

Supporting Information

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

Fengxia Geng,[†] Renzhi Ma,[†] Yasuo Ebina,[†] Yusuke Yamauchi,[†] Nobuyoshi
Miyamoto,[‡] Takayoshi Sasaki^{†,*}

[†] *International Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1
Namiki, Tsukuba, Ibaraki 305-0044, Japan*

[‡] *Department of Life, Environment and Materials Science, Fukuoka Institute of Technology, Wajiro-
Higashi, Higashi-ku, Fukuoka 811-0295, Japan*

* Fax: (+81) 29-854-9061; E-mail: SASAKI.Takayoshi@nims.go.jp

Figure S1. Optical microscope image and SAXS data for crystals swollen in DMAE solutions of very low concentrations, $N/H^+ = 0.1$. The swelling is heterogeneous, and therefore the crystals under optical microscope showed iridescence and the SAXS profile only included a weak and diffuse peak.

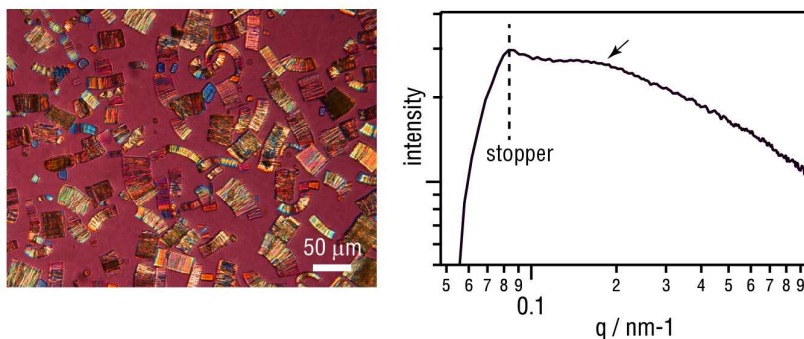


Figure S2. Optical microscope images for crystals swollen in tertiary amine solutions of all concentrations, $N/H^+ = 0.3, 0.5$ and 0.7 .

