Formation of highly ordered porphyrin adlayers induced by electrochemical potential modulation†

Soichiro Yoshimoto,‡*[a] Nozomi Yokoo,[a] Takamitsu Fukuda,[b] Nagao Kobayashi*[b] and Kingo Itaya*[ac]

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Molecular self–assembly of porphyrin derivatives formed with intermolecular hydrogen bonding on the surface of Au(111) electrode in acidic solution can be controlled by varying the number of peripheral carboxy groups and the applied electrochemical potential.

The construction of molecular network architectures with intermolecular hydrogen bonds is significant both for surface design and for controlling surface properties.[1–3] Adlayers of benzene carboxylic derivatives, such as terephthalic acid and trimesic acid (TMA) on highly oriented pyrolytic graphite (HOPG),[2] Pt(111),[3] Cu(100)[4] and Au(111)[5,6] surfaces, have been investigated extensively through the use of scanning tunneling microscopy (STM) not only under ultrahigh vacuum (UHV), but also in air and within solution under atmospheric conditions. Hydrogen bond based network structures provide a potential pathway to the design of host–guest interfaces, because the cavity size can be controlled through careful selection of the component molecules. Two-dimensional nanoporous networks produced with hydrogen bonding or metal–ligand coordination in UHV are known to preferentially bind fullerene molecules as a guest.[7,8] Yokoyama and co-workers have previously reported on the formation of porphyrin (Por) based supramolecular assemblies using CN- or COOH-substituted (3,5-di-*t*-butylphenyl)Por (TBPP) molecules adsorbed on Au(111), in which the dipole–dipole interactions between the CN-moieties and the hydrogen bonding between the carboxy groups are the principal driving force for the assembly formation.[9]

In this paper, we report the structure of self-assembled, two carboxy-substituted cobalt(II) Por derivatives, CoCTPP and CoTCPP (Chart 1), formed on Au(111) in acidic solution through intermolecular hydrogen bonding, and we demonstrate, based on the result of *in situ* STM observations at room temperature, that the architecture can be controlled by varying the number of peripheral carboxy groups on the Por ligand and the applied electrode potential.

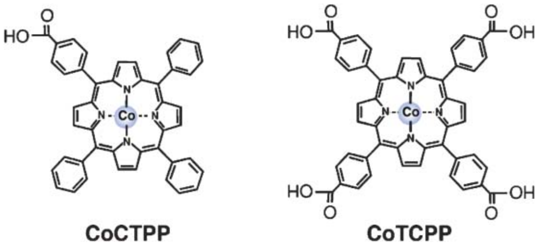

Chart 1 Chemical formulae of 5-(4-carboxyphenyl)-10,15,20-tri(phenyl)porphyrin cobalt(II) (CoCTPP) and tetrakis(4-carboxy-phenyl)-porphyrin cobalt(II) (CoTCPP), respectively.

CoCTPP can be prepared by means of a mixed condensation reaction of benzaldehyde, methyl terephthalaldehyde, and pyrrole under reflux in propionic acid, followed by chromatographic separation and hydrolysis with KOH under reflux in THF/H_2O. CoTCPP can be synthesized by carrying out the same sequence of reactions in the absence of terephthalaldehyde. Fig. 1 shows an STM image of a CoCTPP adlayer formed on an Au(111) surface acquired at 0.7 V (near open circuit potential), after the CoCTPP adlayer was prepared by immersing the Au(111) electrode into a benzene solution containing CoCTPP.[10] Individual CoCTPP molecules can be readily recognized with bright spots on a terrace. It should be noted that the domain size of CoCTPP is smaller than that of cobalt tetraphenyl Por (CoTPP) on Au(111), indicating an influence of carboxy group.[11] After the CoCTPP-covered surface was observed at 0.7 V, the CoCTPP array immediately disappeared when the potential was scanned to and held at 0.2 V, indicating that a marked change took place in the CoCTPP

