10}$ were first synthesized according to previous reports using K_2SO_4 as a flux as well as a solute.[17,18] Slow cooling from a mixed system of K_2SO_4-$CaSO_4$-Nb_2O_5 yielded large crystals; however, they sometimes reached mm-scale sizes and aggregated heavily, making them unsuitable for swelling. We found that monodisperse platelet crystals with lateral size of several tens of microns could be obtained when $CaCO_3$ was used instead of $CaSO_4$ as the source of Ca to make a starting mixture of K_2SO_4-$CaCO_3$-Nb_2O_5 (5:4:3 in mol). The mixture was ground in an agate mortar and placed in a Pt crucible followed by heating in an electric furnace at 1300 °C for 24 h. The detailed preparation conditions are given in ESI S-1.† After removing the flux with water and filtering the product, crystals with sizes of 25-53 μm were classified by sieving. The X-ray diffraction (XRD) profile of the collected crystals (Fig. 1a) could be indexed on the basis of the orthorhombic system (refined unit cell dimensions: a = 0.3871(1), b = 0.7709(3), and c = 2.9486(8) nm), consistent with those reported in previous studies.[19] No impurities were detected.

The sample was then treated with a 5M HNO_3 solution to convert it to the protonated form.[19] The XRD profile for the obtained crystals again agreed well with the previously reported data for the acid-exchanged phase, $HCa_2Nb_3O_{10}\cdot1.5H_2O$.[19] Chemical analysis (Table S-3) revealed the substantial removal of interlayer K^+, indicating the nearly full exchange (98.3%) with protons. The euhedral rectangular crystal shape was maintained, as shown in Figs. 1b and S-3b of ESI.† Note that the crystals thus synthesized are monodisperse and well-shaped with sizes in the range of 25-53 μm, in sharp contrast to samples prepared from the conventional solid-state calcination method (Fig. S-4).†

To examine the swelling behavior, 0.2 g of the $HCa_2Nb_3O_{10}\cdot1.5H_2O$ crystals was reacted with 100 cm^3 of the aqueous solution of tetrabutylammonium hydroxide (TBAOH), which is known to be an effective delaminating agent for various layered compounds.[20,21] The TBAOH concentrations were adjusted in the range of 0.00037 to 0.01828 M, corresponding to the dose of TBA ions needed to equal 0.1 to 5 times the exchangeable proton content of $HCa_2Nb_3O_{10}\cdot1.5H_2O$.

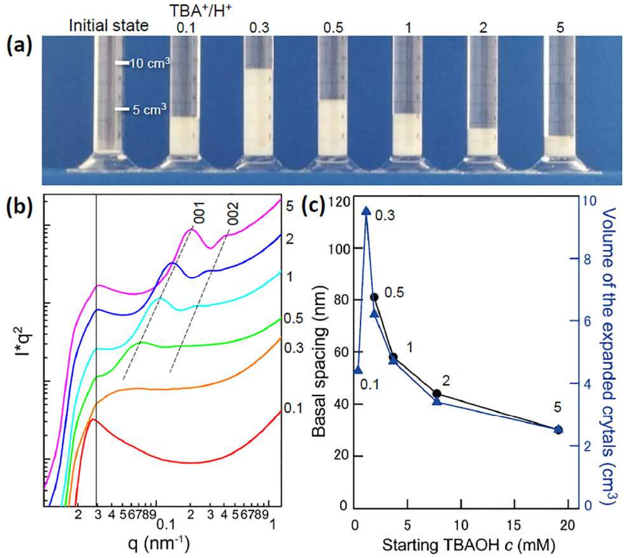

Fig. 2 Photograph showing the expanded samples in TBAOH solutions. The leftmost cylinder contains the dried single crystal sample without added solution. The transparent parts in the cylinders of other samples are filled with supernatants. (b) SAXS profiles of the swollen crystals in TBAOH solutions with various concentrations. The data for the variation in $I \times q^2$ vs. the scattering vector q are plotted. I is the scattering intensity. The basal spacing is calculated by the formula $d = 2\pi / q$. The black solid line represents the position for a stopper of the direct beam. (c) The basal spacing and macroscopic volume of the expanded crystals as a function of the starting TBAOH concentrations. Digits beside the data points indicate the corresponding TBA^+/H^+ values.

