

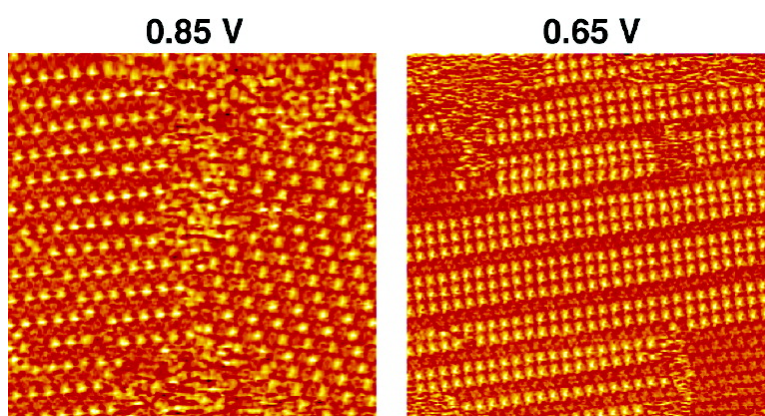
Article

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J. Am. Chem. Soc., **2004**, 126 (27), 8540-8545 • DOI: 10.1021/ja0485210 • Publication Date (Web): 19 June 2004

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Two-Dimensional Supramolecular Organization of Copper Octaethylporphyrin and Cobalt Phthalocyanine on Au(111): Molecular Assembly Control at an Electrochemical Interface

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Abstract: Mixed adlayers of 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine copper(II) (CuOEP) and cobalt(II) phthalocyanine (CoPc) were prepared by immersing Au(111) substrate in a benzene solution containing CuOEP and CoPc molecules, and they were investigated in 0.1 M HClO₄ by cyclic voltammetry (CV) and in-situ scanning tunneling microscopy (STM). The composition of the mixed adlayer consisting of CuOEP and CoPc molecules was found to vary depending on the immersion time. CoPc molecules displaced CuOEP molecules during the modification process with increasing immersion time, and the CuOEP molecules were completely replaced with CoPc molecules in the mixed solution after a long modification time. The two-component adlayer consisting of CuOEP and CoPc, which has a structure with the constituent molecules arranged alternately, was found to form either a $p(9 \times 3\sqrt{7}R - 40.9^\circ)$ or a $p(9 \times 3\sqrt{7}R - 19.1^\circ)$ structure, each involving two molecules on the Au(111) surface. The surface mobility and the molecular reorganization of CuOEP and CoPc were accelerated by modulation of the electrode potential. Different surface structures were produced at different electrode potentials, and hence potential modulation should allow a precisely controllable phase separation to take place in aqueous HClO₄.

Introduction

It is now recognized that precise control of molecular assemblies on a substrate is one of the key foundations for successfully producing nanoscale molecular devices. The formation and characterization of ordered adlayers of porphyrin and/or phthalocyanine at metal surfaces are of great importance from the fundamental and technological points of view, because these molecules are closely relevant to the fields of biology, photosynthesis, electrocatalysis, and molecular devices.^{1,2} Recently, some interesting molecular assemblies of porphyrins and phthalocyanines have been investigated in ultrahigh vacuum (UHV) by scanning tunneling microscopy (STM).^{3–7} For example, Yokoyama and co-workers observed similar small

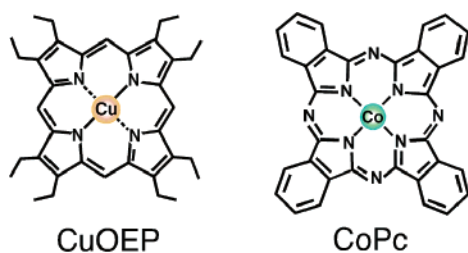
clusters and chains of CN-substituted porphyrins on Au(111) at the low temperature of 63 K.³ Hipps and co-workers found the formation of well-ordered regions with an entirely new structure with a 1:1 composition of cobalt(II) hexadecafluorophthalocyanine (F₁₆CoPc) and nickel(II) tetraphenyl-21*H*,23*H*-porphine (NiTPP) on Au(111) by vapor-phase deposition in UHV.⁴ F₁₆CoPc and NiTPP molecules were distinguished from each other by the difference in brightness of the central metal ions between the F₁₆CoPc and NiTPP molecules. The CoPc molecules are easily identified by the strong tunneling current that results from orbital-mediated tunneling through the half-filled d_{z²} orbital of the Co²⁺ ion: a bright spot appears at the center of each molecule.⁵ 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. Supramolecular structures constructed of fullerene (C₆₀) and chloro[subphthalocyaninato]boron(III) (SubPc) were found on Ag(111) in UHV by de Wild and co-workers.⁶ Highly ordered domains of “edge-on”- and “face-on”-oriented Zn porphyrin hexamer assemblies were controlled on a highly oriented pyrolytic graphite (HOPG) by the addition of coordinating axial ligands, which control the supramolecular architecture formed.⁷ We recently found that an alternate mixed layer consisting of cobalt(II) phthalocyanine (CoPc) and copper(II)

