

Ordered Arrays of Molecular Monolayers of Macrotricyclic Ammonium Cage Hosts as Chloride Receptors

Kazuhiko Ichikawa,* Masanori Yamada, and Naohito Ito

Abstract: In a study of the chloride-ion-assisted assembling process at the interface between the NaCl(001) surface and water, atomic force microscopy (AFM) images showed an ordered array of the chloride receptors **1** ($[\text{Me}_4\text{N}_4(\text{C}_5\text{H}_{10})_3(\text{C}_6\text{H}_{12})_3]^{4+}$) or **2** ($[(\text{PhCH}_2)_4\text{N}_4(\text{C}_5\text{H}_{10})_3(\text{C}_6\text{H}_{12})_3]^{4+}$); these cage hosts can encapsulate Cl^- into their own cavities. On the other hand, a molecular monolayer of fluoride receptor **3** ($[(\text{PhCH}_2)_4\text{N}_4(\text{C}_5\text{H}_{10})_6]^{4+}$) was observed in the AFM image, but the interaction between the monolayer and the surface of NaCl(001) was so weak that no ordered array of these cage hosts was observed in the

AFM image; the intramolecular cavity of **3** is too small to encapsulate Cl^- . The ordered array of cage hosts **1** or **2** was established as a result of their self-assembly through their encapsulation of Cl^- belonging to the metastable monatomic layer at the interface between the NaCl(001) surface and water as well as through their steric fit controlled by their own *exo* hydrophobic groups.

Keywords: atomic force microscopy • cage compounds • ordered array • self-assembly • supramolecular chemistry • surface chemistry

Introduction

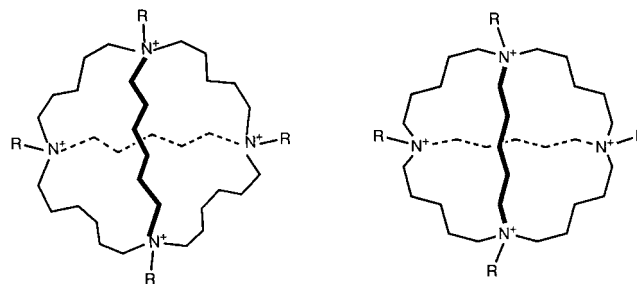
Molecular recognition of anionic substrates by artificial receptors is an area of intense current research due to the importance of anions in biochemical processes.^[1] Ordered arrays and crystals of anion-encapsulation host cages give useful insights into the noncovalent interactions which play an important role in building supramolecular structure.^[2, 3] The creation of molecular assemblies by means of specific non-covalent couplings (crystal engineering) has recently become a hot topic.^[3]

Scanning tunneling and atomic force microscopies (STM and AFM) are useful for the observation of the surface structures of various materials with atomic or molecular resolution. Both STM and AFM have been of benefit in two types of studies: 1) the study of two-dimensional arrays of the molecules adsorbed on the lattice sites of substrates, for example, of porphyrins on iodide-modified Ag(111)^[4] and of cyclodextrins on molybdenum disulfide.^[5] The regular array of these molecules is controlled by the lattice matching with the surface structure of the substrate. 2) As an alternative case, the electrostatic, hydrogen-bonding, and hydrophobic inter-

actions among molecules in water give rise to their self-assembly and organization at the interface. Thus, the two-dimensional molecular patterns of organic acid on hydrocalcite at the solid–liquid interface and of dialkylmelamine on barbituric acid at the air–water interface were constructed through molecular recognition of hydrogen bonds without any assistance from the lattice structure of substrate.^[6, 7]

This paper reports the ordered array of chloride-receptor cage hosts at the surface of an NaCl crystal. The ordered array resulted from self-assembly associated with the encapsulation of a chloride ion into each cage host and was controlled by the steric fit among the *exo* hydrophobic groups of the cage hosts.

