

Host–guest recognition of calcium by crown-ether substituted phthalocyanine array on Au(111): relationship between crown moieties and gold lattice

Soichiro Yoshimoto,^a Koji Suto,^a Kingo Itaya^{*a} and Nagao Kobayashi^{*b}

^a Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba-yama 04, Sendai 980-8579, Japan. E-mail: itaya@atom.che.tohoku.ac.jp; Fax: +81-22-214-5380; Tel: +81-22-214-5380

^b Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan. E-mail: nagaok@mail.tains.tohoku.ac.jp; Fax: +81-22-217-7719; Tel: +81-22-217-7719

Received (in Cambridge, UK) 25th June 2003, Accepted 15th July 2003

First published as an Advance Article on the web 28th July 2003

High-resolution scanning tunneling microscopy has revealed that, of the four crown-ether moieties of 15-crown-5-ed phthalocyanine array on Au(111) surface, only two crown-ether voids at diagonal positions, where the void centers and hollows surrounded by three gold atoms match exactly, trap two Ca²⁺ ions.

Metallophthalocyanines (MPcs) have been studied extensively for use in gas sensors,^{1,2} liquid crystals,¹ organic semiconductors,¹ electrocatalysis,³ and as field effect transistors (FET).¹ Among the various MPc structures that can be obtained via peripheral substitution, crown-ether-substituted Pc derivatives have the unique property of complexing with various alkali and inorganic cations.¹ Formation and characterization of ordered adlayers of MPcs at interfaces are important from both an academic and an industrial standpoint. Recently, scanning tunneling microscopy (STM) has been widely accepted as a powerful tool for understanding the structure of adlayers of molecules in solution.^{4–6} For example, the adlayer of H₂Pc molecules functionalized by four dibenzocrown-ether rings with enantiomerically pure (*S*)-3,7-dimethyloctyl chains was prepared on highly oriented pyrolytic graphite (HOPG) from a mixed organic solution, and was observed under ambient conditions by STM.⁷ Ohira *et al.* prepared Langmuir films of K⁺-free and K⁺-included dibenzo-18-crown-6 molecules, which they transferred onto Au(111) and have used STM to observe directly the difference in appearance of two separately-prepared adlayers in HClO₄ solution.⁸ In this study, we describe how 15-crown-5-ed CoPc adsorbed on a Au(111) surface accommodates Ca²⁺ ions in two crown-ether moieties located at opposite (or *trans*) positions with respect to the Pc ligand. The synthesis of the 15-crown-5-ed CoPc has been described in our previous papers.⁹ An Au(111) electrode was prepared by the Clavilier method.¹⁰ The gold electrode was annealed in a hydrogen flame and then quenched in ultrapure water saturated with hydrogen. The electrode was then immersed in a saturated solution of 15-crown-5-ed CoPc in benzene and ethanol (9 : 1) for 5 min. The 15-crown-5-ed CoPc-modified electrode was then rinsed with ultrapure water and transferred into an electrochemical STM cell.

Fig. 1a shows a typical high-resolution STM image obtained in an area of 9 × 9 nm². It is clear that the 15-crown-5-ed CoPc molecules form a well-ordered adlayer on Au(111). In addition to the information that is related to the symmetry and the structure of 15-crown-5-ed CoPc arrays, this STM image reveals a great deal of information concerning the internal molecular structure. The shape of the observed features in the image clearly corresponds to the molecular structure of 15-crown-5-ed CoPc. Each molecule can be seen as a propeller-shaped feature with the brightest spot located within the 16 atom Pc cyclic polyene, and four additional bright rings located at the corners of each 15-crown-5-ed CoPc molecule. It is clear that all the Pc molecules are oriented in the same direction on the Au(111) surface. The corners of each 15-crown-5-ed CoPc

