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Published on Web 11/13/2002

Manipulation and Characterization of Xenon−Metalloporphyrin Complexation with a Scanning Tunneling Microscope

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Received June 11, 2002

Abstract: The formation of a series of Xe−CuEtioI [Cu(II) etioporphyrin I] complexes on Cu(001) surface was identified by scanning tunneling microscopy (STM) at cryogenic condition. The binding sites of xenon to CuEtioI molecule were directly revealed by high-resolution STM images in combination with controlled manipulation. The interaction between xenon atoms and CuEtioI in the on-top configuration is suggestive of a charge-induced dipole interaction. The structural parameters obtained with the STM complement results from spectroscopic studies of van der Waals complexes.

Introduction

Although chemistry is largely concerned with reactions in which bonds are broken and formed, interactions between molecules are responsible for many important chemical, physical, and biological processes in the condensed phase. An understanding of intermolecular interactions will not only provide us with a deeper insight into the occurrence of fundamental phenomena such as solvation and crystallization, it is also critical for optimization of molecular design associated with molecular recognition and supramolecular chemistry.

Molecular complexes with rare gas atoms are regarded as simple model systems for probing the microscopic intermolecular and intramolecular interactions. Structural and dynamical studies of these weakly bound species provide detailed information for constructing the intermolecular potential energy surfaces. In the past decades, high-resolution spectroscopic studies and molecular beam technology provided a large amount of data that could be very helpful in refining both quantitative description and qualitative understanding of the structures, binding energies, and inter- and intramolecular vibrations of molecular complexes.[1] In combination with quantum chemistry calculations, intermolecular potential energy surfaces in many of these molecular complexes have been accurately determined, greatly improving our understanding of the nature of atomic and molecular interactions at close range.

Structure determination is an important step in the elucidation of molecular complexes. Only with a clear structure in hand can one further pursue the study of the potential energy surface and energy distribution processes and, ultimately, elucidate chemical reactions for the complexes. High-resolution rotational spectroscopy combined with electronic spectroscopy provide precise information on the structure of these complexes. However, the process of predicting the equilibrium geometry on the basis of the available spectral data has often been complicated by the interplay of nonrigidity and large amplitude internal motions in these weakly bound species.[2] These motions might cause considerable differences between geometries obtained using different calculational methods, even with the same set of rotational constants.[3] Additionally, as the size of these complexes increase, an accurate structural determination becomes more difficult because of the enormous requirement of the calculations. It is desirable to have a reference structure from which nonrigid characteristics and large amplitude motions can be incorporated.

In this paper, we report the observation by STM of the formation of a series of xenon−metalloporphyrin complexes on the Cu(001) surface at cryogenic conditions. Combining STM imaging with its manipulation capability, we directly elucidated the structures and binding strength of these molecular complexes. The interaction between xenon atoms and CuEtioI is suggestive of a charge-induced dipole interaction. The study of the binding of rare gas atoms to the metal ion of a molecule is expected to contribute to our understanding of solvation phenomena[4] and chemical bonds in the weakly bound systems.[1]

Experimental Section

The experiments were carried out with a home-built STM system mounted in a vacuum chamber with a base pressure of 6×10^{-11} Torr.[5] The single-crystal Cu(001) surface was cleaned by repeated cycles of Ne^+ sputtering and annealing at 800 K. Electrochemically etched W tips were cleaned in-situ by Ne^+ sputtering, followed by annealing.