The cage hosts $[\text{Me}_4\text{N}_4(\text{C}_5\text{H}_{10})_3(\text{C}_6\text{H}_{12})_3]^{4+}$ (**1**), $[(\text{PhCH}_2)_4\text{N}_4(\text{C}_5\text{H}_{10})_3(\text{C}_6\text{H}_{12})_3]^{4+}$ (**2**), and $[(\text{PhCH}_2)_4\text{N}_4(\text{C}_5\text{H}_{10})_6]^{4+}$ (**3**) have the characteristic feature of four positive binding sites around the center, the capabilities of both encapsulation of and selectivity for chloride or fluoride ions,

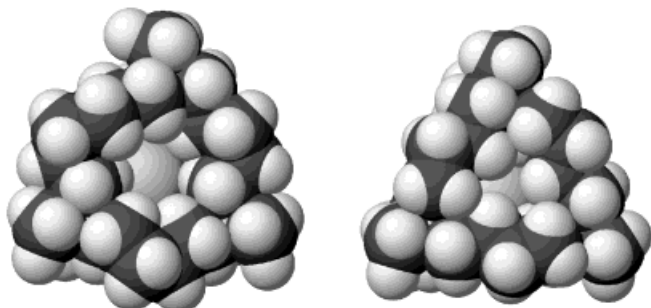


1: R=CH₃
2: R=C₆H₅CH₂

3: R=C₆H₅CH₂

[*] Prof. K. Ichikawa, M. Yamada, N. Ito
Division of Material Science
Graduate School of Environmental Earth Science
Hokkaido University, Sapporo 060 (Japan)
Fax: (+81) 11-757-5995
E-mail: ichikawa@env.hines.hokudai.ac.jp

and a variety of noncovalent recognitions which result from their own *exo* hydrophobic groups. Since the selectivity for chloride or fluoride ions can be determined by the size of intramolecular cavity, which can be controlled by varying the number of cyclic methylene groups, **1/2** and **3** selectively recognized chloride and fluoride ions, respectively, by encapsulating them into their intramolecular cavities.^[8–11] Scheme 1



Scheme 1. Space-filling molecular structure of **1**·Cl⁻ viewed from a (C₅H₁₀)(C₆H₁₂)₂ face (left) and a (C₅H₁₀)₃ face (right).

illustrates the different sizes of quasitetrahedral faces bounded by (C₅H₁₀)₃ and (C₅H₁₀)(C₆H₁₂)₂ (in this case the face is surrounded by one (CH₂)₅ chain and two (CH₂)₆ chains); the structures were obtained by X-ray crystallography.^[11] The chloride receptors **1** and **2** can encapsulate a Cl⁻ into their own cavities, and the fluoride receptor **3** can encapsulate a F⁻ and no Cl⁻. The ¹H, ¹⁹F, and ³⁵Cl NMR data for the aqueous solutions of **2**·4BF₄⁻ + NaCl and **3**·4BF₄⁻ + (CH₃(CH₂)₃)₄NF have shown that the cage hosts **2** and **3** have high encapsulation and selectivity for chloride and fluoride ions, respectively.^[10, 11]

It is very interesting to fix a molecular monolayer of the chloride-receptor cage hosts on an NaCl(001) surface from the point of view of the deposition of cage hosts on a substrate

Abstract in Japanese:

マクロトリサイクリック第四級アンモニウムイオンは分子内にできた cavity にハライドイオンを包接することができるハライドイオンレセプターである。そこで塩化物イオンレセプターである **1**、**2** とフッ化物イオンレセプターである **3** を用いて、NaCl(001) と水との界面におけるハライドイオンの包接挙動と単分子膜配列を原子間力顕微鏡 (AFM) を用いて観察を行った。その結果、**1**、**2** は NaCl(001) と水との界面において形成される、準安定な非平衡イオン配列の塩化物イオンを分子内 cavity への包接を伴う分子認識を通して規則正しい周期性を持った配列を形成することが観察された。また、この場合 *exo*-疎水基の効果によって **1** と **2** の配列には大きな周期性の違いがみられた。一方、フッ化物イオンレセプターである **3** は分子内 cavity が小さく、界面における塩化物イオンを分子内 cavity に包接できないため NaCl(001) 表面との相互作用が非常に弱く、周期性を持った配列を観察することができなかった。