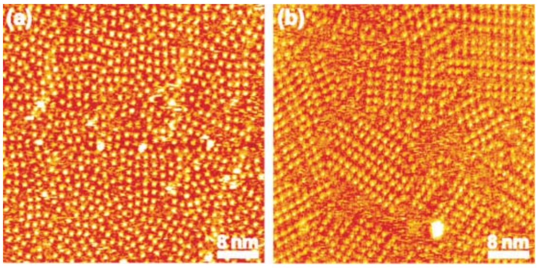

Fig. 1 Large-scale (50 × 50 nm^2) STM images of CoCTPP array formed on Au(111), acquired at (a) 0.7 V and (b) 0.2 V *vs.* RHE in 0.1 M $HClO_4$. Tip potentials and tunneling currents were 0.45 V and 10.0 nA for (a) and 0.44 V and 0.94 nA for (b), respectively.

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[a] *Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 6-6-04 Aoba, Sendai 980-8579, Japan. E-mail: itaya@atom.che.tohoku.ac.jp; Fax: +81-22-795-5868; Tel: +81-22-795-5868*
[b] *Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan. E-mail: nagaok@mail.tains.tohoku.ac.jp; Fax: +81-22-795-7719; Tel: +81-22-795-7719*
[c] *Core Research Evolutional Science and Technology organized by Japan Science and Technology Agency (CREST-JST), Kawaguchi Center Building, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

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‡ Present Address. National Institute of Advanced Industrial Science and Technology (AIST), Central 6, 1–1–1 Higashi, Tsukuba, Ibaraki 305-8566, Japan. Tel: +81-29-861-6167 Fax: +81-29-861-6177; E-mail: so-yoshimoto@aist.go.jp (S. Yoshimoto)

adlayer at this potential. Several domains with molecular rows consisting of two bright spots appeared on the terrace within 1 min. It is noteworthy that the highly ordered adlayer of CoCTPP dimer became disordered as shown in Fig. 1a when the potential was shifted back to a value more positive than 0.5 V. The structure of the CoCTPP adlayer, therefore, clearly depends upon the electrochemical potential, and potential modulation provides the key to controlling the formation of hydrogen bond-based structures in acidic solution. It should be noted that this pattern of potential-induced structural change was not observed in the case of CoTPP. A highly ordered domain was maintained even at potentials close to the hydrogen evolution potential.[11] Note that the Co(II) ions create the brightest spots in the image because of a strong tunneling current passing through the partially filled d_{z^2} orbital.[12] However, at 0.7 V the central Co ion is in the state of Co(III) formed by the electrochemical oxidation (Fig. 1a). Upon oxidation of Co(II) to Co(III) at 0.7 V the electron within the d_{z^2} orbital is lost, and the cobalt ions are observed as dark spots. However, Co(III)Por complexes are known to be unstable. Since our STM measurements were carried out in solution under atmospheric conditions, it is conceivable that dioxygen coordinated to the Co(III) to form the more stable Co(III)CTPP–O_2 complex. In fact, a slight difference in height amplitude between STM image shown in Fig. 1a and that shown in Fig. 1b was found, *i.e.*, the corrugation height was approximately 0.4 nm at 0.7 V whereas it was 0.3 nm at 0.2 V. The strong π-donating axial ligand led to smaller Co hyperfine couplings, and the π-electrons were localized on the oxygen moiety, which possibly provided a new tunneling pathway. The possibility of formation of the Co(III)–O_2 complex was also found in the highly ordered crown ether-substituted CoPc array on Au(111).[13]