The molecular structure of Cu(II) etioporphyrin I (1,3,5,6-tetramethyl-2,4,6,8-tetraethylporphine, CuEtioI) is shown in Figure 1A. CuEtioI is favorable for optical study because of its intense absorption band at around 400 nm, which is readily accessible by photoexcitation.[6] Its properties are representative of porphyrins, an important class of

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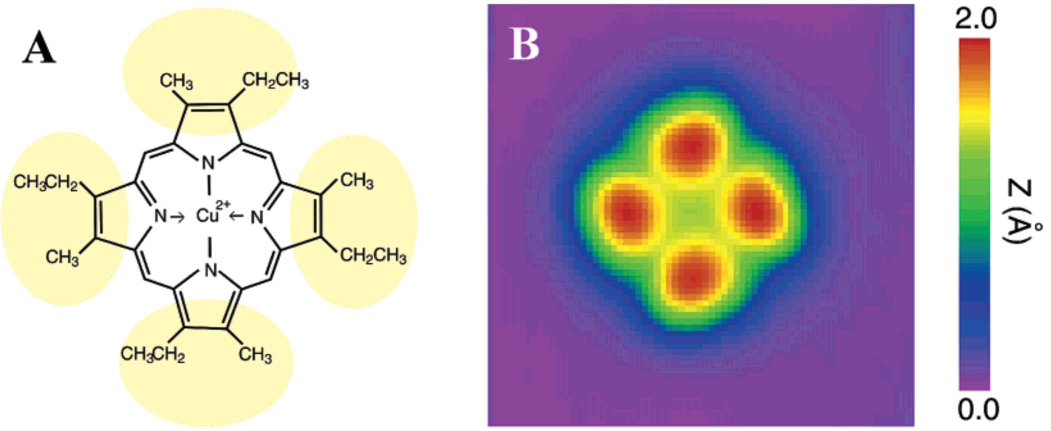

Figure 1. (A) Molecular structure of CuEtioI. (B) STM topographic image of CuEtioI adsorbed on Cu(001) at 11 K. The scanned area is 33.0 Å by 33.0 Å. The sample was biased at 0.25 V relative to the tip, and the tunneling current was set at 0.1 nA. The round features superimposed on the molecular structure in Figure 1A schematically represent the positions of the four lobes in the corresponding STM image of CuEtioI.

molecules. CuEtioI also serves as a model for studying the bonding of single molecules to a metal-containing inorganic complex. The present experiments provide a contrast with the study of bonding on an extended Cu surface.

CuEtioI was purchased from Porphyrin Corp. and was purified by multiple sublimation in the vacuum chamber before use. In the experiment, CuEtioI was thermally evaporated in situ onto the clean Cu(001) surface at 11 K. The coverage and adsorption positions of CuEtioI molecules were determined by STM. The Cu(001) surface was then exposed to xenon (99.999%, Spectra Gases Inc.) via a variable leak valve. Imaging and manipulation by STM were performed at 11 K. All the STM images presented in this paper were processed with plane fit only.

Results and Discussion

The adsorption behavior of CuEtioI on the Cu(001) surface has previously been well-characterized.[5] In brief, the CuEtioI molecule appears as a set of four protruding lobes with an apparent height of 2 Å and overall diameter of 15 Å in constant current STM topographs, as shown in Figure 1B. The agreement with features in the images of other porphyrin[7,8] and phthalocyanine molecules[9] suggests that the molecule lies flat upon adsorption on the Cu(001) surface. The central region of the molecule, where Cu^{2+} is situated, appears as a depression with respect to the surrounding lobes. The Cu^{2+} ion is not resolved in the STM image.

The molecular image of CuEtioI could be better understood by comparing with the image for Ni(II) octaethylporphyrin (NiOEP) self-assembled on the Au(111) surface.[10] In the STM image, the eight ethyl groups at the periphery of the NiOEP molecule were found to have a prominent contrast with respect to the porphyrin ring. This observation was attributed to the out-of-plane orientation of ethyl groups and their hyperconjugative interactions with the electronic states of the porphyrin ring.[11] The distances between the lobes in Figure 1B closely match the physical dimensions of the CuEtioI molecule. The asymmetry in each of the lobes can be similarly attributed to the modulation of the electronic structure (presumably the frontier orbitals) of the porphyrin ring by the arrangement and electronic structure of the methyl and ethyl groups (see Figure 1A). However, since the alternately distributed methyl and ethyl groups of CuEtioI encounter less steric strain than the eight ethyl groups in NiOEP, the four ethyl groups of CuEtioI could lie in the porphyrin plane, leading to the less pronounced lobe features for CuEtioI. On the other hand, the STM contrast of the central metal ion in metal phthalocyanines and porphyrins has been attributed to the presence of metal ion *d* orbital character near the Fermi level.[12] Since both the occupied (half-filled $d_{x^2-y^2}$) and unoccupied orbitals of Cu^{2+} are located about 1 eV above the Fermi level,[13] while the LUMO of the porphyrin ring might be closer, a weak contrast compared with the porphyrin ring in the STM image is expected for the Cu^{2+} ion in CuEtioI.