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Chart 1. Chemical Formula of CuOEP and CoPc

tetraphenyl-21*H*,23*H*-porphine (CuTPP) was formed on reconstructed Au(100)–(hex) but not on reconstructed Au(111), suggesting that the supramolecular assembly consisting of two chemical components also depends on the crystallographic orientation of Au.⁸ Thus, the formation of characteristic structures of noncovalent intermolecular interactions, such as a dipole–dipole interaction with a CN group,³ electrostatic interaction,⁴ and supramolecular assembly,^{6,7} is of importance both in building nano-arrays and in designing surfaces.

In the field of electrochemistry, it is necessary to design high-quality films for the development of fuel cells. Two-component films consisting of porphyrins and/or phthalocyanines have been examined, because such mixed films consisting of iron(III) tetra-(4-*N*-methylpyridyl) porphyrin and iron(III) phthalocyanine derivatives produce a higher activity for O₂ reduction.⁹ However, the relationship between mixed adlayers and their electrocatalytic activities has been not clarified in aqueous solutions at the nanoscale. Therefore, it is important to understand and control the properties of bimolecular adlayers in aqueous solutions under electrochemical conditions, because the molecule–substrate interaction can be modulated by surface charge density.¹⁰

In the present work, we prepared mixed adlayers by immersing an Au(111) substrate into a benzene solution containing both CoPc and copper(II) octaethylporphyrin (CuOEP) (see Chart 1) to investigate the structure of the adlayers composed of those molecules, because CuOEP and CoPc molecules can be discriminated from each other by the difference in image brightness between the central metal ions of those molecules.^{4,5,11a,b}

Experimental Section

CoPc and CuOEP were obtained from Aldrich. Benzene (spectroscopy grade) was purchased from Kanto Chemical Co. and used without further purification. The CoPc- and CuOEP-mixed benzene solution was prepared by adding a 100 μM CuOEP benzene solution into a benzene solution saturated with CoPc. The aqueous solution was prepared with HClO₄ (Cica-Merck, ultrapure grade) and ultrapure water (Milli-Q; ≥18.2 MΩ·cm).

The Au(111) electrode was prepared by the Clavilier method.¹² The aligned gold single-crystal bead was cut and successively polished with

finer grades of alumina paste, and the electrode was then annealed at ca. 950 °C for at least 12 h in an electric furnace to remove mechanical damages. Binary adlayers of CoPc and CuOEP were formed by immersing Au(111) for 1–20 min in a ca. 3 μM CuOEP benzene solution saturated with CoPc (less than 10 μM), after the Au electrode was annealed in hydrogen flame and quenched into ultrapure water saturated with hydrogen.¹¹ The modified Au(111) electrode was then rinsed with ultrapure water and transferred into an electrochemical or STM cell.

Cyclic voltammetry was carried out at 20 °C using a potentiostat (HOKUTO HAB-151, Tokyo) with the hanging meniscus method in a three-compartment electrochemical cell in N₂ atmosphere. Electrochemical STM measurements were performed by using a Nanoscope E (Digital Instruments, Santa Barbara, CA) with a tungsten tip etched in 1 M KOH. To minimize residual faradaic current, the tungsten tips were coated with nail polish. STM images were taken in the constant-current mode with a high-resolution scanner (HD-0.5J). All potentials are referred to the reversible hydrogen electrode (RHE). One of the (111) facets on the gold single-crystal bead was used as the substrate for electrochemical STM.¹¹