that consists of their guests. Since a big difference exists for the lattice matching between the ordered array of cage hosts of **2** or the crystalline structure of **2**·4Cl⁻·3H₂O^[11] and the NaCl(001) surface, the ordered array of cage hosts cannot be established as an epitaxial growth on the NaCl(001) surface, where Cl⁻ is their guest. The observed nonequilibrium and flexible structure of the monatomic layer at the interface between NaCl(001) surface and water^[12] is favorable for the chloride-ion-assisted assembly and the steric fit of **1** or **2**; flexible means that since the two-dimensional number density of ions in the metastable layer is lower than that of the NaCl(001) surface, the chloride ions in the above-mentioned monatomic layer may themselves be displaced under the effect of molecular recognition of chloride receptors **1** or **2**.

Results and Discussion

Figure 1 shows the AFM image of the ordered array of **1** at a surface of the NaCl crystal (10 × 10 nm² area): the unit structure of the array is a square of the size of 1.05 × 1.05 nm². The separation between peaks in the cross-section profiles in Figure 1 is about twice as long as the distance between like ions for the ionic arrangement of the NaCl(001) surface. The corrugation amplitude of the cross-section profiles is twice or more than twice as high as the difference between the ionic

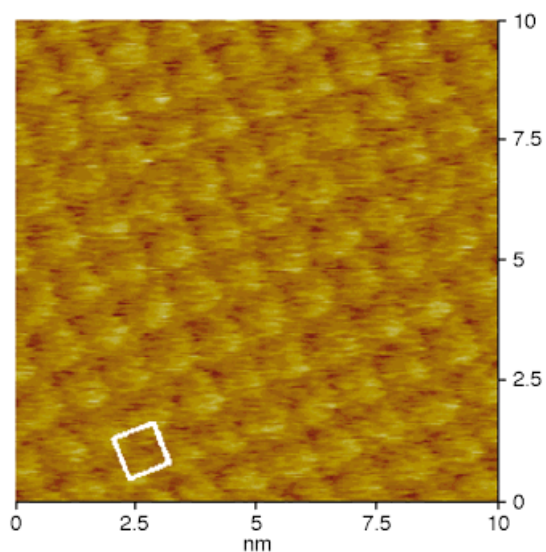


Figure 1. Unfiltered molecular resolution AFM image for the ordered array of cage hosts **1** on the NaCl crystal surface. The bright spots correspond to the protrusions of each cage host. The white square in the image indicates a unit structure of the array.

radii of sodium and chloride ions at the NaCl(001) surface. Therefore, it was concluded that the observed AFM image is not reflected from the lattice structure of the NaCl(001) surface. Figure 2 shows the AFM image (20 × 20 nm² area) for the ordered array of **2** on a surface of a NaCl crystal. The array of the bright spots indicates a parallelogram as a unit structure of the array which has the size of 2.05 × 2.20 nm². The separations between the bright spots in both directions are about four times as long as the lattice constant of the NaCl

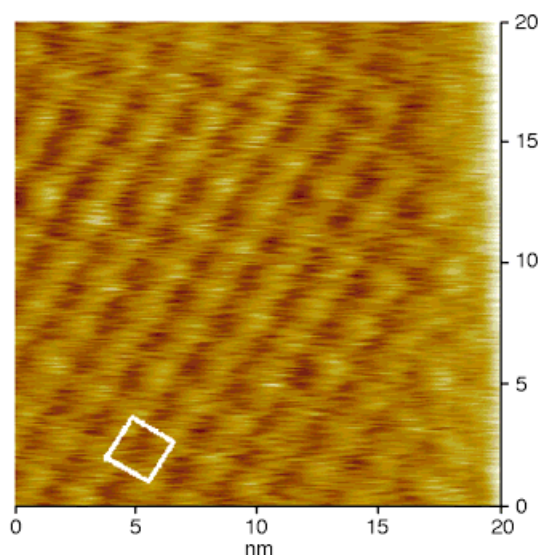


Figure 2. Unfiltered molecular resolution AFM image for the ordered array of cage hosts **2** on the NaCl crystal surface. The white parallelogram in the image indicates a unit structure of the array.

crystal. The corrugation amplitude of the cross-section profiles is more than five times as high as that of NaCl crystal. Therefore, the observed AFM image does not correspond to the lattice structure of NaCl(001) surface. The dark spots in Figure 2 correspond to indentions attributed to the much smaller NaCl(001) surfaces: the spots were too narrow and low to observe an atomic-resolution AFM image. The two-dimensional number densities n_s of the bright spots for the cage hosts **1** or **2**, obtained from the AFM images of Figures 1 and 2, are 0.94 nm^{-2} and 0.23 nm^{-2} , respectively, because of the different steric fits due to the different sizes of the *exo* hydrophobic groups CH_3 and $\text{C}_6\text{H}_5\text{CH}_2$ of **1** and **2**, respectively.