Because of its closed-shell electronic structure, xenon interacts weakly with most metal surfaces.[14] Even at 11 K, we were unable to observe individual xenon atoms because of their high mobility on the Cu(001) surface. At high coverages, xenon atoms start to aggregate into two-dimensional islands. The hexagonal close-packed xenon atoms inside the islands could be easily resolved with an interatomic distance of 4.3 Å. However, the blurring edges of the islands reflect the weak lateral interactions, that is, the dispersion forces, between xenon atoms.

The identification of xenon atoms and determination of their binding sites on the adsorbed CuEtioI were established by comparing the STM images of the same area before and after dosing xenon. The most distinguishing variation is the appearance of protrusions either on top of the molecule or at the kink sites formed by two adjacent lobes of the CuEtioI molecule. As shown in Figure 2A, protrusions appeared on top of three of the four CuEtioI molecules in this image. We have determined

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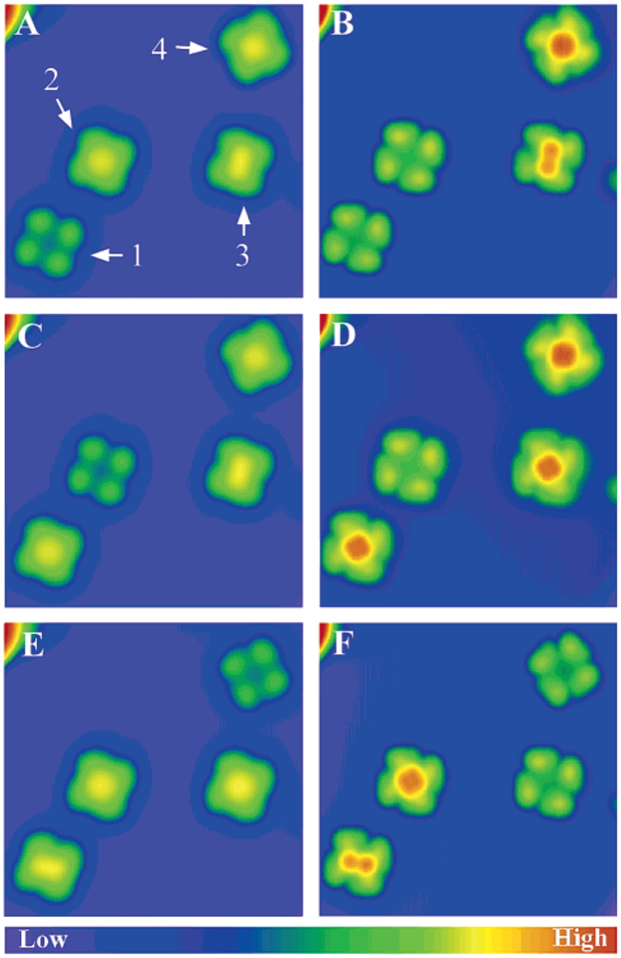

Figure 2. A sequence of STM topographic images showing the manipulation and formation of mononer and dimer Xe−CuEtioI complexes on Cu(001) at 11 K. The size of each image is 73.4 Å by 73.4 Å. The images were taken with a sample bias of 0.25 V and tunneling current of 0.1 nA. A single color palette is applied to all the images in order to illustrate the resolution and contrast variations associated with the transfer of a Xe atom onto and off the STM tip. The palette represents a range of 3.8 Å of surface corrugation. Images A, C, and E were recorded with a bare tip. Enhanced resolution and image contrast in images B, D, and F were obtained after transferring a xenon atom to the tip. The sequence of manipulation started with image A, showing CuEtioI (molecule 1), a xenon atom on CuEtioI (molecules 2 and 4), and a xenon dimer on molecule 3.

that these protrusions correspond to xenon atoms adsorbed on top of the Cu^{2+} ion of CuEtioI molecules.