After equilibrating overnight, the sample exhibited a significant volume expansion, as observed from the white sediment at the bottom of the graduated cylinder (Fig. 2a). 0.2 g of the crystal before the reaction occupied a negligible volume, or approximately 0.05 cm^3 based on its density of 3.76 g cm^{-3}. In contrast, a macroscopic increase in sample volume was observed after the treatment with the TBAOH solution. The volume increased at the initial stage with increasing TBA^+ dose, showing a maximum of 9.5 cm^3 at TBA^+/H^+ = 0.3. At higher TBAOH concentrations, a gradual decrease in volume was observed.

Small angle X-ray scattering (SAXS) profiles were collected to obtain microscopic information of the expanded samples (Fig. 2b). A set of peaks were detected for the samples at TBA^+/H^+ = 0.5–5. These peaks are attributable to the first- and second-order reflections of the highly swollen layered structure. The sample with TBA^+/H^+ = 5 showed better-defined peaks with a well-expanded basal spacing of 30 nm. With decreasing TBA^+/H^+ values, the peaks shifted toward smaller angles, indicating further expansion. The maximum layer expansion was observed at TBA^+/H^+ = 0.5 with a basal spacing of 81 nm. In this case, the interlayer expansion is almost 50-fold compared to that of the starting phase (1.63 nm). Furthermore, the well-defined reflection accompanying the second-order peak at high TBAOH concentrations implies a high structural regularity of the expanded crystal. Normalization of the change in the basal spacing according to the increase in the sample volume indicated a close correlation between these variables (Fig. 2c); this suggests that such a massive interlayer expansion takes place

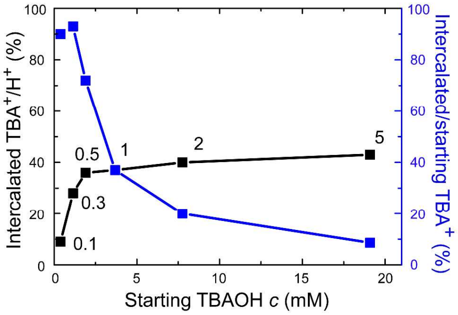

Fig. 3 The amount of intercalated TBA^+ expressed as a percentage relative to the amount of H^+ in the crystal as a function of the starting TBAOH concentrations (black line). The blue line plots the ratio of intercalated TBA^+/starting TBA^+ in solutions.

homogeneously across the crystal. In contrast, the peaks became diffuse or undetectable at $TBA^+/H^+ = 0.3$. Considering the maximum sample volume, it may be reasonable to assume that the sample with $TBA^+/H^+ = 0.3$ has a very large interlayer separation of ~100 nm or above (based on an extrapolated value in Fig. 2c). As the interlayer separation becomes larger, the stacking order will naturally decrease. This trend as well as the detection limit of the SAXS measurement may be responsible for our inability to determine the interlayer spacing value at this TBAOH concentration. The absence of the diffraction feature for the sample with $TBA^+/H^+ = 0.1$ is probably due to insufficient TBA^+ intercalation, which will be discussed later. Notably, the sample volume at this condition did not follow the trend of other samples.

