

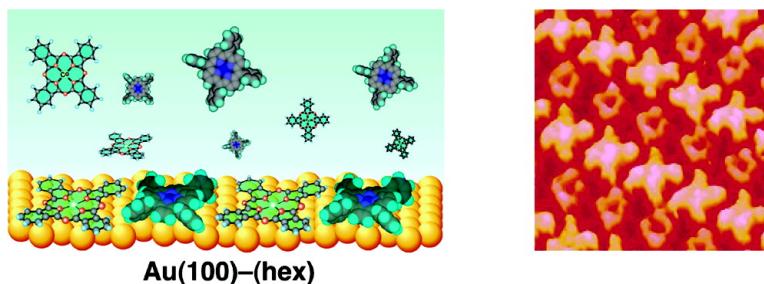
Communication

**Two-Dimensional Self-Organization of Phthalocyanine and Porphyrin: Dependence on the Crystallographic Orientation of Au**

Koji Suto, Soichiro Yoshimoto, and Kingo Itaya

*J. Am. Chem. Soc.*, **2003**, 125 (49), 14976-14977 • DOI: 10.1021/ja038857u • Publication Date (Web): 14 November 2003

Downloaded from <http://pubs.acs.org> on March 30, 2009



**More About This Article**

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



## Two-Dimensional Self-Organization of Phthalocyanine and Porphyrin: Dependence on the Crystallographic Orientation of Au

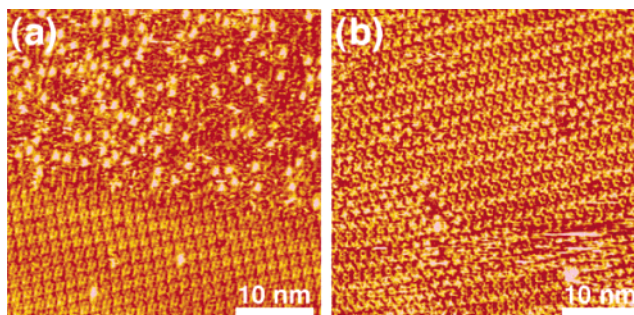
Koji Suto,<sup>†</sup> Soichiro Yoshimoto,<sup>†</sup> and Kingo Itaya<sup>\*,†,‡</sup>

Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba-yama 04, Sendai 980-8579, Japan, and Core Research Evolutional Science and Technology Organized by Japan Science and Technology (CREST-JST), Kawaguchi Center Building, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