A voltage pulse method was developed successfully to transfer a xenon atom between the STM tip and Ni(110)[15] and Cu(211) surfaces.[16] This approach was employed in our experiment to further investigate the stability and equilibrium structure of the Xe−CuEtioI complexes. The STM tip was first placed over the center of molecule 2 (as labeled in Figure 2A). After the feedback was turned off, a bias pulse of −0.8 V for 100 ms was applied to the sample. The tip was found to retract (tunneling gap increased) by about 0.5 Å after the feedback was turned on again, indicating a conductance variation in the tunnel junction. Figure 2B is an image obtained after rescanning the same area. The tip resolution was significantly enhanced compared with that of Figure 2A. The enhanced spatial resolution of the STM tip is attributed to the spatially localized atomic orbital of xenon adsorbed on the tip apex.[17] The chirality of CuEtioI molecules, which is derived from the asymmetric positions of the methyl and ethyl substituents in the porphyrin ring, was readily distinguished. In addition, the protrusion in the center of molecule 2 disappeared so that the characteristic four-lobe structure of CuEtioI was clearly revealed. The xenon atom previously adsorbed on top of the CuEtioI molecule has been transferred to the tip by the voltage pulse.

To verify this transfer, the tip was then positioned above the center of molecule 1 and a voltage pulse of +0.8 V for 100 ms was applied to the sample. The tunneling gap was found to decrease at the end of the pulsing process. The rescanned image (Figure 2C) revealed that the tip resolution has decreased and a protrusion similar to that previously observed on molecule 2 in Figure 2A now appeared on molecule 1. The decrease of the tip resolution is due to the change from a Xe-terminated tip to a bare metal tip. The newly formed molecule 1 is a CuEtioI molecule with a single xenon atom bound to the Cu^{2+}.

Another interesting feature in Figure 2B is that there appears to be two xenon atoms (two central protrusions) coadsorbed on molecule 3. To confirm this configuration, the STM tip (without a Xe atom on it) was positioned over the elongated protrusion in Figure 2C and a negative pulse of −0.8 V for 100 ms was applied. The subsequent image in Figure 2D clearly revealed that one of the two protrusions previously on molecule 3 has been removed. A single xenon atom was adsorbed on top of each molecule (1,3, and 4) and the tip.

Two more transfer processes were performed between Figure 2D and E, illustrating the reproducibility and control of the process. The xenon atom on the tip, previously transferred from molecule 3 in Figure 2C, was first put down on molecule 2. Then, the xenon atom on molecule 4 was transferred to the tip. The Xe-terminated tip was then positioned right above the xenon-binding molecule 1 and a positive pulse (+0.8 V, 100 ms) was applied, leading to the addition of a second Xe atom bound to molecule 1. A rescan of the surface revealed an image (Figure 2E) showing an elongated protrusion in the center of molecule 1. After another xenon atom was transferred from molecule 3 to the tip, the two xenon atoms bound to molecule 1 were clearly resolved (Figure 2F). When Figure 2B is compared with Figure 2F, the xenon dimer on CuEtioI shows two equivalent orientations rotated by 90°. These equivalent configurations were observed after the xenon manipulation procedure was repeated. The two Xe atoms in the dimer can also move together in concert, resulting in a 90° rotation, which occurs frequently during imaging process. The distance between the two xenon atoms in the dimer for both configurations is 4.3 Å, the same as the interatomic distance in the hexagonal close-packed overlayer.