The equilibration data of guest species is important to understand the swelling phenomenon, which is involved by the intercalating TBA^+ and water as well as H^+ in the crystal. The concentration of TBA^+ in the solution was determined by acid-base titrations before and after equilibration, and the intercalated amount of TBA^+ was deduced from the concentration difference. The uptake rapidly increased as the initial TBA^+ dose increased up to $TBA^+/H^+ = 0.5$ (Fig. 3). In this region, over 90% of the applied TBA^+ was taken up into the crystal, and the remaining concentration of TBA^+ in the solution was low or nearly zero. When $TBA^+/H^+ > 0.5$, the uptake reached saturation at a value corresponding to the replacement of ~40% of H^+ in the crystal, and the concentration of TBA^+ in the solution increased. The saturation uptake of 40% may be understood by the structural consideration on the layer surface coverage with TBA ion.[22,23] The projected size of TBA ion is estimated as 0.61 to 0.71 nm^2, depending on its orientation (Fig S-5).† These values are 4.1 to 4.8 times larger than the unit cell area of the perovskite layer, meaning 0.21 to 0.24 TBA ions are needed to cover the layer surface. Since the sheet has two faces, front and back, incorporation of TBA ion should be double (0.42 to 0.48TBA), which is similar to the experimental value.

The obtained data reveal that the amount of intercalated TBA^+ is too small to account for the observed interlayer separation of several tens of nm. Thus, the huge expansion should be understood by the insertion of a large volume of water into the interlayer galleries, similar to our recent finding for the swelling of the layered titanate in various amine solutions.[1,2] As an example, we estimate the stoichiometry of the swollen phase at $TBA^+/H^+ = 0.5$, where a maximum swelling of 81 nm was observed. The host layer has a square unit basal area of 0.149 nm^2 (= 0.3855 x 0.3855 nm^2) which accommodates one formula weight of $Ca_2Nb_3O_{10}^-$. The swollen crystal has an interlayer columnar space with a height of 79.5 nm (assuming an oxide layer thickness of 1.5 nm). Based on the equilibration data, 0.36 of TBA ions is accommodated in the interlayer region. It is reasonable to assume that the remaining space,[23] which is estimated to be 11.74 nm^3, will be occupied exclusively by water molecules. Based on the density of water, 393 water molecules are included in the interlayer space, resulting in a formula of $TBA_{0.36}H_{0.64}Ca_2Nb_3O_{10}\cdot393H_2O$. This means that the swollen crystal is composed of 92.1 wt% water, 1.1 wt% TBA^+, and 6.8 wt% oxide layers. Notably, even a very small amount of TBA^+ introduced in the interlayer space could cause a large interlayer separation by penetrating a huge amount of water and stabilize the greatly expanded structure.

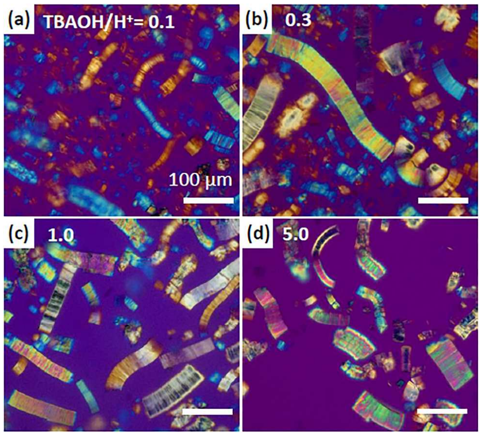

Fig. 4 Polarized optical microscopy images (color tint plate is inserted) of the swollen crystals in the TBAOH solutions with different concentrations.

The swelling degree gave the maximum value when the TBA^+ uptake reached saturation and showed monotonous decrease with further increase in the initial TBA^+ concentration, as revealed from Fig. 2 and 3. A similar trend was observed in the layered titanate (Fig. S-6),† strongly suggesting a common swelling mechanism working in the both layered systems. The saturated uptake to determine the maximum swelling should depend on various factors of the layered hosts such as acidity, layer architecture, *etc*. The shrinkage in basal spacing afterwards may be understood by the increase in osmotic pressure from the outside of crystals associated with the increase in TBA^+ concentration.