Received October 3, 2003; E-mail: itaya@atom.che.tohoku.ac.jp

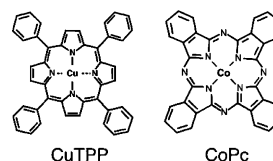
Two-dimensional (2D) molecular assemblies on surfaces are one of the key technologies for nanoscale electronics devices. Formation and characterization of ordered adlayers of porphyrin or phthalocyanine or both at metal surfaces are of great importance from the fundamental and technological points of view, as these molecules are closely related to the fields of biology, photosynthesis, electrocatalysis, and molecular devices.<sup>1–4</sup> Recently, some supermolecular assemblies of porphyrins and phthalocyanines have been investigated on Au(111) in ultrahigh vacuum (UHV) by scanning tunneling microscopy (STM).<sup>5–7</sup> For example, Yokoyama and co-workers observed similar small clusters and chains of CN-substituted porphyrins on Au(111) at the low temperature of 63 K.<sup>5</sup> Hipps and co-workers found the formation of well-ordered regions with an entirely new structure with 1:1 composition of cobalt(II) hexadecafluorophthalocyanine (F<sub>16</sub>CoPc) and nickel(II) tetraphenyl-21*H*,23*H*-porphine (NiTPP) on Au(111) by vapor-phase deposition in UHV.<sup>6</sup> F<sub>16</sub>CoPc and NiTPP molecules were discriminated by the difference in brightness of center metal ion between F<sub>16</sub>CoPc and NiTPP molecules.<sup>6</sup> The CoPc molecules are easily identified by the strong tunneling current that results from orbital-mediated tunneling through the half-filled d<sub>z<sup>2</sup></sub> orbital of the Co<sup>2+</sup> ion: they exhibit a bright spot at the center of each molecule. The remarkable contrast in tunneling current afforded by the difference in electronic configuration of transition metal ions allows one to clearly discriminate between species for chemical identification at the molecular level. Very recently, supermolecular structures constructed of C<sub>60</sub> and chloro[subphthalocyaninato]boron(III) were found on Ag(111) in UHV by de Wild and co-workers.<sup>7</sup> Thus, the formation of characteristic structures is of importance both in building nanoarrays and in designing surfaces. However, to our knowledge, the dependency of binary adlayers upon the crystallographic orientation of the Au surface has not yet been clarified. To obtain information on other crystal planes is important for controlling the surface structure and their properties. In this work, we prepared a mixed adlayer by immersing an Au single crystal into a benzene solution containing CoPc and CuTPP, and compared the binary adlayer of CoPc and CuTPP on Au(111) with that on Au(100) substrate. The study was focused on the formation of a 2D alternate bimolecular structure on a reconstructed Au(100) surface by immersion of the electrode into a benzene solution containing both CoPc and CuTPP (Chart 1).

Figure 1a shows a typical large-scale STM image of a CoPc and CuTPP mixed adlayer formed on Au(111) acquired at 0.75 V in 0.1 M HClO<sub>4</sub>. The terrace was completely covered with two different phases, a disordered region (upper part) and a highly ordered region (lower part), as shown in Figure 1a. The reconstructed rows could be seen through the highly ordered molecular



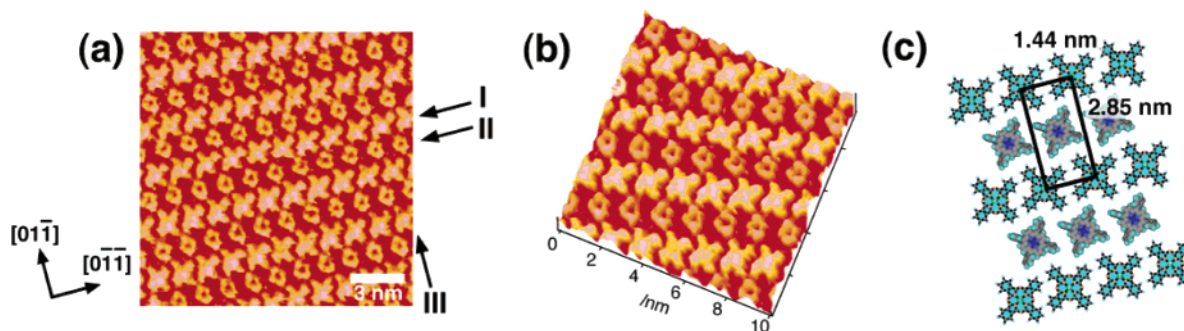
**Figure 1.** Large-scale (40 × 40 nm<sup>2</sup>) STM images of CoPc and CuTPP mixed adlayer formed on Au(111) (a) and Au(100)–(hex) (b) in 0.1 M HClO<sub>4</sub> acquired at 0.75 V versus RHE. Potential of the tip and tunneling current were 0.4 V and 1.2 nA, respectively.