At substantially higher exposures of xenon to the surface, a new complex was observed, consisting of one CuEtioI molecule with four xenon atoms bound on top. The CuEtioI molecules were usually trapped inside the two-dimensional xenon islands. The four xenon atoms bonded on top of CuEtioI are arranged in a square-planar structure, with a nearest xenon−xenon distance of 4.3 Å. It should be noted that the configuration with three xenon atoms bound on top of CuEtioI was not observed. Attempts were not successful to either add a third xenon atom to the Xe dimer−CuEtioI complex or remove only one xenon

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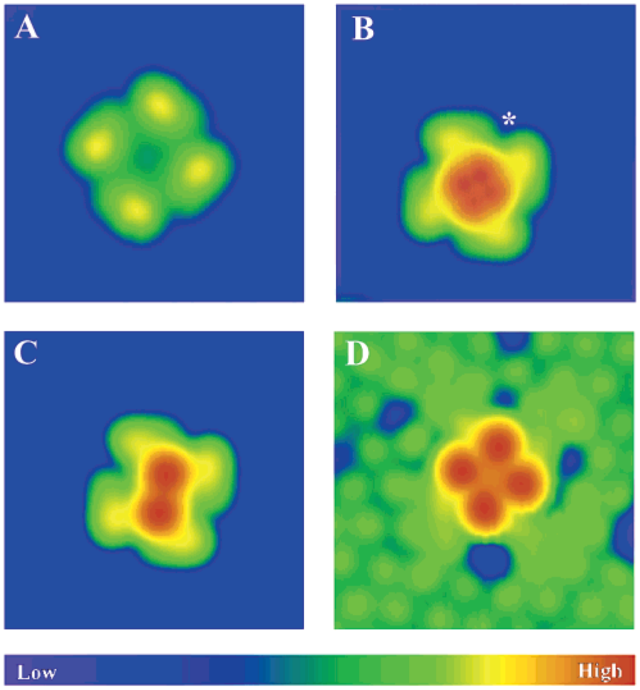

Figure 3. High-resolution STM images of (A) CuEtioI, (B) Xe@CuEtioI, (C) Xe_2@CuEtioI, and (D) Xe_4@CuEtioI formed on Cu(001) at 11 K. The Xe_4@CuEtioI in Figure 3D is not isolated but trapped in a two-dimensional island of xenon atoms, which appear as green balls in the image. The size of each image is 31.0 Å by 31.0 Å. All the images were acquired at 0.25 V and 0.1 nA with a Xe-terminated tip. The color palette represents a height variation of 3.8 Å. The asterisk in Figure 3B indicates the tip position during STM−IETS measurements.

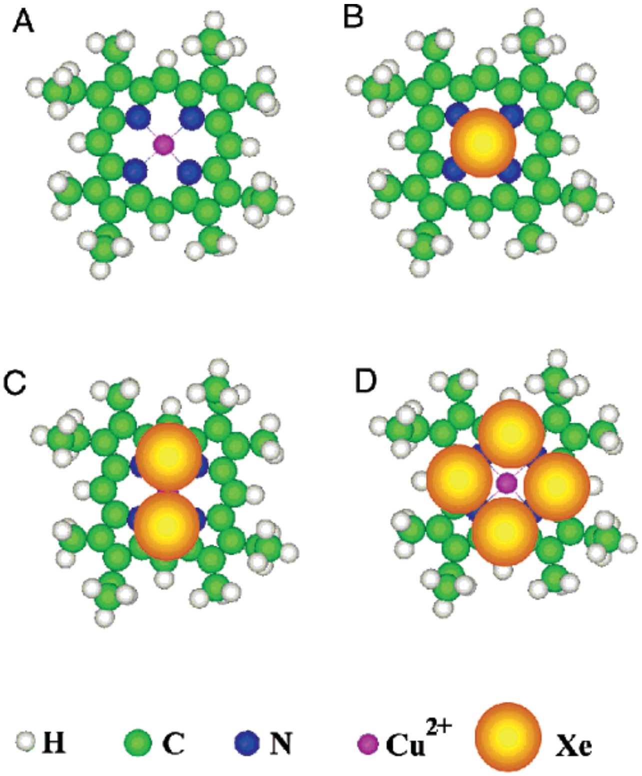

Figure 4. Schematic structures of (A) CuEtioI molecule and (B−D) Xe−CuEtioI complexes deduced from the corresponding images in Figure 3.

atom from the Xe tetramer−CuEtioI molecule by the STM tip. Negative voltage pulses applied to the Xe tetramer−CuEtioI often lead to the simultaneous removal of two xenon atoms to form Xe dimer−CuEtioI. The xenon atoms in the Xe dimer−CuEtioI could then be removed one by one.