Figure 3 shows that the height ($0.50 \pm 0.03 \text{ nm}$) of the steps of the ordered array of cage host **1** is not equal to the height ($0.30 \pm 0.01 \text{ nm}$) of the observed steps in AFM images of NaCl(001) surfaces covered with both air and water (Figures 1 and 3 in ref. [12]), which corresponds to half the unit cell length (0.284 nm). This observation demonstrates that the ordered array of **1** or **2** was constructed by molecular recognition associated with the encapsulation of chloride ions which belonged to the metastable monatomic layer at the interface between NaCl(001) surface and water. For aqueous solutions containing $1 \cdot 4\text{BF}_4^-$, the crystal growth proceeds by ion agglomeration at the many steps observed in Figure 3: the agglomeration is produced by motion of the chloride ions, both encapsulated and unencapsulated by cage hosts **1**, and sodium ions on the terraces of the interface between the NaCl(001) surface and water. Here, the cage hosts **1** or **2** were able to become components of the interface only through their own encapsulation of the chloride ions. For aqueous solutions of $1 \cdot 4\text{Cl}^-$ (or $\text{Cl}^- \subset 1 \cdot 3\text{Cl}^-$), $2 \cdot 4\text{Cl}^-$ (or $\text{Cl}^- \subset 2 \cdot 3\text{Cl}^-$), and $3 \cdot 4\text{BF}_4^-$, on the other hand, all the observed steps had a height of 0.3 nm , which was equal to the height observed in the AFM images of NaCl(001) surfaces covered with either air or water.^[12] The chemical species

$\text{Cl}^- \subset 1$, $\text{Cl}^- \subset 2$, and **3** cannot encapsulate the chloride ions. Since the chloride-encapsulating cage hosts **1** or **2** and the free cage host **3** were unable to participate in the ion motion, the height of steps was necessarily equal to that produced by the ion motion of Cl^- and Na^+ , covered with water, on terraces. Here, these monolayers are simply held in place by electrostatic forces between the positively charged ammonium ions and the metastable monatomic layer of Na^+ and Cl^- at the interface between the NaCl(001) surface and water. Here, the cross-section profile of the observed molecular monolayer showed the height of their cage hosts. But it was impossible to observe an ordered array pattern of a molecular layer of $\text{Cl}^- \subset 1$, $\text{Cl}^- \subset 2$, or free **3** because such a layer would be disrupted by the scanning force of not less than 10 nN , which is a minimum value for observation of the ordered array of cage hosts. As a conclusion, the observation of the ordered array of **1** or **2** can be explained mainly in terms of the chloride-ion-assisted assembly associated with encapsulation of Cl^- in the nonequilibrium and flexible structures of the monatomic layer at the interface between the NaCl(001) surface and water.

The AFM images of Figures 1 and 2 have been simulated on the basis of the following assumed possible processes: 1) Since the AFM images showed the nonequilibrium structure at the interface between the NaCl(001) surface and water,^[12] the structure of the NaCl(001) surface can transform to the nonequilibrium and flexible structure after an aqueous