Results and Discussion

Immersion Time Dependence. The CuOEP and CoPc binary adlayers were prepared on the Au(111) surface with varying immersion times in the benzene solution. Figure 1a–c shows typical STM images of the binary adlayers formed on Au(111) at immersion times of 4, 6, and 20 min, respectively. As can be seen in Figure 1a, the adlayer at the immersion time of 4 min was composed of well-ordered and disordered segments over the entire surface of the terrace. The well-ordered portion was composed of hexagonally packed CuOEP molecules. According to the previous papers by Hipps' group,^{4,5} CuOEP and CoPc molecules can be discriminated from each other by the difference in the mode of the d_{z²} orbital between the Cu ion and Co ion. In this system, the center spot in each CuOEP appeared dark, whereas that of CoPc was brightest. The STM image in Figure 1a shows that the surface concentration of CoPc was the same as that of CuOEP. However, approximately 30–40% of the scan area was covered with CoPc molecules. Actually, the adlayer structure prepared with a short immersion time (less than 2 min) revealed that a CuOEP adlayer was formed predominantly on Au(111), suggesting that CoPc molecules displace the CuOEP molecules during the modification process with increasing immersion times. It is demonstrated that the molecular assembly of CuOEP on the Au surface forms more quickly than that of CoPc. As reported in our recent papers on CoOEP^{11d} and FeOEP,^{11e} the OEP adlayer was formed for only 10 s in 5–100 μM benzene solution containing either CoOEP or FeOEP molecules, indicating that the adlayer structure of OEP is independent of the metal ion. Preliminary results for the adlayer prepared from 1:1 (50 μM) mixed benzene solution containing ZnOEP and ZnPc demonstrated that only the highly ordered ZnOEP adlayer was formed on Au(111), suggesting that the interaction between ZnOEP molecules is much stronger than that between ZnPc molecules.¹³ Therefore, the highly ordered adlayer of CuOEP formed on Au(111) is attributed to be kinetically controlled. A close-up view of the CuOEP- and CoPc-mixed array is shown in Figure 1b. It is seen that CoPc molecules displaced CuOEP molecules in the

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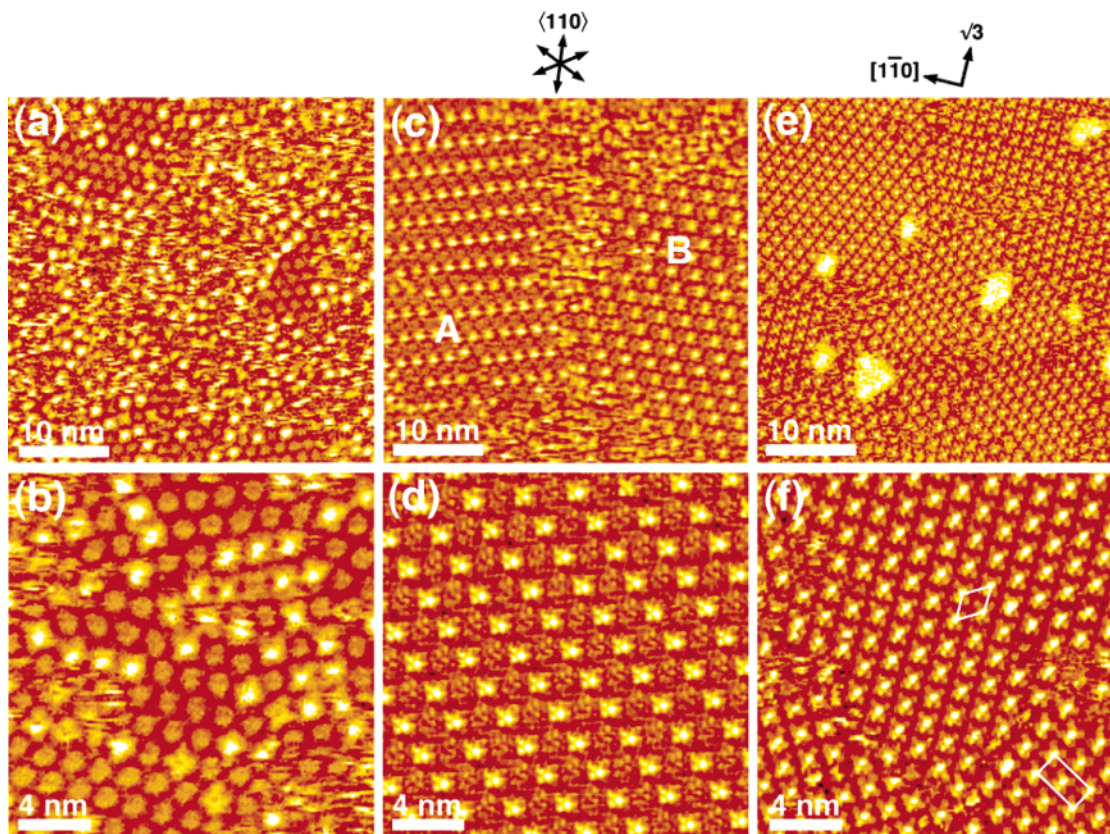


Figure 1. Typical large-scale ($40 \times 40 \text{ nm}^2$) and higher resolution ($20 \times 20 \text{ nm}^2$) STM images, acquired at 0.85 V vs RHE in 0.1 M HClO_4 , of CuOEP and CoPc binary arrays on Au(111) prepared by immersion in ca. $3 \mu\text{M}$ CuOEP benzene solution saturated with CoPc. The immersion times were 4 min (a and b), 6 min (c and d), and 20 min (e and f), respectively. The tip potential was 0.45 V (a), 0.47 V (b), and 0.35 (c) vs RHE. Tunneling currents were 0.8 nA (a), 0.75 nA (b), 2.0 nA (c), 0.85 nA (d), and 10 nA (e and f), respectively. The set of three arrows indicates the lattice directions of the Au(111) substrate.