molecule are arranged in a side-by-side configuration, *i.e.* the crown rings of the nearest neighbor molecules are closely positioned with respect to each other. In the 15-crown-5-ed CoPc molecule, the central and the four additional spots observed are attributed to the central cobalt ion and the 15-crown-5-ether rings, respectively. As reported by Hipps' group using ultrahigh vacuum (UHV)-STM system¹¹ and by our group using *in situ* STM in solution,¹² the center of each 15-crown-5-ed CoPc molecule appears as the brightest spot in the STM image because of the tunneling being mediated by a half filled d_{z²} orbital between the Au surface and the tip.¹¹ On the basis of the cross-sectional profile, the distance between the centers of diagonal spots in a molecule was found to be 2.02 ± 0.05 nm. A comparison between the molecular arrays and the step lines running along the Au lattice revealed that the molecular rows were aligned along the atomic row and the √3 directions. The unit cell was superimposed as a rectangular lattice in Fig. 1a. The intermolecular spacing between 15-crown-5-ed CoPc molecules aligned in the [110] (arrow I) and the √3 (arrow II) directions were found to be 2.34 ± 0.07 and 2.03 ± 0.05 nm, respectively, which corresponds to 8 and 4√3 times the Au lattice constant. Therefore, commensurate *p*(8 × 4√3R-30°) structure is assigned to the unit cell. These observed distances are slightly larger than the lattice parameters of the bulk crystal structure, which are 2.05 nm and 1.8 nm, in the case of a rectangular lattice.¹³ A possible structural model of *p*(8 × 4√3R-30°) is shown in Fig. 1b, with the unit cell indicated with solid lines. In order to determine the location of the adsorption sites, we have considered the effect of moving the unit cell in parallel directions with respect to the Au(111)-(1 × 1) substrate and found that the geometry drawn in Fig. 1b gives the most symmetric configuration. In this model, the central Co²⁺ ions and all the crown-ether moieties are situated at 2-fold bridge sites. In this configuration, each Pc molecule adsorbed on Au(111) has 2-fold symmetry.

Once the formation of a well-defined adlayer of 15-crown-5-ed CoPc in pure 0.05 M HClO₄ had been confirmed by STM, we added a 0.05 M HClO₄ solution containing 10 mM Ca²⁺ dropwise into the electrochemical STM cell, in order to directly observe the impact of Ca²⁺ ion on the 15-crown-5-ed CoPc adlayer. A high-resolution STM image is shown in Fig. 1c. It is clear from this image that all the molecules are oriented in the same direction on Au(111). The unit cell is identical to that obtained in HClO₄ solution in the absence of Ca²⁺, *i.e.*, *p*(8 × 4√3R-30°). Each 15-crown-5-ed CoPc molecule exhibits a characteristic shape with the brightest spot at the center, except for the molecule located on the left side of the center of the image, in which the central Co²⁺ appears to be missing. In the absence of Ca²⁺, four additional spots were observed at the corners, whereas in the presence of Ca²⁺, only two additional bright spots are observed at diagonal positions with respect to the Pc ligand as marked by two circles in Fig. 1c, as a result of two Ca²⁺ ions being trapped by crown ether rings. Careful inspection of the ordered arrays revealed that the diagonal axis