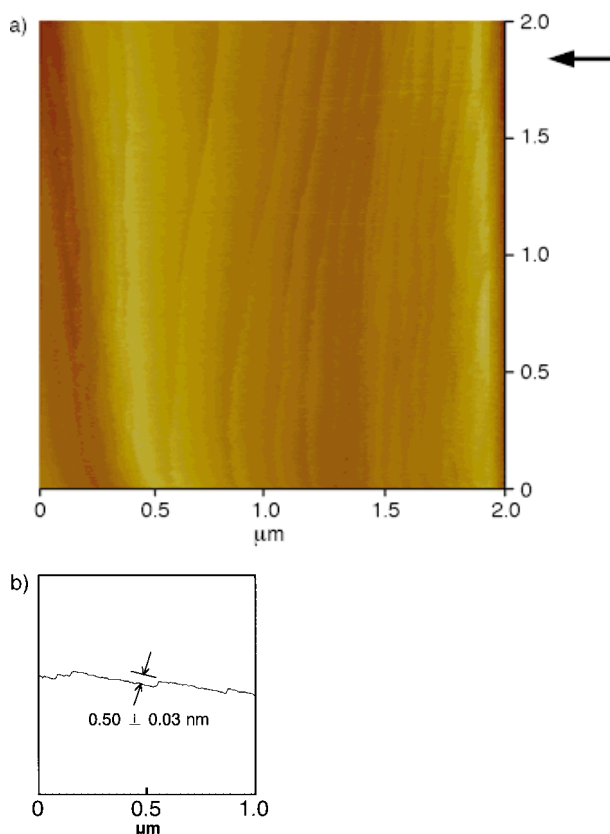


Figure 3. a) Many steps in an AFM image of the NaCl surface used for Figure 1. b) Cross-section profile in the direction of the arrow in (a). The height ($0.50 \pm 0.03 \text{ nm}$) of steps is not equivalent to that of the monatomic layer of the NaCl(001) surface shown in Figures 1 and 3 of ref. [12].

solution of $1 \cdot 4\text{BF}_4^-$ or $2 \cdot 4\text{BF}_4^-$ has been dropped onto the NaCl(001) surface. 2) Compound **1** or **2** can then encapsulate a chloride ion which belongs to the nonequilibrium structure of the interface between NaCl(001) surface and water. 3) As the chloride ion can be encapsulated only through the face of quasitetrahedral $(\text{C}_5\text{H}_{10})(\text{C}_6\text{H}_{12})_2$ (see Scheme 1), this face must be face down on the interface. 4) The three positive sites of the nitrogen atoms at the three apices of a face of $(\text{C}_5\text{H}_{10})(\text{C}_6\text{H}_{12})_2$ recognize each chloride ion in the nonequilibrium structure of the interface covered with water as a result of electrostatic interaction. In fact, the distances 0.66–0.70 nm between nitrogen atoms in the X-ray crystal structure of $2 \cdot 4\text{Cl}^-$ correspond approximately to the distances 0.63–0.74 nm between chloride ions in the nonequilibrium structure (see Figure 4 in ref. [12]). 5) The possible orientation of the cage hosts **1** or **2** is controlled by the effect of the steric fit of the *exo* hydrophobic groups R. 6) The ordered array of the cage hosts established by the anion-assisted assembling

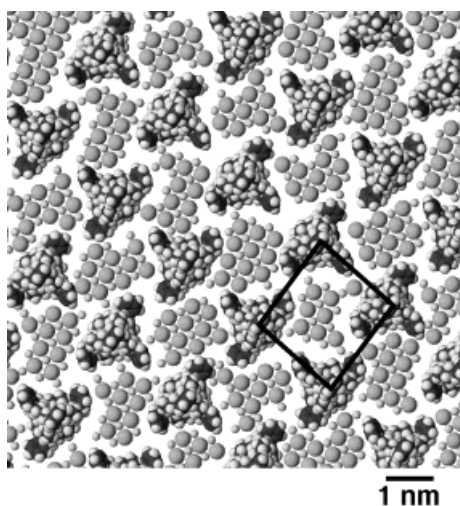
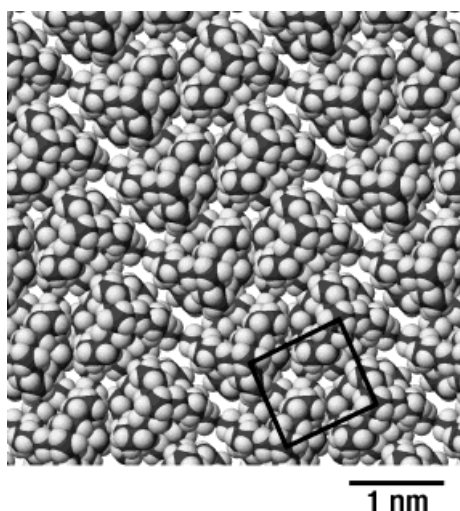