hexagonal domain. The corrugation height was found to be 0.3 and 0.1 nm for the CoPc and CuOEP molecules, respectively. Cross-sectional profiles showed that both molecules formed a monolayer, not multilayers. The difference in corrugation height is attributable to the difference in electronic state between Cu and Co ions. When the modification with CuOEP and CoPc was allowed to continue for 6 min, a completely different, new domain appeared on the terrace as shown in Figure 1c. The terrace was now covered with two different domains. In the STM image acquired in an area of $40 \times 40 \text{ nm}^2$, highly ordered molecular rows were clearly recognized as stripes consisting of bright and dark lines. 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 parallel to the so-called $\sqrt{7}$ direction of the Au(111) lattice. Molecular rows between two domains A and B crossed each other at an angle of ca. 108° . Molecular rows in both domains are aligned along the $\sqrt{7}$ direction of the Au(111) lattice, but the relationship between the two domains is such that they constitute a set of rotational mirror images. A typical size of the domain consisting alternately of CuOEP and CoPc was ca. $30 \times 30 \text{ nm}^2$. Reconstructed rows of the Au(111) substrate were not found under the CuOEP and CoPc mixed adlayer, suggesting that the underlying Au surface became (1×1) . Such an alternate binary array was not observed with the CoPc- and CuTPP-mixed adlayer on Au(111); that is, the terrace was completely covered with two different phases, a disordered region and a highly ordered region.⁸ The binary

adlayers of CuOEP and CoPc might be controllable by the difference in either packing arrangements of CuTPP (square) and CuOEP (hexagonal) or in the molecular interaction between CoPc and CuOEP and that between CoPc and CuTPP molecules, because CuOEP is almost a flat plane molecule, whereas CuTPP is bulky due to the rotation of phenyl groups. When the immersion time was longer than 20 min, the terrace was completely covered with CoPc molecules only. A typical domain size of the CoPc adlayer formed on the Au(111)- (1×1) surface was 10–15 nm. Careful inspection of the highly ordered arrays of the CoPc molecule formed on the Au(111)- (1×1) reveals that islands are often observed at domain boundaries, as shown in Figure 1e. In the higher resolution STM image of the CoPc adlayer shown in Figure 1f, several domains are seen, in which each CoPc molecule can be recognized as a propeller-shaped image. Two adlayer structures composed of commensurate $c(5 \times 6\sqrt{3})\text{rect}$ and $(3\sqrt{3} \times 3\sqrt{3})R30^\circ$ were clearly seen on the atomically flat terrace as described in our previous paper.^{11b} The change in adlayer composition with immersion time revealed that CoPc molecules displace the CuOEP molecules during the modification process with increased immersion times, suggesting that the adsorption of CoPc onto Au(111) surface is thermodynamically more stable than that of CuOEP.

Further details of the internal structure, orientation, and packing arrangement of the binary CuOEP and CoPc mixed adlayer are seen in the high-resolution STM image for an area of $15 \times 15 \text{ nm}^2$ in Figure 2, which shows that alternate molecular rows are present uniformly on Au(111). A high-