Figure 3A−D shows the high-resolution images, acquired with a Xe-terminated tip, of a CuEtioI molecule and the three xenon complexes. The schematic structures of these complexes deduced directly from the corresponding STM images are shown in Figure 4A−D.

The nature of the interactions between xenon atoms and CuEtioI in these unconventional complexes is an interesting question. In noble gas chemistry, direct bonds between noble gas atoms and metal cations have only been observed in a few cases.[18−20] On the other hand, complexes of these closed-shell atoms with neutral or charged molecules have been widely identified by spectroscopic methods.[1−3,21−23] These complexes, however, are generally regarded as van der Waals species, since the bond energies are of the order of a few hundred wavenumbers. The presence of the charge on a metal ion is expected to increase the interaction energy by an order of magnitude because of a charge-induced dipole force, as evidenced in some metal ion-rare gas clusters in the gas phase.[22,23]

The binding energy of xenon to CuEtioI could be estimated from the xenon manipulation processes. This energy is approximately equal to the magnitude of the voltage pulse for transferring a xenon atom from CuEtioI molecule to the tip, provided the tip is sufficiently far from the sample.[24] In our experiment, voltage pulses of 0.75−0.90 V were applied with close to unity transferring probability. The interaction in Xe−CuEtioI is therefore estimated to be a fraction of an electronvolt, which is comparable with the binding energy of a rare gas atom to a metal cation in the gas phase.[23]

Rare gas atoms tend to bind to the most electropositive site in the molecule.[25] Although metalloporphyrin is a neutral species, it is still likely that the local electric field in the vicinity of Cu^{2+} could strongly polarize xenon, which has a particularly large polarizability. The rare gas atom then binds to the cation through its electronic polarization.[21−23] The nature of the interaction between xenon and CuEtioI is attributed to a charge-induced dipole.

A nodal cross along the Cu−N bond directions is visible in the STM image of the single Xe atom bound on top of CuEtioI (Figure 3B). This feature can be observed in the bias range from −0.5 V to 0.5 V with a Xe-terminated tip. The mechanism is not yet clear. One tentative explanation is that the image is representative of the coupling of certain electronic states of the Xe atom and those of Cu^{2+}, such as the d_{xz} and d_{yz} orbitals, which have a relatively larger spatial distribution towards xenon than the $d_{x^2-y^2}$ along the Cu−N bond directions. Another possible interpretation of this image is that the xenon atom is not adsorbed directly on the top of the Cu^{2+} ion as an axial ligand. Instead, it is tilted a little toward the two N atoms of two adjacent pyrrole rings. Apparently, the xenon atom in this configuration has four equivalent positions. Becuase of the finite