Figure 4. Simulations of the observed arrays of cage hosts **1** (top) or **2** (bottom). The square and parallelogram of solid lines correspond to the unit structures in Figures 1 and 2, respectively. The observed indentations in the ordered array of the chloride-encapsulating cage hosts **1** or **2** correspond to the NaCl(001) surfaces which were divided into pieces and transformed from the nonequilibrium structure after the evaporation of water.

process of steps 1–5 can be frozen by the evaporation of the water. However, the nonequilibrium structure at a bare region of NaCl surface can be preserved only under water and returned to the equilibrium structure of the NaCl(001) surface after evaporation.^[12] 7) The molecular structure of **1** or **2** encapsulating a chloride ion was given by X-ray diffraction.^[11] 8) The *exo* hydrophobic group CH_3 or $\text{C}_6\text{H}_5\text{CH}_2$ was assumed to stand perpendicular to the NaCl surface. 9) The BF_4^- counterions exist apart from **1** or **2**: they were not encapsulated into **1** or **2** as deduced from the ^{19}F NMR experiments.^[10]

Figure 4 shows that the possible arrays of **1** and **2** thus simulated do indeed resemble the observed arrays (see Figures 1 and 2). The two-dimensional number densities, n_s , of **1** and **2** were calculated to be 0.87 and 0.22 nm^{-2} from the top and bottom of Figure 4, respectively: they should be compared with the observed densities 0.94 and 0.23 nm^{-2} from the AFM images. The big difference between their densities results from the different steric fits due to the different sizes between the *exo* hydrophobic groups CH_3 and $\text{C}_6\text{H}_5\text{CH}_2$. The sizes of the unit structures calculated for each array of **1** or **2** agree acceptably with the values obtained from the observed AFM images of the arrays of **1** and **2**.

Conclusions

The ordered array of cage hosts **1** ($[\text{Me}_4\text{N}_4(\text{C}_5\text{H}_{10})_3(\text{C}_6\text{H}_{12})_3]^{4+}$) or **2** ($[(\text{PhCH}_2)_4\text{N}_4(\text{C}_5\text{H}_{10})_3(\text{C}_6\text{H}_{12})_3]^{4+}$) was produced as a result of their self-assembly through the process of their own encapsulation of chloride ions, which belong to the nonequilibrium and flexible structures of the monatomic layer at the NaCl–water interface, and through the process of their steric fit controlled by their own *exo* hydrophobic groups. Since the cage hosts of **3** ($[(\text{PhCH}_2)_4\text{N}_4(\text{C}_5\text{H}_{10})_6]^{4+}$) cannot encapsulate Cl^- , the molecular monolayer of **3** was disrupted by the minimum scanning force needed to observe the ordered array of the cage hosts.

Experimental Section

The novel cage hosts of the macrotricyclic ammonium salts, $1 \cdot 4\text{BF}_4^-$, $2 \cdot 4\text{BF}_4^-$, $3 \cdot 4\text{BF}_4^-$, $1 \cdot 4\text{Cl}^-$, and $2 \cdot 4\text{Cl}^-$ were dissolved in pure water or aqueous solutions of CH_3OH (50% v/v). The aqueous solutions, in which the concentrations resulted in numbers of solute species equal to the total number of chloride ions at the NaCl(001) surface (ca. 1 cm^2 area), were put onto the surface and left under air to dry for more than one day. In the AFM experiments the scanning force to observe the ordered array of **1** or **2** was 10–20 nN; the image acquisition time was less than about 20 s.^[13] The molecular monolayer of **3** was disrupted by the scanning force of 10 nN, which was the minimum possible for the observation of the ordered array of cage hosts **1** or **2** by the contact mode.

Acknowledgments: One of the authors (M.Y.) thanks Dr. M. Alamgir Hossain for the loan of all the samples of cage hosts used in this work.

Received: May 26, 1997 [F704]

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