**Chart 1.** Chemical Formulas of Copper(II) Tetraphenyl-21*H*,23*H*-porphine (CuTPP) and Cobalt(II) Phthalocyanine (CoPc)



layer at the lower part. The highly ordered phase composed of only CuTPP molecules could be discriminated, whereas some brightest spots were observed in the upper part of Figure 1a. According to the STM image, the disordered phase seems to consist of an assembly of CoPc and CuTPP molecules. However, under the experimental conditions, the surface concentration of CoPc is much smaller than that of CuTPP. Actually, the adlayer structure prepared with a short immersion time (less than 2 min) revealed that a CuTPP adlayer was predominantly formed on Au(111), suggesting that CoPc molecules displace the CuTPP molecules during the modification process with increased immersion times. According to the recent paper by Hipps' group, the binary adlayer consisting of CoPc and NiTPP prepared in UHV revealed a densely packed, apparently well-defined structure, which is compositionally disordered.<sup>6b</sup> The difference between adlayer structures formed in UHV and in solution might depend on the difference in the interaction between CoPc and CuTPP molecules. On the contrary, the stripes composed of alternate bright and dark lines are observed on Au(100)–(hex) as shown in Figure 1b. In the STM image acquired in a large area of 40 × 40 nm<sup>2</sup>, highly ordered molecular rows can be clearly recognized as bright and dark lines, respectively. Even a superficial look at any of the presented STM images reveals that the binary molecular arrays are two-dimensionally well-organized. Each molecular row consisting of stripes runs nearly parallel to the <110> atomic lattice direction of Au(100) substrate. The terrace was

<sup>†</sup> Tohoku University.  
<sup>‡</sup> CREST-JST.



**Figure 2.** High-resolution STM image ( $15 \times 15 \text{ nm}^2$ ) of CoPc and CuTPP mixed adlayer formed on Au(100)–(hex) surface in 0.1 M HClO<sub>4</sub> acquired at 0.75 V versus RHE (a), height-shaded view ( $10 \times 10 \text{ nm}^2$ ) (b), and structural model of the CoPc and CuTPP mixed adlayer (c). Potential of the tip and tunneling current were 0.45 V and 1.2 nA, respectively.

entirely covered with the binary adlayer with two domains crossing at an angle of almost 90°. A typical length of stripes (bright or dark line) was found to be 50 nm. Domains of alternate CoPc and CuTPP molecular chains were observed in an area of more than 150 nm. The binary adlayers of CoPc and CuTPP might be controllable by the difference in either potential of zero charge or local charge density of the reconstructed row between Au(111)–( $\sqrt{3} \times 22$ ) and Au(100)–(hex). Although further investigations of the dependence on the crystallographic orientation are needed, a clear difference between bimolecular adlayers on Au(111) and those on Au(100) surfaces was found by using the wet deposition method in the present study.

Further detail of the internal structure, orientation, and packing arrangement of the binary CoPc and CuTPP mixed adlayer is seen in the high-resolution STM image of an area of  $15 \times 15 \text{ nm}^2$  shown in Figure 2a. It can be seen that alternate molecular rows are uniformly formed on Au(100)–(hex). An individual CoPc molecule marked by arrow I can be recognized as a propeller-shaped image with a central brightest spot and four additional spots at the corners. These bright spots can be attributed to the benzene moieties in the CoPc molecule as reported in our recent paper.<sup>8</sup> It is clear that all CoPc molecules are oriented in the same direction on Au(100)–(hex). On the contrary, each dark row indicated by arrow II is observed as a ring in which the center is a dark spot, indicating that it is a CuTPP molecule. As described above, the difference in brightness at the centers of CuTPP and CoPc molecules is clearly explained by the difference in the mode of occupation of d orbitals.<sup>9</sup> Thus, the central cobalt ion in each CoPc molecule appeared as a bright spot in the image, whereas the copper ion in each CuTPP molecule appeared as a dark spot. On the basis of the cross-sectional profile, the intermolecular spacing between CoPc molecules and between CuTPP molecules aligned in the directions of arrow I and II were both measured to be  $1.44 \pm 0.05 \text{ nm}$ , whereas the distance between CoPc molecules indicated by arrow III was found to be  $2.85 \pm 0.07 \text{ nm}$ . These two values correspond to almost 5 and 10 times the Au lattice constant, respectively. The details of morphology of each molecule are clearly displayed in the height-shaded view in Figure 2b. A structural model of CoPc and CuTPP mixed adlayer formed on the Au(100)–(hex) surface is presented in Figure 2c. The exact relation between the CoTPP adlayer and the underlying Au(100)–(hex) lattice could not be determined in the present study. When Au(100)–( $1 \times 1$ ) was used as the substrate, not the alternate bimolecular structure but a disordered structure was found. The well-ordered, alternate packing arrangement of CoPc and CuTPP molecules formed on Au(100)–(hex) was