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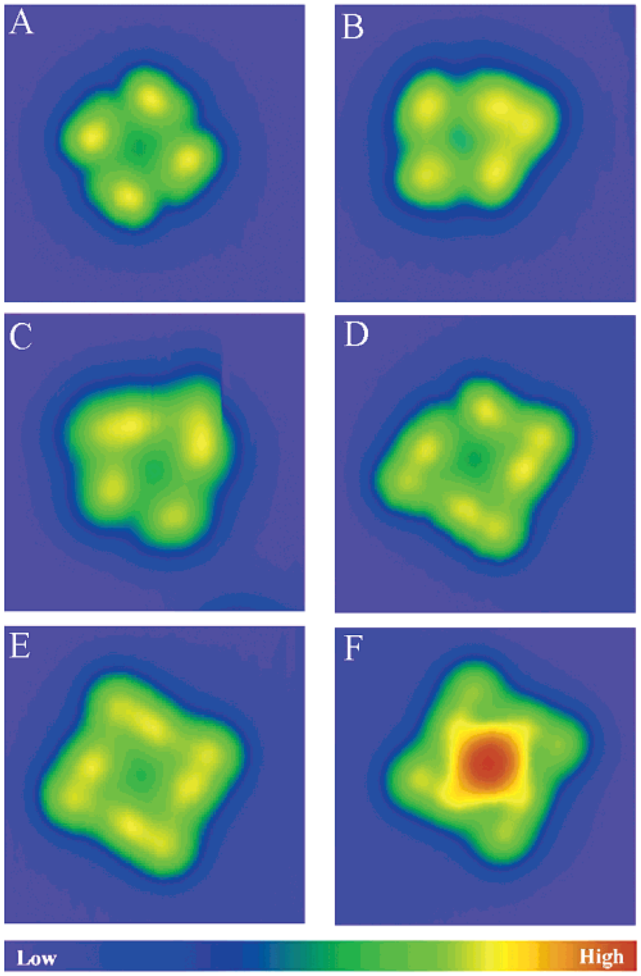

Figure 5. STM images of different molecules on Cu(001) at 11 K: (A) CuEtioI, (B) a xenon atom bonded at the periphery of CuEtioI (Xe*CuEtioI), (C) Xe$_2$*CuEtioI, (D) Xe$_3$*CuEtioI, (E) Xe$_4$*CuEtioI, (F) CuEtioI with 4 xenon atoms bonded at the periphery and one xenon atom bonded on top (Xe$_4$*Xe@CuEtioI). The size of each image is 33.8 Å by 33.8 Å. The imaging conditions were 0.25 V and 0.1 nA.

temperature or the imaging process, with the assumption that tunneling electrons could excite the xenon atom to overcome the small energy barrier between different positions, the xenon image in Figure 3B could be interpreted as the averaged image of the xenon atom hopping among the four equivalent positions around the molecule. On the basis of this assumption and the steric effect, the two xenon atoms in the Xe dimer−CuEtioI are situated between two pyrrole rings and 180° apart (Figure 3C). This configuration would be more energetically favorable than the two positions along the two opposite Cu−N bond directions or at two adjacent sites.

Inelastic electron tunneling spectroscopy with STM (STM−ETS) was also performed on the Xe−CuEtioI complex in comparison with the previous vibrational study of CuEtioI on Cu(001).[5] The STM−IETS measurement of the one xenon atop CuEtioI complex showed a peak at 359 meV in the second derivative of the tunneling current, d^2I/dV^2, when the tip was positioned between two neighboring lobes and close to the molecule (as labeled in Figure 3B). This value is identical with the methine bridge C−H stretch mode of the CuEtioI molecule.[5] However, because of the broadness of the C−H stretch in STM−IETS and the insensitivity of the methine group to the