Su *et al.* have recently reported that the adlayer structure of TMA on an Au(111) surface in $HClO_4$ was determined by the applied electrode potential.[6] The potential-induced phase transition at about 0.85 V was ascribed to reorientation of the TMA molecule from the surface plane to a more perpendicular position caused by a protonation/deprotonation reaction of the carboxy groups.[6] The adlayer of tetrapyridyl Por (TPyP) on Au(111) has also been reported to undergo reorientation caused by a change in surface interaction at negative potentials.[14] No change in orientation was observed in our study, however, probably because of the influence of the strong hydrophobic interaction between the phenyl moieties of CoCTPP. Charge density at the electrochemical interface contributes to the interaction between CoCTPP and substrate, although deprotonation at the carboxy group in each CoCTPP molecule presumably takes place at anodic potentials. Further details of the internal structure, orientation and packing arrangement of the CoCTPP adlayer can be observed in the close-up view of a 10 × 10 nm^2 area (Fig. 2a), which was recorded at 0.2 V (Fig. 2a). Each CoCTPP molecule can be readily identified based on the bright spot associated with the Co(II) ion, which is surrounded by several less intense spots associated with the structure of CTPP ligand. At 0.2 V, the central cobalt ion is completely reduced from the superoxide coordinated Co(III) to Co(II). Molecular chains of CoCTPP can be observed in the dark areas between bright rows, which consist of two CoCTPP molecules. The morphological detail of each molecule is displayed in the height-shaded view (Fig. 2b). The intermolecular distance between nearest neighbor CoCTPP molecules was estimated, based on the cross-sectional profile, to be 1.45 ± 0.05 nm for the direction along the red (or blue) arrow. This value is comparable to the intermolecular distance in the CoTPP adlayer, which is controlled by hydrophobic interaction between the phenyl moieties.[11] The intermolecular distance between the nearest neighbors in the dimer rows consisting of a set of CoCTPP molecules, and the corresponding distance in the dimer rows in the dark stripe (indicated by the blue and green arrows, respectively), were approximately 1.6 and 2.0 nm, respectively. The row in the wide, dark stripe observed in the STM image appears to be associated with the formation of hydrogen bonds between nearest neighbor CoCTPP molecules. When the length of the hydrogen bond (*ca.* 0.265 nm)[15] and the molecular size are taken into consideration, however, the nearest neighbor distance of 2.0 nm between two carboxy groups is too short to be reasonable.[3,16] We therefore propose that the surface molecule of CoCTPP form a hydrogen bond with the next nearest neighbor CoCTPP molecule in the dark row. This proposed structure leads to an intermolecular distance of 2.4 nm (Fig. 2c).

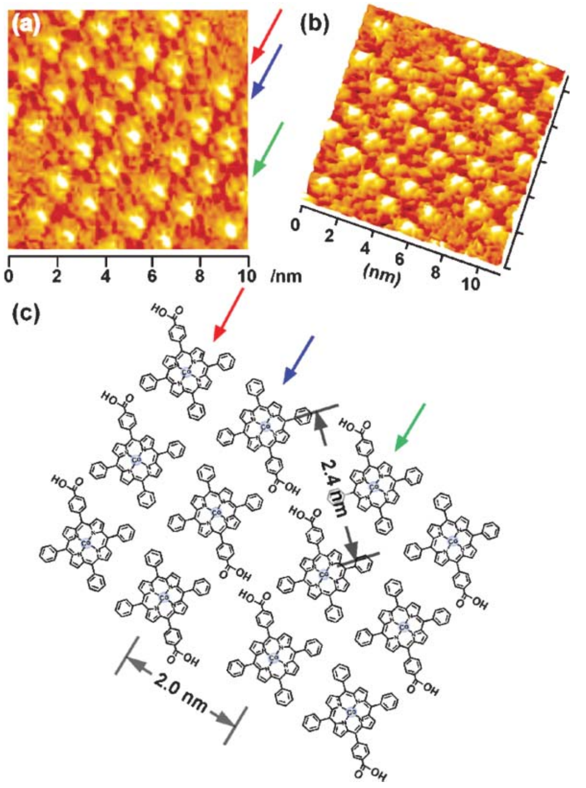

Fig. 2 (a) High-resolution (10 × 10 nm^2) STM image and (b) height-shaded view of a CoCTPP array on Au(111) surface in 0.1 M $HClO_4$ acquired at 0.2 V *vs.* RHE. Tip potential and tunneling current were 0.44 V and 2.0 nA, respectively. (c) Proposed model for the formation of CoCTPP dimers on Au(111) through hydrogen bonding.