consistently observed in the potential range between 0.8 and 0 V. The Au(100)–(hex) surface was stabilized by the adsorption of CoPc and CuTPP in 0.1 M HClO<sub>4</sub> at potentials near OCP. However, the ordered domain of mixed CoPc and CuTPP molecules was disordered at potentials higher than 0.9 V. Some Au islands were found to form on the terraces, indicating that lifting of reconstruction, i.e., structural transition from (hex) to ( $1 \times 1$ ) was induced by applied potentials.<sup>10</sup> The details will be described in a separate contribution.<sup>11</sup> These results show that the adlayer structure depends strongly upon the underlying Au lattice, suggesting that the reconstructed Au(100)–(hex) surface is a key factor in controlling alternate CoPc and CuTPP molecular chains. The two-component structure of CoPc and CuTPP consisting of molecular wires was alternately arranged on the reconstructed Au(100)–(hex) surface, and the adlayer structure was determined clearly by high-resolution STM in aqueous HClO<sub>4</sub>.

**Acknowledgment.** 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. We acknowledge Dr. Y. Okinaka for his assistance in writing this manuscript.

**Supporting Information Available:** Experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Balzani, V. Ed. *Electron Transfer in Chemistry* WILEY–VCH: New York, 2001; Vol. 3.
- (2) Collman, J. P.; Wagenknecht, P. S.; Hutchison, J. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1537 and references therein.
- (3) Jortner, J.; Ratner, M. Eds. *Molecular Electronics*; IUPAC: Oxford, 1997.
- (4) Guillaud, G.; Simon, J.; Germain, J. P. *Coord. Chem. Rev.* **1998**, *178–180*, 1433.
- (5) Yokoyama, T.; Yokoyama, S.; Kamikado, T.; Okuno, Y.; Mashiko, S. *Nature* **2001**, *413*, 619.
- (6) (a) Hipsps, K. W.; Scudiero, L.; Barlow, D. E.; Cooke, M. P., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 2126. (b) Scudiero, L.; Hipsps, K. W.; Barlow, D. E. *J. Phys. Chem. B* **2003**, *107*, 2903.
- (7) de Wild, M.; Berner, S.; Suzuki, H.; Yanagi, H.; Schlettwein, D.; Ivan, S.; Baratoff, A.; Günterodt, H.-J.; Jung, T. A. *ChemPhysChem* **2002**, *3*, 881.
- (8) (a) Yoshimoto, S.; Tada, A.; Suto, K.; Narita, R.; Itaya, K. *Langmuir* **2003**, *19*, 672. (b) Yoshimoto, S.; Tada, A.; Suto, K.; Itaya, K. *J. Phys. Chem. B* **2003**, *107*, 5836.
- (9) (a) Lu, X.; Hipsps, K. W.; Wang, X.; Mazur, U. *J. Am. Chem. Soc.* **1996**, *118*, 7197. (b) Scudiero, L.; Barlow, D. E.; Mazur, U.; Hipsps, K. W. *J. Am. Chem. Soc.* **2001**, *123*, 4073.
- (10) Magnussen, O. M.; Hotlos, J.; Behm, R. J.; Batina, N.; Kolb, D. M. *Surf. Sci.* **1993**, *296*, 310.
- (11) Suto, K.; Yoshimoto, S.; Itaya, K. Manuscript in preparation.

JA038857U