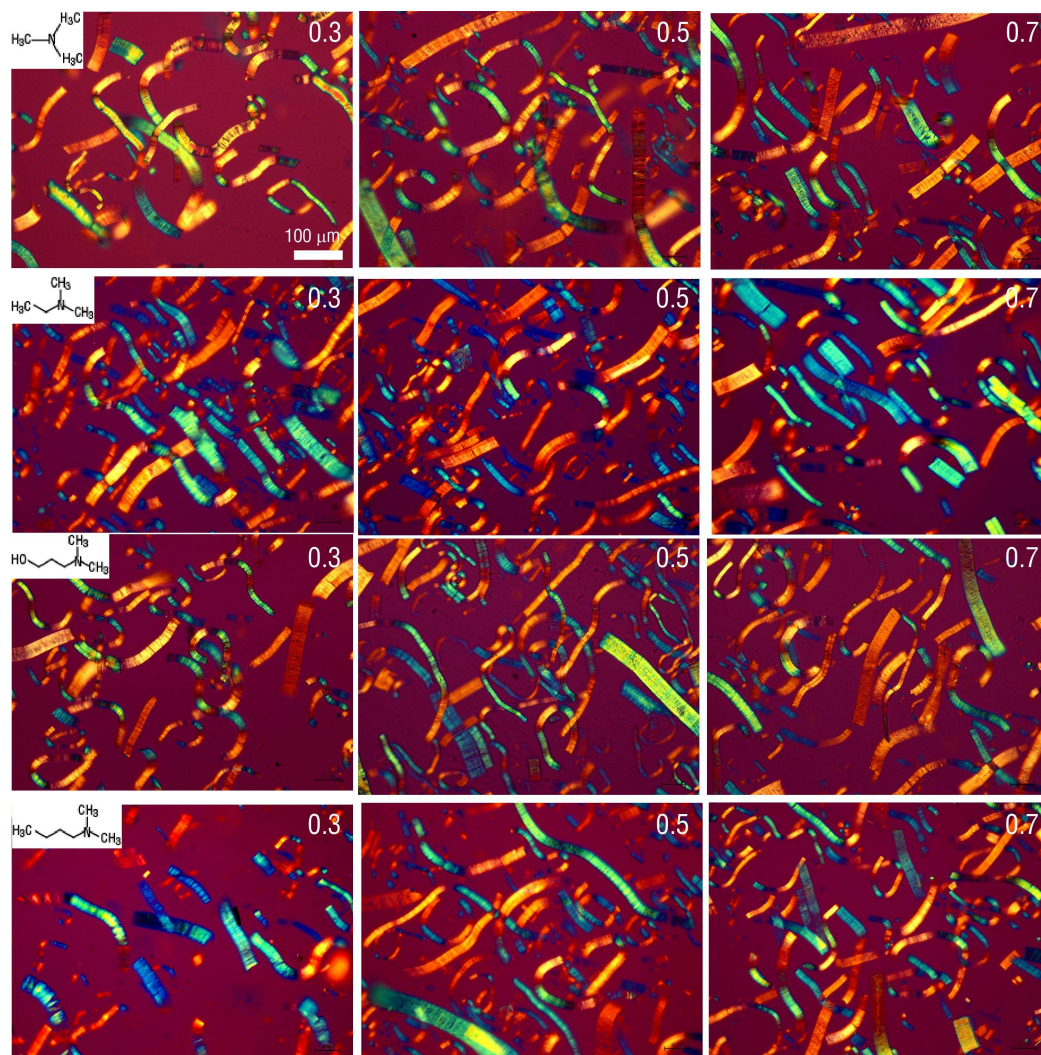


Table S1. The table lists intercalated amount of tertiary amines and quaternary ammonium hydroxides in solutions at concentration of $N/H^+=0.3, 0.5$, and 0.7 obtained by titration. The values correspond to relative proportion of the uptake with respect to the cation-exchange capacity.

amine ratio	tertiary amine				quaternary ammonium hydroxide			DMAE
	TMA	DMEA	DMAP	DMBA	TMAOH	DEDMAOH	TBAOH	
0.7	0.39	0.36	0.39	0.36	0.41	0.41	0.30	0.39
0.5	0.37	0.35	0.36	0.35	0.40	0.38	0.28	0.37
0.3	0.26	0.27	0.28	0.26	0.29	0.29	0.25	0.27

TMA=Trimethylamine, DMEA=2-dimethylethylamine, DMAP=3-dimethylamino-1-propanol, DMBA= N,N-dimethylbutylamine, TMAOH= tetramethylammonium hydroxide, DEDMAOH= diethyldimethylammonium hydroxide, TBAOH= tetrabutylammonium hydroxide.

Figure S3. Optical microscope images for crystals swollen in quaternary ammonium hydroxide solutions of all concentrations, $N/H^+ = 0.3, 0.5$ and 0.7 .