The effect of applied potential on the structure of CoTCPP adlayers on Au(111) surface was examined in the same manner as described above for CoCTPP. At anodic potentials, the adlayer structure was found to be disordered (not shown). A characteristic, highly ordered square packing arrangement of the two-dimensional network array was formed, however, when the potential was held at a value more negative than 0.5 V (Fig. 3a). The reconstructed rows of the Au(111) surface were also observed

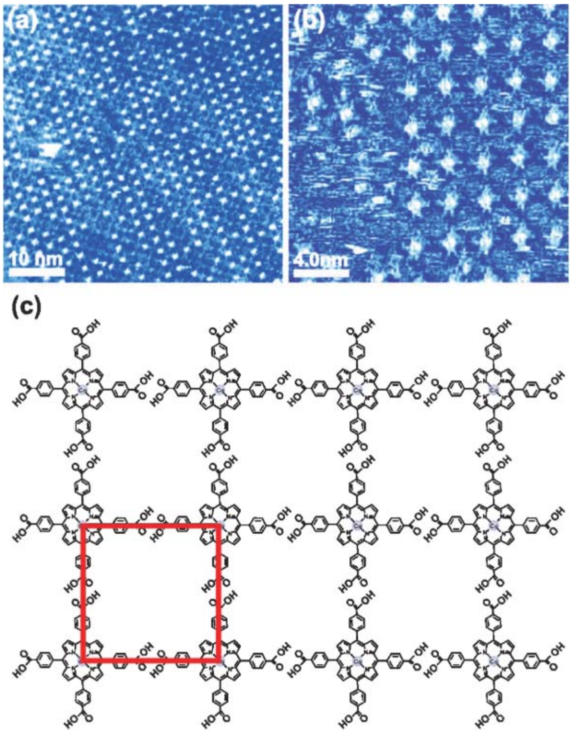

Fig. 3 (a) Large-scale (50 × 50 nm^2) and (b) high-resolution (20 × 20 nm^2) STM images of CoTCPP array formed on Au(111) acquired at (a) 0.1 V and (b) 0.85 V (stepped from 0.2 V) *vs.* RHE in 0.1 M $HClO_4$. Tip potentials and tunneling currents were 0.45 V and 0.8 nA for (a) and 0.47 V and 0.83 nA for (b), respectively. (c) Structural model of highly ordered square packing array formed by potential modulation of the CoTCPP adlayer on Au(111).

through the CoTCPP layer, suggesting that the CoTCPP and the underlying Au substrate are incommensurate with respect to each other. The array structure is therefore based on electrochemically-induced interaction between the CoTCPP molecules. The fact that the ordered CoTCPP array is removed during scanning at a tunneling current greater than 1.0 nA is an additional evidence that there is only a weak interaction between CoTCPP and the Au substrate. It is safe to conclude that the adlayer is stable for at least 5 min (Fig. 3b), as we were able to obtain a high-resolution STM image at 0.85 V after the potential was first held at 0.2 V. Each individual CoTCPP molecule can be identified based on the bright spot for the Co(II) ion surrounded by less intense spots at the corners associated with the TCPP ligand. The intermolecular distance between the individual CoTCPP complexes is 2.45 ± 0.08 nm. The streaks observed in regions surrounded by four CoTCPP molecules are probably related to the incorporation of a highly mobile "trapped H_3O^+". A model for the hydrogen bonding of this two–dimensional network structure is shown in Fig. 3c. The orientation of each CoTCPP molecule appears to be determined by the formation of hydrogen bonds between four adjacent carboxy groups (Fig. 3c). It should be noted that this network structure is almost identical to the crystal structure reported for ZnTCPP.[15] The fact that the CoTCPP adlayer structure observed at negative potentials on Au(111) is different from that of stearic acid co-adsorbed H_2TCPP arrays on HOPG,[17] suggests that the packing arrangement of TCPP is strongly influenced by the presence of a central metal atom.

In conclusion, we have demonstrated that the ordered arrays of mono- or tetra-carboxy-substituted Por derivatives formed on the Au(111) surface in acidic solution depends to a remarkable extent both on the number of peripheral substituents and on the modulation of applied potential, and that electrochemical control of the self-assembly of Por complexes is an effective method for constructing novel surface architectures.