The morphology of the expanded crystals produced at TBA^+/H^+ = 0.1, 0.3, 1, and 5 was observed by polarized optical microscope (Fig. 4). Each platelet crystal was greatly elongated in the direction perpendicular to the basal plane, like an accordion. In the sample with $TBA^+/H^+ = 0.1$, unreacted platelet crystals were observed along with the swollen crystals. This may be regarded as a sort of biphasic process, which is frequently observed in normal intercalation reactions. The swollen crystals tended to show better-defined edges when the TBAOH concentration increased. On the other hand, the swollen crystals with $TBA^+/H^+ < 0.3$ showed rather blurred contours. This trend may be related to the decrease in structural order along the progress of the swelling, which is recognized from the SAXS analysis as discussed above.

The length of the swollen crystals showed the wide spread in all the samples as seen from histograms (Fig. S-7)† counted from the

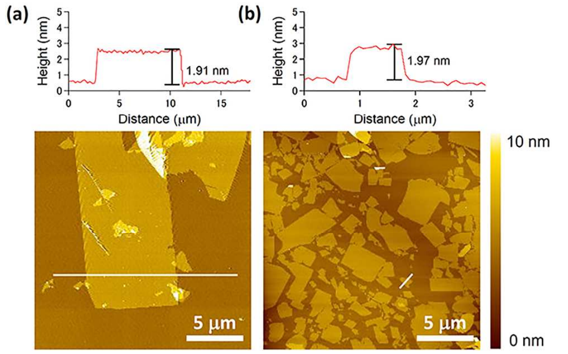

Fig. 5 Thickness profiles and AFM images of nanosheet products on the Si substrate. Nanosheets were derived from (a) flux-grown crystals and (b) calcined powders. The thickness is equal to each other within the precision of the measurements, and is consistent with the previously reported value (1.8 ± 0.1 nm).[24]

images. The largely varied thickness of the starting platelet crystals is partly responsible for the wide distribution of the swollen crystal length. But a more important reason may be fragmentation of the swollen crystals because the distribution in the histogram is more or less similar to each other although the degree of swelling as well as the macroscopic sample volume was significantly different for these samples. It would be natural that the highly elongated crystals incorporating a large volume of water into the interlayer galleries become less stable to be broken into shorter pieces. Our recent study on the layered titanate showed such a tendency and revealed that the TBA ion particularly promotes fragmentation and delamination as the ultimate end. Still it is amazing that the sample with TBA^+/H^+ = 0.3, which showed the maximum macroscopic volume, contained highly elongated crystals of >300 μm, suggesting an enormous degree of swelling. As discussed above, the extrapolation of the SAXS data (Fig. 2a)† suggests such an extremely high degree of swelling, although it could not be directly detected.

A real-time movie (ESI Video 1)† supports the idea that the swollen sample is crystalline and can undergo reversible swelling/shrinking actions. The platelet crystals underwent immediate swelling upon addition of the TBAOH solution and subsequently returned to their initial platelet crystal state upon treatment with HCl solution.

Finally, the exfoliation of the swollen crystals into unilamellar nanosheets was explored. The swollen crystals in the TBAOH solution were subjected to external force via shaking by hand three times per day for 1 week. To monitor nanosheet formation, 10 cm^3 of suspension was centrifuged at 1500 rpm for 10 min to remove intact swollen crystals or those not cleaved into thinner crystallites. A Si substrate primed with polycation was then immersed into the supernatant diluted one hundredth to detect the delaminated product. As shown in Fig. 5a, AFM analysis showed sheet-like objects with a unique height of 1.91 nm, revealing their unilamellar nature. The nanosheets obtained from the swollen crystals were characterized by their defined square contours as well as their large sizes of approximately 10 μm. It is important to note that the nanosheets derived from the polycrystalline sample of $KCa_2Nb_3O_{10}$ were generally irregular in shape and rather small, with maximum dimensions of several micrometers (Fig. 5b and Fig. S-8b).† These results demonstrate a promising possibility to produce large, high-quality nanosheets that are expected to be useful in various applications.