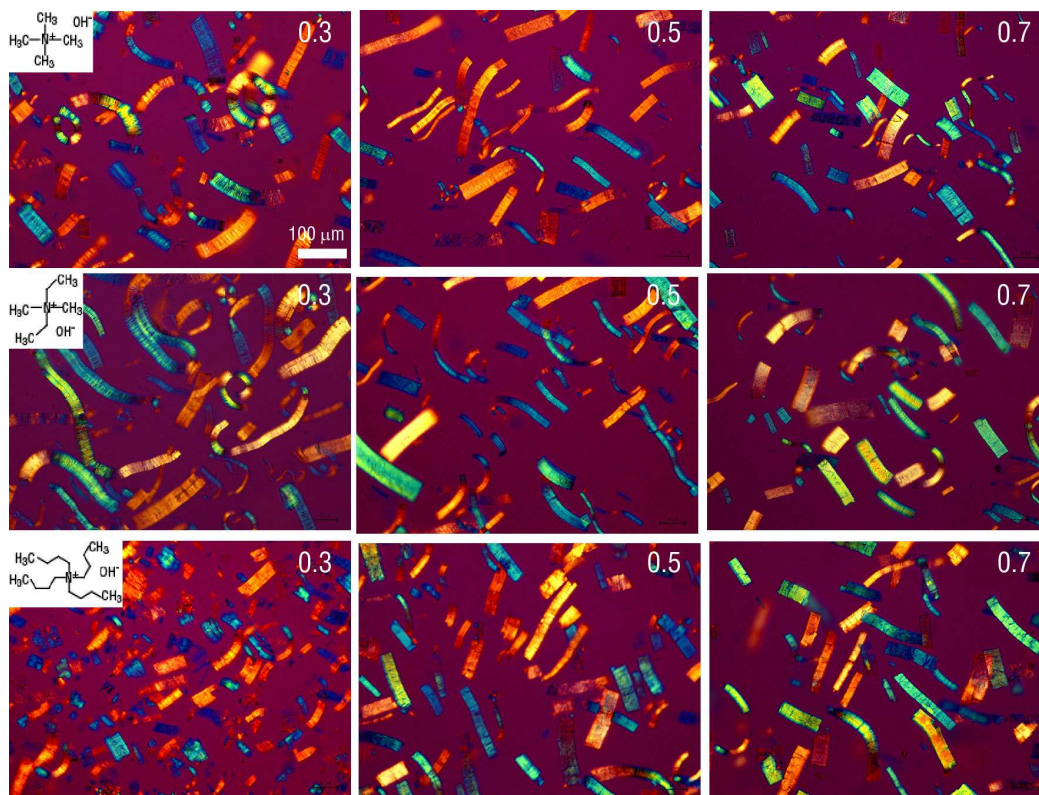


Figure S4. The TBA ions in a near-spherical shape have a cationic size of ~ 0.8 nm, and for close-packing each ion occupies an area of 0.557 nm^2 . One unit cell is 0.114 nm^2 ($0.38 \times 0.30 \text{ nm}^2$), and consequently each cell can hold 0.20 TBA^+ , close to experimental observations.

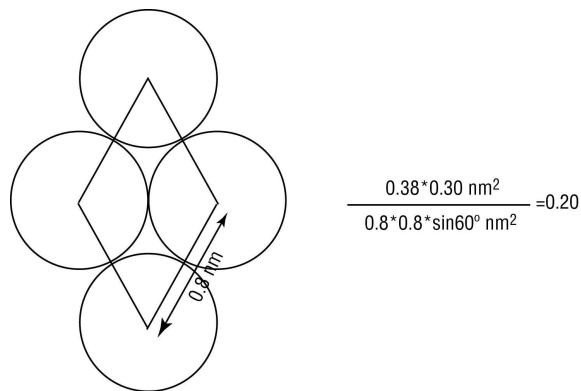


Figure S5. X-ray diffraction patterns for intercalation phases formed upon action with tetrakis(decyl)ammonium hydroxide and hexadecyltrimethylammonium hydroxide solutions. The samples were dried before measurement. The diagrams show strong and sharp $(0k0)$ reflections (up to 6), a typical feature of macromolecule intercalation. The spacings were calculated averagely from $[(d_{060} \times 6 + d_{050} \times 5 + d_{040} \times 4 + d_{030} \times 3 + d_{020} \times 2 + d_{010})/6]$, which gave 2.94 nm and 2.89 nm for tetrakis(decyl)ammonium hydroxide and hexadecyltrimethylammonium hydroxide, respectively, corresponding to monolayer intercalation.