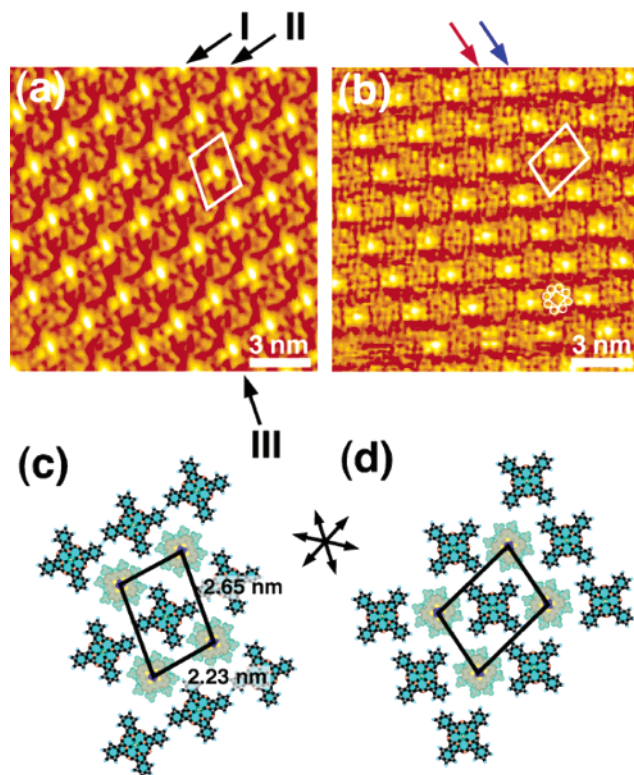


Figure 2. High-resolution ($15 \times 15 \text{ nm}^2$) STM images (a and b) of alternate binary CuOEP and CoPc arrays on Au(111) in 0.1 M HClO₄ acquired at 0.85 V vs RHE and corresponding proposed models (c and d). Tip potentials and tunneling currents were 0.35 V and 5.5 nA (a) and 0.45 V and 0.85 nA (b), respectively. Structural models are for the CuOEP and CoPc binary adlayers on the Au(111) surface with superimposed $p(9 \times 3\sqrt{7} - 40.9^\circ)$ (c) and $p(9 \times 3\sqrt{7} - 19.1^\circ)$ (d) unit cells. The set of three arrows indicates the lattice directions of the Au(111) substrate.

resolution STM image obtained in domain A in Figure 1c is displayed in Figure 2a. Note that the scan angle was rotated by ca. 20° with respect to that of Figure 1b to obtain an image with a clearer resolution. Individual CoPc molecules in the row marked by arrow I are propeller-shaped with the brightest spot at the center and four additional spots at the corners. These bright spots are attributed to the benzene moieties in the CoPc molecule as reported in our previous paper.^{11b} It is clear that all CoPc molecules are oriented in the same direction on Au(111). On the contrary, each molecule in the dark row marked by arrow II is in the shape of a ring with a central dark spot, indicating that it is a CuOEP molecule. As reported by Hipps' group in UHV⁵ and by our group in solution,¹¹ the center of each CoPc molecule appears as the brightest spot in the STM image because of the tunneling being mediated by a half-filled d_{z^2} orbital between the Au surface and the tip. However, at 0.8 V, the central Co ion is in the state of Co(III) formed by the electrochemical oxidation (Figure 1a). Because the d_{z^2} orbital should be empty in this oxidation state, another mechanism must be considered to explain the tunneling at the center of the Co(III)Pc molecule. It is generally known that the Co(III) porphyrin is unstable, and, to make it more stable, the addition of an axial ligand, such as O₂ like a super oxide anion, O₂⁻, is necessary.^{14a} Furthermore, the water molecule might coordinate with Co(III)-

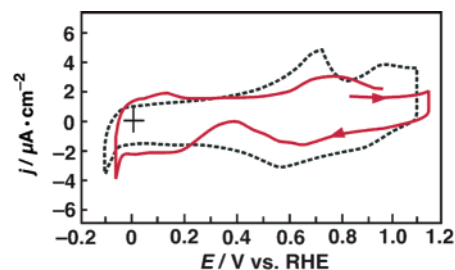


Figure 3. Cyclic voltammograms of bare Au(111) (dotted line) and the CuOEP- and CoPc-mixed adlayer formed on Au(111) (solid line) electrodes in 0.1 M HClO₄. The mixed CuOEP and CoPc adlayer was formed by immersing Au(111) for 6 min in ca. $3 \mu\text{M}$ CuOEP benzene solution saturated with CoPc. The potential scan rate was 50 mV s^{-1} .

Pc in an aqueous solution, because the complexes such as [CoTPP(H₂O)₂]ClO₄ or [CoOEP(H₂O)₂]ClO₄ are also known.^{14b} Because our STM measurements were carried out in solution containing air, it is feasible that O₂ molecules dissolved in solution were eventually attached to Co(III) ions to stabilize the Co(III)Pc molecule. It is known that the stronger σ -donating axial ligands lead to the smaller Co hyperfine coupling, promoting the localization of π -electrons on the oxygen.^{14a} This π -orbital might act as a new tunneling pathway, which could increase the tunneling current at the central position of Co(III)Pc. This accounts for the observation that the central cobalt ion in each CoPc molecule appeared bright in the image, whereas the copper ion in each CuOEP molecule appeared dark. From the cross-sectional profile, the intermolecular distance between CoPc molecules aligned in the direction of arrow I (Figure 2a) and that between CuOEP molecules aligned in the direction of arrow II were both measured to be $2.23 \pm 0.06 \text{ nm}$, whereas the distance between CoPc molecules aligned in the direction of arrow III was found to be $2.63 \pm 0.08 \text{ nm}$. These values correspond to $3\sqrt{7}$ and 9 times the Au lattice constant, respectively. An adlattice is superimposed with solid lines in Figure 2a. In addition to the information concerning the symmetry and the structure of CuOEP and CoPc arrays, this STM image reveals a great deal of information concerning the internal molecular structure. The shape of the molecules in the dark rows of Figure 2a was unclear. When the usual tunneling current lower than 1 nA was used, the molecular row of CuOEP indicated by the red arrow in Figure 2b was clearly resolved as a well-defined chemical structure. On the contrary, the shape of each CoPc molecule in the rows indicated by the blue arrow was variant under these conditions. The adlattice of the two-component adlayer consisting of CuOEP and CoPc shown in Figure 2b was identical to that shown in Figure 2a, however. It has a $p(9 \times 3\sqrt{7} - 19.1^\circ)$ structure, which is a mirror image of $p(9 \times 3\sqrt{7} - 40.9^\circ)$. Structural models of $p(9 \times 3\sqrt{7} - 40.9^\circ)$ and its mirror image structure, $p(9 \times 3\sqrt{7} - 19.1^\circ)$, are proposed in Figure 2c and d, respectively. The unit cells are represented by solid lines. The effect of moving the unit cell in parallel directions with respect to the Au(111) substrate was taken into consideration. In those models, the center of each molecule was assigned to a 2-fold bridge site (Au atoms are not shown here).