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Notes and references

1 (*a*) S. De Feyter and F. C. De Schryver, *Chem. Soc. Rev.*, 2003, **32**, 139; (*b*) S. De Feyter and F. C. De Schryver, *J. Phys. Chem. B*, 2005, **109**, 4290
2 (*a*) S. Griessl, M. Lackinger, M. Edelwirth, M. Hietschold and W. M. Heckl, *Single Molecules*, 2002, **3**, 25; (*b*) S. J. H. Griessl, M. Lackinger, F. Jamitzky, T. Markert, M. Hietschold and W. M. Heckl, *J. Phys. Chem. B*, 2004, **108**, 11556
3 Y.-G. Kim, S.-L. Yau and K. Itaya, *Langmuir*, 1999, **15**, 7810
4 (*a*) A. Dmitriev, N. Lin, J. Weckesser, J. V. Barth and K. Kern, *J. Phys. Chem. B*, 2002, **106**, 6907; (*b*) A. Dmitriev, H. Spillmann, N. Lin, J. V. Barth and K. Kern, *Angew. Chem., Int. Ed.*, 2003, **42**, 2670; (*c*) M. A. Lingenfelder, H. Spillmann, A. Dmitriev, S. Stepanow, N. Lin, J. V. Barth and K. Kern, *Chem.–Eur J.*, 2004, **10**, 1913
5 Y. Ishikawa, A. Ohira, M. Sakata, C. Hirayama and M. Kunitake, *Chem. Commun.*, 2002, 2652
6 G.-J. Su, H.-M. Zhang, L.-J. Wan, C.-L. Bai and Th. Wandlowski, *J. Phys. Chem. B*, 2004, **108**, 1931
7 S. Stepanow, M. Lingenfelder, A. Dmitriev, H. Spillmann, E. Delvigne, N. Lin, X. Deng, C. Cai, J. V. Barth and K. Kern, *Nat. Mater.*, 2004, **3**, 229
8 (*a*) J. A. Theobald, N. S. Oxtoby, M. A. Phillips, N. R. Champness and P. H. Beton, *Nature*, 2003, **424**, 1029; (*b*) J. A. Theobald, N. S. Oxtoby, N. R. Champness, P. H. Beton and T. J. S. Dennis, *Langmuir*, 2005, **21**, 2038
9 (*a*) T. Yokoyama, S. Yokoyama, T. Kamikado, Y. Okuno and S. Mashiko, *Nature*, 2001, **413**, 619; (*b*) T. Yokoyama, T. Kamikado, S. Yokoyama and S. Mashiko, *J. Chem. Phys.*, 2004, **121**, 11993
10 Experimental details are described in ESI.‡
11 S. Yoshimoto, A. Tada, K. Suto, R. Narita and K. Itaya, *Langmuir*, 2003, **19**, 672
12 (*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
13 S. Yoshimoto, K. Suto, A. Tada, N. Kobayashi and K. Itaya, *J. Am. Chem. Soc.*, 2004, **126**, 8020
14 Y. He, T. Ye and E. Borguet, *J. Am. Chem. Soc.*, 2002, **124**, 11964
15 (*a*) Y. Diskin-Posner and I. Goldberg, *Chem. Commun.*, 1999, 1961; (*b*) I. Goldberg, *Chem. Commun.*, 2005, 1243
16 (*a*) J. Inukai, M. Wakisaka, M. Yamagishi and K. Itaya, *Langmuir*, 2004, **20**, 7507; (*b*) J. Inukai, M. Wakisaka and K. Itaya, *Chem. Phys. Lett.*, 2004, **399**, 373; (*c*) J. Inukai, M. Wakisaka, M. Yamagishi and K. Itaya, *J. Electrochem. Soc.*, 2005, **152**, E35
17 S.-B. Lei, C. Wang, S.-X. Yin, H.-N. Wang, F. Wi, H.-W. Liu, B. Xu, L.-J. Wan and C.-L. Bai, *J. Phys. Chem. B*, 2001, **105**, 10838