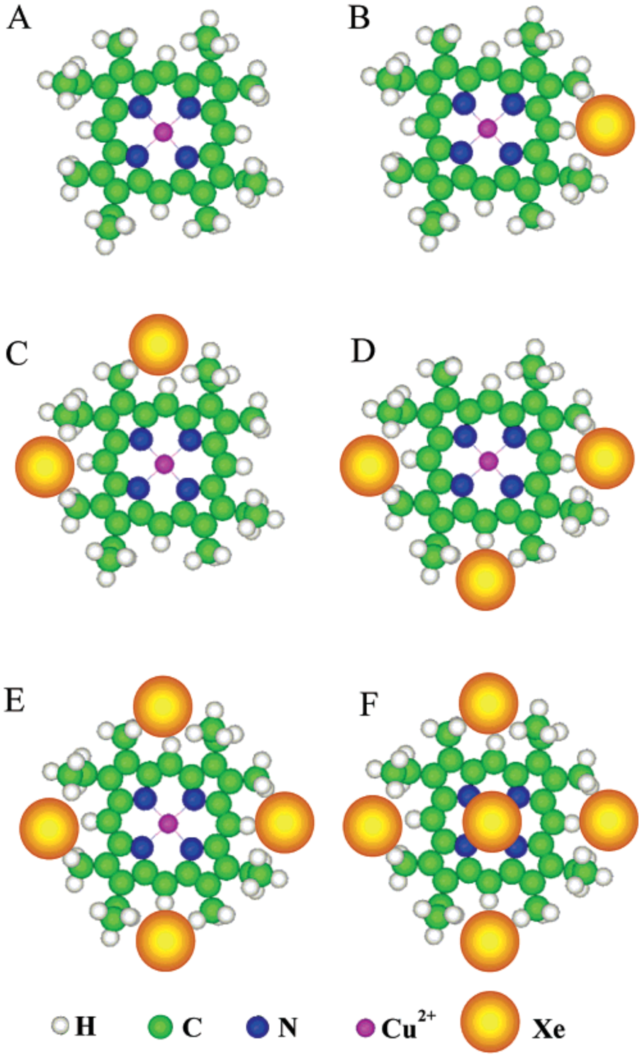

Figure 6. Schematic structure of (A) a CuEtioI molecule and (B−F) Xe−CuEtioI complexes deduced from the corresponding STM images in Figure 5.

CuEtioI redox process,[26] the effect of the xenon atom on the charge distribution of the porphyrin macrocycle might not be detectable from changes in the vibrational peak.

In addition to these complexes with xenon adsorbed on top of CuEtioI, another preferred adsorption site of xenon is at the kink sites formed between a methyl and an ethyl group on the two adjacent pyrrole rings. CuEtioI molecules with different numbers of Xe atoms were observed, as shown in Figure 5. The kink-site xenon was observed to frequently hop to a neighboring site during the imaging process. The Xe atoms adsorbed at the kink site could be deliberately transferred to the STM tip by using the previously described procedure. However, the reverse transfer is seldom successful, most likely because of the low desorption barrier for xenon from the kink site. The schematic structures of these complexes are illustrated in Figure 6. The asymmetry in the xenon adsorption sites, observed in the STM images shown in Figure 5, can be attributed to the relative steric effect of the ethyl and methyl group, shifting the xenon toward the methyl. The adsorption of xenon at the kink sites leads to further elucidation of the chirality

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in the STM image of CuEtioI (Figure 5A). The interaction of CuEtioI with xenon locates the positions of the methyl and ethyl groups.

The Xe−CuEtioI complexes observed in our experiments directly reveal the energetically favorable sites for the binding of Xe atoms, as well as the dynamic and equilibrium structures of these complexes as a function of the number of xenon atom. The coordination configurations of xenon atoms to the CuEtioI molecule in these complexes provide a test ground and serve as a starting point for modeling the interactions in molecular aggregates and clusters with similar structures. Comparing the experimental observations with theoretical calculations would improve our understanding of the intermolecular interactions and optimize force field constants in the calculations.

Conclusions

In conclusion, a series of Xe−CuEtioI complexes formed on the Cu(001) surface was identified by STM at cryogenic conditions. The structures and binding sites of xenon atoms to CuEtioI molecules were directly elucidated by high-resolution STM imaging combined with controlled manipulation. The interaction of xenon with CuEtioI involves a charge-induced dipole of the xenon. The structural information obtained from high-resolution STM images would enable spectral analysis, as well as construction of the potential energy surface of the molecular complexes. The ability to vary the number of atoms or molecules in a complex by STM manipulation makes it possible to observe the evolution of its various structural and dynamic properties with size.

Acknowledgment. We thank X. Xu, W. A. Goddard III, and P. J. Farmer for their helpful discussions. Support of this research by the Chemical Science, Geo- and Bioscience Division, Office of Science, U.S. Department of Energy Grant No. DE-FG03-01ER15157 is gratefully acknowledged.

JA0272639