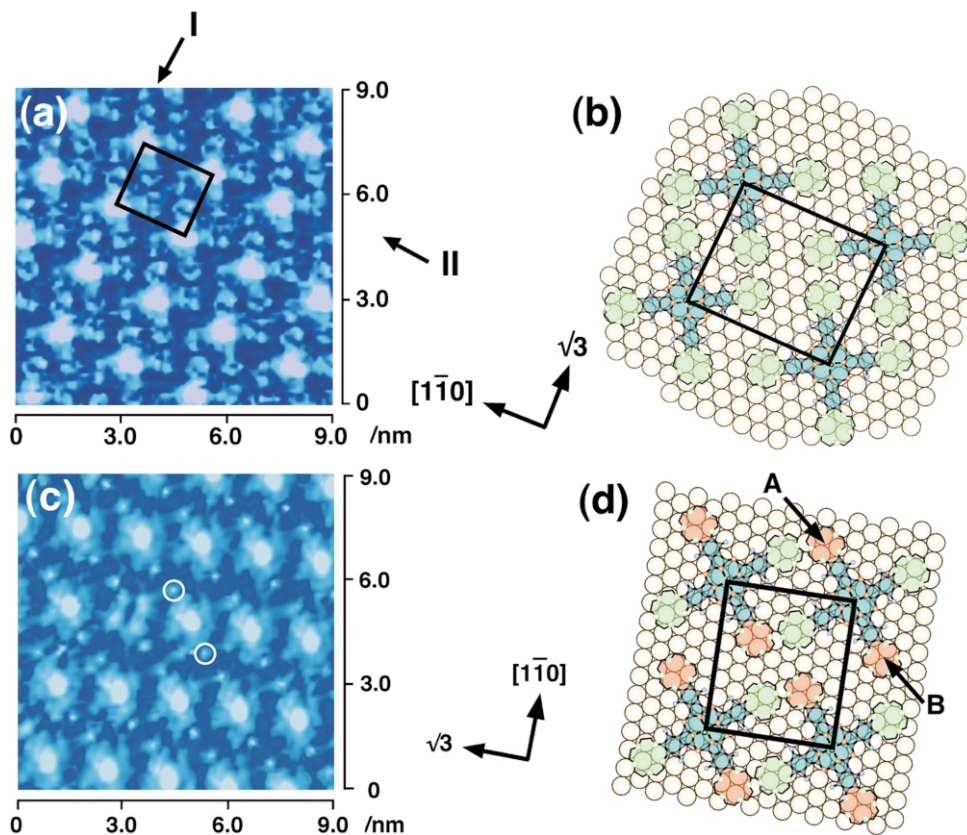


Fig. 1 High-resolution ($9 \times 9 \text{ nm}^2$) STM images and models of 15-crown-5-ed CoPc arrays on Au(111) surface in 0.05 M HClO_4 : (a) and (b) in the absence and (c) and (d) in the presence of 1 mM Ca^{2+} , respectively, acquired at (a) 0.85 V and (c) 0.8 V vs. RHE. Potential of the tip and tunneling current were (a) 0.45 V and 1.0 nA and (c) 0.35 V and 5.0 nA, respectively. Model (b) is for the 15-crown-5-ed CoPc adlayer on Au(111) surface with a superimposed $p(8 \times 4\sqrt{3}R-30^\circ)$ unit cell, and model (d) is for the 15-crown-5-ed CoPc array complexed with Ca^{2+} on Au(111) surface with a superimposed $p(8 \times 4\sqrt{3}R-30^\circ)$ unit cell. In (c), two circles indicate two 15-crown-5 moieties in which Ca^{2+} ions are trapped.

of each 15-crown-5-ed CoPc was rotated anticlockwise by *ca.* 10° compared with the image in Fig. 1a. The result seems to indicate that each 15-crown-5-ed CoPc molecule is rotated slightly after the Ca^{2+} ion is trapped. A schematic model is presented in Fig. 1d. In this model, the central Co^{2+} ions are located at 2-fold bridge sites as shown in Fig. 1c, but the diagonal axis of 15-crown-5-ed CoPc are rotated by *ca.* 10° with respect to the direction of Au atomic row (Fig. 1c). With this rotational angle, the centers of two crown-ether moieties colored in red are situated at the hcp and fcc 3-fold hollow sites (A and B in the model), whereas the other two unoccupied moieties in green are located at near bridge sites. The rotation of the Pc rings after the inclusion of the Ca^{2+} ions is probably caused by a change in the interactions between the crown-ether moieties on neighboring Pc molecules. The crown-ethers which contain trapped Ca^{2+} ions appear to favor three-fold hollow sites. The distance between Au lattice and crown moieties probably plays a significant role in the host-guest recognition. Further investigation is required to fully understand the cause of the rotation of the crown-ether moieties. It should be noted that STM images obtained in the presence of 1 mM K^+ are identical to those obtained in pure HClO_4 . The radius of Ca^{2+} and K^+ ions are 1.98 Å and 2.66 Å, respectively,^{9b} whereas the size of 15-crown-5-ether ring is estimated to be 1.7–2.2 Å.^{9b} K^+ ion appears to be too large to be trapped in 15-crown-5-ether rings.