(2) Potential Dependence. Because characteristic arrangements of CuOEP and CoPc were observed at the immersion time of 6 min, the CV measurements described in this section were also made under the same conditions. Figure 3 shows

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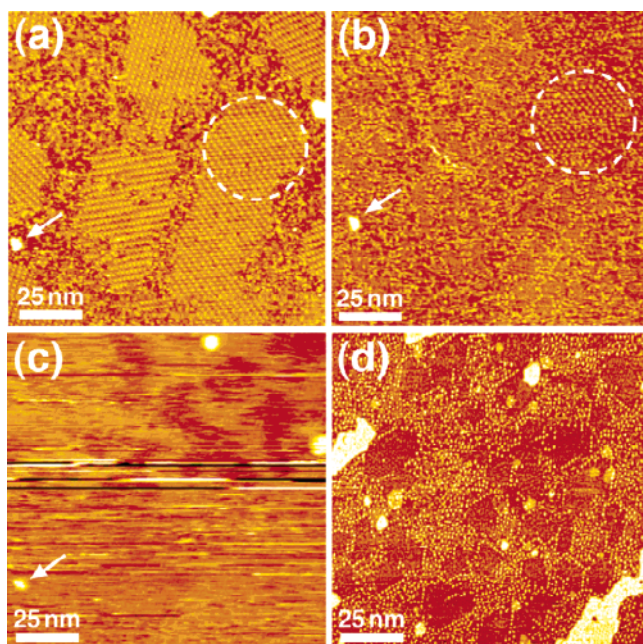


Figure 4. Potential-dependent STM images of the CuOEP- and CoPc-mixed adlayer on the Au(111) surface in 0.1 M HClO₄ acquired in an area of 125 × 125 nm² at 0.8 V (a), 0.6 V (b), 0.35 V (c), and 0.85 V (d), respectively, where the last potential of 0.85 V was applied by stepping from 0.3 V. The potential of the tip and the tunneling current were 0.47 V and 1.0 nA (a–c) and 0.46 V and 0.75 nA (d), respectively.

typical cyclic voltammograms (CVs) of bare (dashed line) and CoPc- and CuOEP-modified (red solid line) Au(111) electrodes in 0.1 M HClO₄ recorded at the scan rate of 50 mV s⁻¹. The voltammogram for bare Au(111) in Figure 3 in the double-layer potential region is identical to that reported previously.¹⁵ For the Au(111) electrode modified with CuOEP and CoPc by immersing into the mixed solution for 6 min, the electrode potential was first scanned positively from 0.82 to 1.15 V, and then the scan direction was reversed. A broader cathodic peak was observed in the potential range between 0.8 and 0.4 V. The reductive peak observed between 0.25 and 0 V is likely to be due to the electrochemical reduction of Co(III) to Co(II) as described in our previous paper.^{11b} The cathodic current commencing at -0.02 V appears to be due to hydrogen evolution and the desorption of molecules. The broad reductive peak in the potential range between 0.8 and 0.4 V was not seen at the CuOEP- or CoPc-modified Au(111) electrode, suggesting either that the electron charge transfer reaction for this peak accompanies a structural change of the mixed adlayer or that a change in the film capacitance is induced by structural changes. Indeed, alternate arrays of CuOEP and CoPc were observed only in the potential range between 1.0 and 0.75 V.