In summary, highly elongated columnar-shaped crystals were derived from size-controlled host crystals of the layered perovskite niobate upon contact with TBAOH solutions. Reaction caused the crystals to greatly expand by up to 50-fold. The massive hydration widened the interlayer distance to several tens of nm in the stacking direction to reach a water content of >90 wt%. The macroscopic and microscopic results demonstrate the regularity of interlayer separation across the crystal and highlight the unusual crystalline nature of highly hydrated perovskite crystals. Furthermore, we showed the possibility of producing large, regularly shaped, and unilamellar 2D materials from the obtained swollen crystals.

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Notes and references

1 F. Geng, R. Ma, A. Nakamura, K. Akatsuka, Y. Ebina, Y. Yamauchi, N. Miyamoto, Y. Tateyama, and T. Sasaki, *Nat. Commun.*, 2013, **4**, 1632.
2 F. Geng, R. Ma, Y. Ebina, Y. Yamauchi, N. Miyamoto, and T. Sasaki, *J. Am. Chem. Soc.*, 2014, **136**, 5491-5500.
3 J-C. P. Gabriel, F. Camerel, B. J. Lemaire, H. Desvaux, P. Davidson, and P. Batail, *Nature*, 2001, **413**, 504-508.
4 N. Miyamoto and T. Nakato, *Adv. Mater.*, 2002, **14**, 1267-1270.
5 V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano, and J. N. Coleman, *Science*, 2013, **340**, 1226419.
6 R. Ma and T. Sasaki, *Acc. Chem. Res.*, 2015, **48**, 136-143.
7 K. Norrish, *Nature*, 1954, **173**, 256-257.
8 G. F. Walker, *Nature*, 1960, **187**,312-313.
9 M. Smalley, *Clay Swelling and Colloid Stability*, CRC Press, Boca Raton, FL, 2006.
10 T. Sasaki and M. Watanabe, *J. Am. Chem. Soc.*, 1998, **120**, 4682-4689.
11 W. G. Garrett and G. F. Walker, *Clays Clay Min.*, 1962, **9**, 557-567.
12 Y. Ebina, K. Akatsuka, K. Fukuda, and T. Sasaki, *Chem. Mater.*, 2012, **24**, 4201-4208.
13 M. Osada and T. Sasaki, *Adv. Mater.*, 2012, **24**, 210-228.
14 Y. Ebina, T. Sasaki, M. Harada, and M. Watanabe, *Chem. Mater.*, 2002, **14**, 4390-4395.
15 T. C. Ozawa, K. Fukuda, K. Akatsuka, Y. Ebina, and T. Sasaki, *Chem. Mater.*, 2007, **19**, 6575-6580.
16 T. Shibata, K. Fukuda, Y. Ebina, T. Kogure, and T. Sasaki, *Adv. Mater.*, 2008, **20**, 231-235.
17 M. Dion, M. Ganne, and M. Tournoux, *Mater. Res. Bull.*, 1981, **16**, 1429-1435.
18 H. Fukuoka, T. Isami, and S. Yamanaka, *J. Solid State Chem.*, 2000, **151**, 40-45.
19 A. J. Jacobson, J. T. Lewandowski, and J. W. Johnson, *J. Less-Common Metals*, 1986, **116**, 137-146.
20 Y. Ebina, T. Sasaki, and M. Watanabe, *Solid State Ionics*, 2002, **151**, 177-182.
21 T. Sasaki, M. Watanabe, H. Hashizume, H. Yamada, and H. Nakazawa, *J. Am. Chem. Soc.*, 1996, **118**, 8329-8335.
22 T. Sasaki and M. Watanabe, *Mol. Cryst. Liq. Cryst.*, 1998, **311**, 417-422.
23 The volume of one TBA^+ is calculated based on the tetrahedral molecular shape with 1.19 nm on a side.
24 M. Osada, K. Akatsuka, Y. Ebina, H. Funakubo, K. Ono, K. Takada, and T. Sasaki, *ACS Nano*, 2010, **4**, 5225-5232.