In conclusion, by using 15-crown-5-ed CoPc molecule, we succeeded in resolving the packing arrangement and the internal molecular structure of each 15-crown-5-ed CoPc molecule adsorbed on the Au(111) electrode. We also, for the first time, succeeded in directly observing the host-guest recognition of Ca^{2+} ions in aqueous HClO_4 by high resolution STM. In the presence of Ca^{2+} , the 15-crown-5-ed CoPc adlayer on Au(111) traps Ca^{2+} ions in two 15-crown-5-ether moieties located diagonally with respect to the Pc ligand.

This work was supported in part by CREST-JST and by the Ministry of Education, Culture, Sports, Science and Technology, a Grant-in-Aid for the Center of Excellence (COE) Project, Giant Molecules and Complex Systems, 2003. The authors acknowledge Dr Y. Okinaka for his assistance in writing this manuscript.

Notes and references

- G. Guillaud, J. Simon and J. P. Germain, *Coord. Chem. Rev.*, 1998, **178–180**, 1433.
- D. Wright, P. Roisin, G. P. Rigby, R. J. M. Nolte, M. J. Cook and S. C. Thorpe, *Sens. Actuators, B*, 1993, **13–14**, 276.
- J. P. Collman, P. S. Wagenknecht and J. E. Hutchison, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1537 and references therein.
- A. A. Gewirth and B. K. Niece, *Chem. Rev.*, 1997, **97**, 1129.
- K. Itaya, *Prog. Surf. Sci.*, 1998, **58**, 121.
- D. M. Kolb, *Angew. Chem. Int. Ed.*, 2001, **40**, 1162.
- P. Samorfi, H. Engelkamp, P. Witte, A. E. Rowan, R. J. M. Nolte and J. P. Rabe, *Angew. Chem. Int. Ed.*, 2001, **40**, 2348.
- A. Ohira, M. Sakata, C. Hirayama and M. Kunitake, *Org. Biomol. Chem.*, 2003, **1**, 251.
- (a) N. Kobayashi and Y. Nishiyama, *Chem. Commun.*, 1986, 1462; (b) N. Kobayashi and A. B. P. Lever, *J. Am. Chem. Soc.*, 1987, **109**, 7433; (c) N. Kobayashi, *Coord. Chem. Rev.*, 2002, **227**, 129.
- J. Clavilier, R. Faure, G. Guinet and R. Durand, *J. Electroanal. Chem.*, 1980, **107**, 205.
- (a) X. Lu, K. W. Hipps, X. D. Wang and U. Mazur, *J. Am. Chem. Soc.*, 1996, **118**, 7197; (b) K. W. Hipps, X. Lu, X. D. Wang and U. Mazur, *J. Phys. Chem.*, 1996, **100**, 11207; (c) X. Lu and K. W. Hipps, *J. Phys. Chem. B*, 1997, **101**, 5391.
- (a) S. Yoshimoto, A. Tada, K. Suto, R. Narita and K. Itaya, *Langmuir*, 2003, **19**, 672; (b) S. Yoshimoto, A. Tada, K. Suto and K. Itaya, *J. Phys. Chem. B*, 2003, **107**, 5836.
- C. Sirlin, L. Bosio, J. Simon, V. Ahsen, E. Yilmazer and Ö. Bekaroğlu, *Chem. Phys. Lett.*, 1987, **139**, 362.