After confirming that a well-defined adlayer composed of alternate CuOEP and CoPc molecular rows was formed and also that an expected CV profile was obtained in pure 0.1 M HClO₄, the potential was held constant at various potentials. We first observed a structural change of the CuOEP- and CoPc-mixed adlayer by potential stepping. Figure 4a–d shows large-scale STM images of 125 × 125 nm² acquired at 0.8, 0.6, 0.35, and 0.85 V, respectively. The white arrow in each STM image

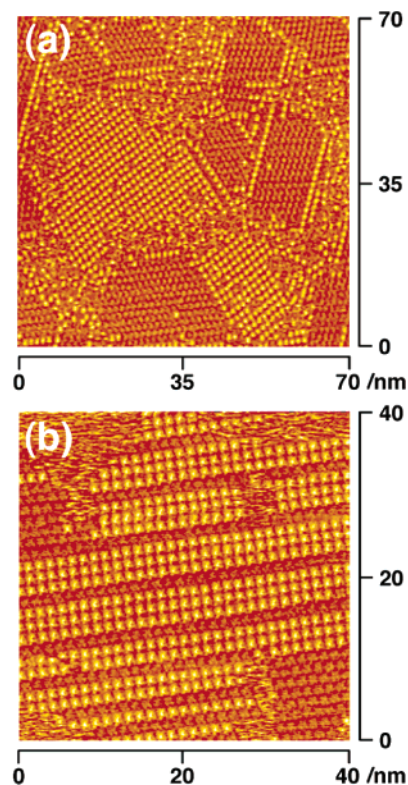


Figure 5. Typical STM images of binary CuOEP and CoPc arrays on the Au(111) surface in 0.1 M HClO₄ acquired at (a) 0.45 V and (b) 0.65 V after stepping the potential from 0.85 V in an area of 70 × 70 nm² (a) and 40 × 40 nm² (b), respectively. The potential of the tip and the tunneling current were 0.35 V and 4.5 nA, respectively.

points at the same location. In Figure 4a, the terrace was covered with several ordered domains and disordered regions. Domains aligned in the $\sqrt{7}$ directions can be seen on the atomically flat terrace. The white circle indicates one of the well-defined regions where the molecular rows are arranged alternately. When the electrode potential was held at 0.6 V, the ordered domains gradually became smaller. As indicated by the white circle in Figure 4b, the ordered area barely remained. Dark regions consisting of CuOEP molecules were formed, suggesting that the two-dimensional organization of CuOEP is more stable than that of CoPc. At 0.35 V, the STM image became unclear, indicating that the molecules are probably highly mobile on the surface because of a structural change. A few minutes later, the phase-separated domain began to appear on the terrace. However, the electrode potential was returned to 0.85 V because the resolution deteriorated. The phase-separated domains were stable when the potential was returned to 0.85 V. As can be seen in Figure 4d, two separated domains consisting of bright and dark domains were observed on the terrace, although their locations were different. The bright region was composed of disordered CoPc molecules, whereas the dark area was composed of hexagonally ordered CuOEP molecules.

We attempted to control the domain size and composition by other methods such as the potential scan at a slow rate to a slightly anodic potential. Figure 5a shows a typical STM image of a CuOEP and CoPc adlayer formed on the Au(111) surface after the potential was held constant at 0.45 V following the scan from 0.8 V at a scan rate of 10 mV s⁻¹. This STM image shows that the structure changed drastically upon this potential manipulation; that is, the alternate packing structure of binary

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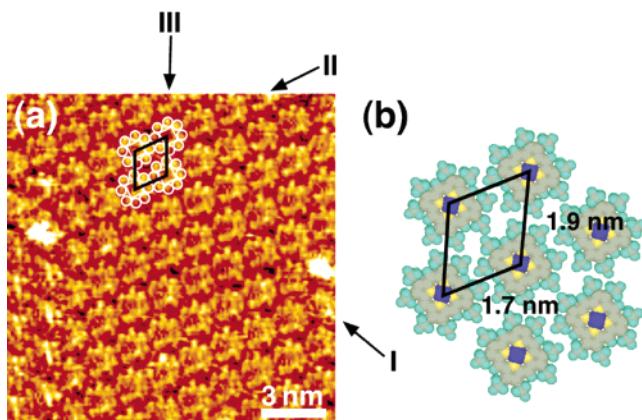


Figure 6. High-resolution STM image ($15 \times 15 \text{ nm}^2$) (a) and structural model (b) of a region of on Au(111) surface covered with arrays of CuOEP in 0.1 M HClO_4 acquired at 0.85 V vs RHE after electrochemical phase separation. The tip potential and tunneling current were 0.46 V and 6.4 nA, respectively.