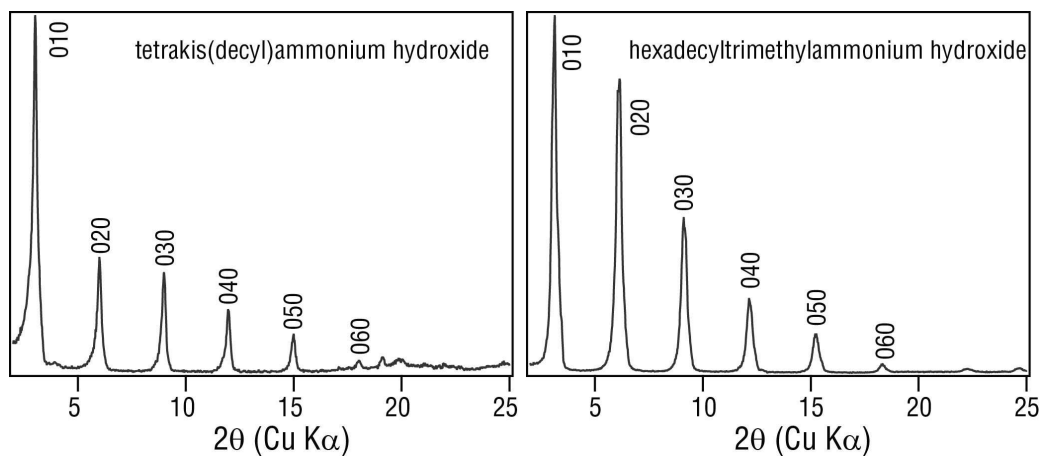


Figure S6. Optical microscope images and SAXS profiles for crystals swollen in primary amine solutions of all concentrations, $N/H^+ = 0.5, 1, 5, 10$.

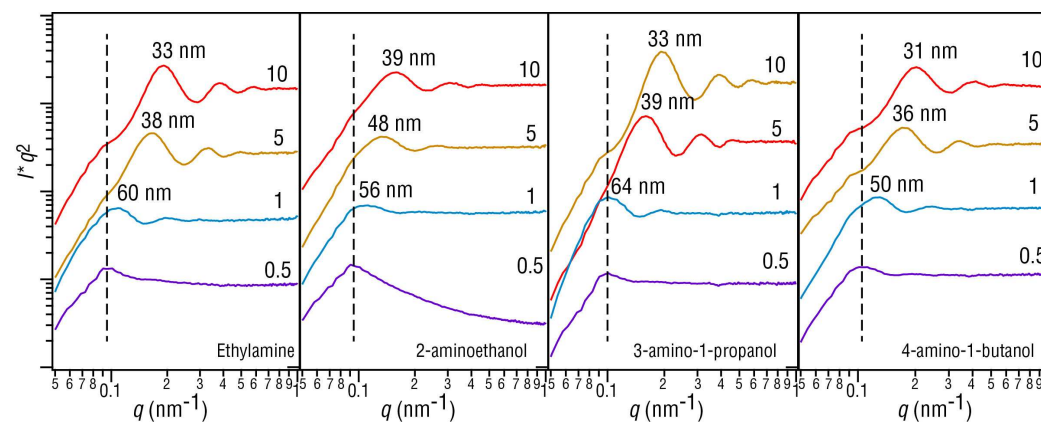
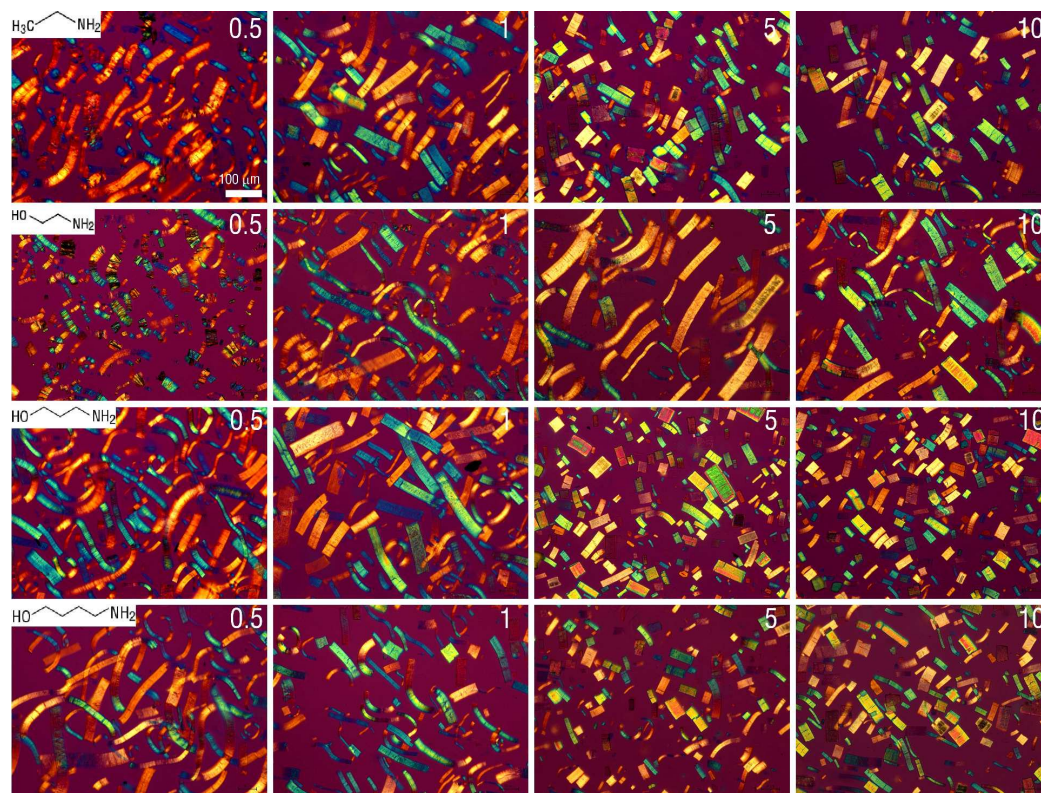


Figure S7. When the crystals are immersed in methylamine solution, obvious volume increase or osmotic swelling was not observed. Instead, XRD characterization studies showed that the interlayer spacings shift from 0.88 nm for original protonated titanate oxide to 0.93 nm. A related protonated titanate, $\text{H}_{1.07}\text{Ti}_{1.73}\text{O}_4 \cdot \text{H}_2\text{O}$, was reported to incorporate a series of n-alkylammonium ions, and the layer-to-layer distance propped up by methylamine was also 0.93 nm (*Chem. Mater.* 1998, 10, 4123). This suggests that some protons in the gallery are replaced by methylammonium ions, forming the corresponding intracrystalline phase.

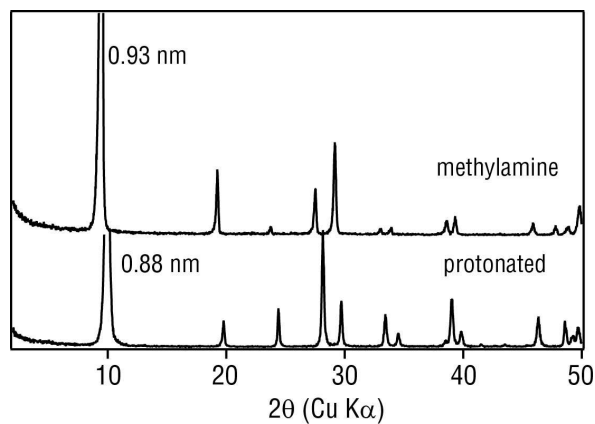


Table S2. In solutions near the maximum swelling, the outside concentration is practically zero, and the solution in the gallery space generates osmotic pressure of close to one atmospheric pressure.

DMAE	Outside		Inside	
	C (mol/L)	Pressure (atm)	C (mol/L)	Pressure (atm)
0.3	0.000238	0.006	0.040	0.979
0.5	0.001012	0.025	0.048	1.174
0.7	0.002496	0.061	0.056	1.370

TMA	Outside		Inside	
	C (mol/L)	Pressure (atm)	C (mol/L)	Pressure (atm)
0.3	0.00013	0.006	0.0367	0.898
0.5	0.00067	0.033	0.0714	1.747
0.7	0.00211	0.103	0.0919	2.248

TBA	Outside		Inside	
	C (mol/L)	Pressure (atm)	C (mol/L)	Pressure (atm)
0.3	0.00038	0.019	0.0305	0.746
0.5	0.00176	0.086	0.0487	1.192
0.7	0.00332	0.162	0.0643	1.573