CuOEP and CoPc disappeared, and a new structure was formed on the terrace, in which arrays of bright domains with square lattice and dark domains with quasi-hexagonal lattice were arranged alternately. In the bright domain composed of CoPc molecules, a highly ordered array with square packing arrangement was found. Also, bright CoPc molecular rows ran parallel to the CuOEP domain. Figure 5b shows a typical STM image of a mixed CuOEP and CoPc adlayer formed on the Au(111) surface after the potential was held at 0.65 V for 30 min. In this case, one-dimensional (1D) molecular chains of CuOEP were clearly observed as dark gaps between bright rows consisting of two or three CoPc molecular rows. The intermolecular distance between CoPc molecules was about 1.4 nm, corresponding to that of close-packed CoPc molecules with a square unit cell as described in previous publications.^{5a,b,11b} These results show that the adlayer structure depends strongly upon electrochemical potential, suggesting that potential modulation is a key factor controlling alternate CuOEP and CoPc molecular chains. The similar ordering of porphyrins at negative potentials was reported by Borguet and co-workers to result from a change in surface interactions.¹⁶ The reason the phase separation takes place is not clear. One possible reason is the difference in charge distribution resulting from either the central metal ion (Cu ion and Co ion) or the chemical framework (OEP and Pc). As described in our recent papers, it was found that the FeOEP adlayer on Au(111) was highly mobile in potentials more negative than 0.4 V due to the reduction of Fe(III) to Fe(II),^{11e} whereas the CoOEP adlayer on Au(111) was observed in the potential region between 0 and 0.95 V.^{11d} Although further investigation on the effect of chemical framework with the same central metal is needed to understand this point, reorganization of each CuOEP and CoPc molecule probably depends on a central metal ion.

Figure 6a shows a close-up view of the ordered CuOEP array in the electrochemically induced domain, revealing the internal molecular structure and the molecular orientation in the ordered domain. The molecules CuOEP were arranged hexagonally, and the center of each CuOEP molecule was observed as a dark spot. Each CuOEP molecule can be recognized as a square with additional spots at the corners corresponding to eight ethyl

groups. It is clear that CuOEP molecules possess the same orientation in all molecular rows. The intermolecular distance along row I or II was found to be $1.72 \pm 0.06 \text{ nm}$. The intermolecular distance along row III was $1.98 \pm 0.08 \text{ nm}$. As was described in the previous papers dealing with NiOEP on Au(111) in UHV by Hipps and co-workers¹⁷ and CoOEP^{11d} and FeOEP^{11e} on Au(111) in solution by our group, two different orientations can be seen for those molecules in molecular rows; that is, individual molecules were arranged alternately with a rotation angle of ca. 15° . However, the packing arrangement of CuOEP was slightly different in this case, resulting from the difference in surface concentration between the alternate mixed layer (total amount of molecules) and the CuOEP single layer. The surface concentration of the mixed layer was calculated to be $5.7 \times 10^{-11} \text{ mol cm}^{-2}$ from the unit cell of either $p(9 \times 3\sqrt{7}R - 40.9^\circ)$ or $p(9 \times 3\sqrt{7}R - 19.1^\circ)$ including two molecules, which is smaller than that of the close-packed CuOEP layer ($8.7 \times 10^{-11} \text{ mol cm}^{-2}$)^{11d} or the CoPc layer ($7.9 \times 10^{-11} \text{ mol cm}^{-2}$).^{11b} Therefore, the structural difference between the self-organized CuOEP prepared by immersion into a benzene solution containing CuOEP and the electrochemically induced CuOEP molecules can be attributed to the relaxation between CuOEP molecules.

Finally, in this system, the surface mobility and the molecular reorganization of CuOEP and CoPc were accelerated by modulation of electrode potential. The surface charge density at the electrochemical interface would contribute not only to the interaction between molecule and substrate but also to the interaction between molecules. Such a precise and unique control at electrochemical interfaces is of great interest for further application of porphyrin and phthalocyanine molecular assembly.

Conclusions

The mixed adlayer consisting of CuOEP and CoPc molecules produced on the Au(111) substrate by immersion into a benzene solution of CuOEP saturated with CoPc possesses variable compositions depending upon the immersion time. CoPc molecules displaced the CuOEP molecules during the modification process as the immersion time was increased, and the CuOEP molecules were finally replaced by CoPc molecules when the immersion time extended 20 min. The mixed adlayer consisting of CuOEP and CoPc was found to have a structure with the constituent molecules arranged alternately. The two-component structure of CuOEP and CoPc formed either $p(9 \times 3\sqrt{7}R - 40.9^\circ)$ or $p(9 \times 3\sqrt{7}R - 19.1^\circ)$ including two molecules on the Au(111) surface. Different surface structures are produced at different electrode potentials, and hence potential modulation should allow precisely controllable phase separation to take place in aqueous HClO_4 .

Acknowledgment. This work was supported in part by CREST-JST, by the Ministry of Education, Culture, Sports, Science, and Technology, a by a Grant-in-Aid for the Center of Excellence (COE) Project, Giant Molecules and Complex Systems, 2004. We acknowledge Dr. Y. Okinaka for his assistance in writing this manuscript.

JA0485210

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