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**Sandwich Complexes**

# Superstructure Formation and Rearrangement in the Adlayer of a Rare-Earth-Metal Triple-Decker Sandwich Complex at the Electrochemical Interface**

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The control and design of molecular assemblies by using noncovalent intermolecular interactions, such as hydrogen bonding, metal–ligand coordination, and dipole–dipole, electrostatic, and π–π interactions on surfaces, represents a promising approach for the construction of nanoarchitectures.[1–4] "Bottom-up" strategies based on supramolecular chemistry enable the synthesis of crystals and complexes from the solution phase. Porphyrin and phthalocyanine (Pc) assemblies are some of the most promising building blocks for three-dimensional molecular patterning and the development of new functional properties. In recent years, adlayers of several sandwich compounds such as the bisphthalocyanine double-decker complexes of Y, Ce, Pr, and Er have been investigated at the liquid–solid interface.[5–9] Possible future applications for these rare-earth complexes include their use as organic field-effect transistors, liquid crystals, and chemical sensors.[10] In the case of double-decker heterodimers, several groups have reported a unique property of molecular rotation.[11a,12] This rotation can be controlled by coordination to specific functional groups within the molecule[11] or by the redox properties of the rare-earth central metal.[12] More recently, direct observation of molecular rotation for $Zn^{II}$ porphyrin coordinated to 4-methoxypyridine on Ag(100) was reported by Lambert and co-workers.[13] The insertion of 4-methoxypyridine on the $Zn^{II}$ porphyrin adlayer on Ag(100) provided one of the important factors as a rotational axle. Thus, it is very attractive to understand the formation of superstructure by rotation control and electrochemical properties of these molecules. However, not much attention has been paid so far to those adlayers at electrochemical interfaces. Herein, we report the adlayer of [15]crown-5-ether-substituted Pc (CRPc) and a tetraphenyl porphyrin (TPP) triple-decker complex coordinated by $Eu^{III}$, TPP/CRPc/CRPc (**1**)[14] (Figure 1) on a Au(111) surface to create a three-dimensional functional molecular architecture. Adlayer structures, internal structure, and unique properties of triple-decker Pc complex **1** are demonstrated on the Au(111) electrode surface at the electrochemical interface.

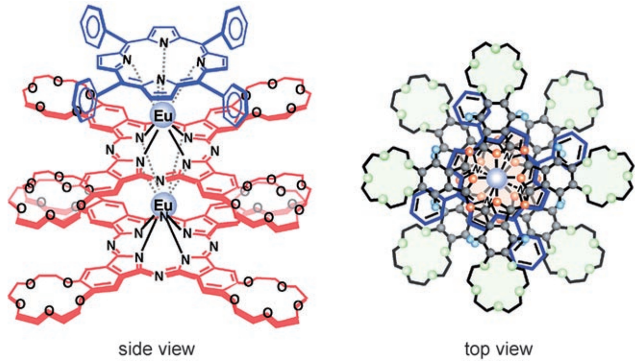

*Figure 1.* Chemical formula of TPP/CRPc/CRPc triple-decker **1**. Top view: Eu central blue sphere; CRPc black structure; TPP dark blue structure.

The resulting adlayer was investigated in acidic solution by using scanning tunneling microscopy (STM) in situ at a potential of 0.77 V (Figure 2a). Although each molecule can be resolved with scan areas as large as $50 \times 50\ nm^2$, it should be noted that the domain size is smaller than that for the adlayer of $Co^{II}$-crown-ether-substituted Pc (CoCRPc) on Au(111), which we reported in our previous paper.[15] The molecules of **1** are arranged in both hexagonal and square patterns. Further details of the internal structure, orientation, and molecular packing are revealed in a close-up view ($15 \times 15\ nm^2$) through careful adjustment of the tunneling currents (Figure 2b). Each triple-decker appears as a dark spot at the center of four additional smaller spots. Although the crown moieties in the topmost CRPc layer are not fully resolved in the tunneling experiment conditions, the overall molecular

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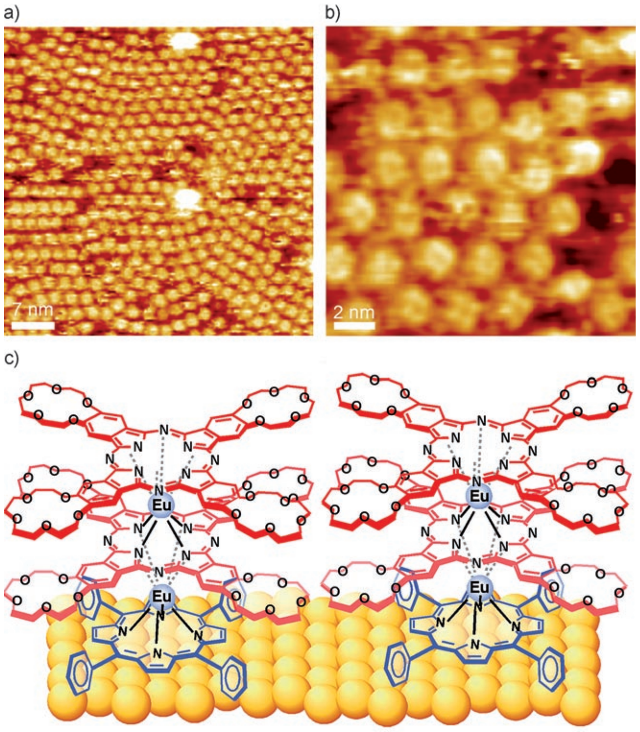

*Figure 2.* Large-scale (50×50 $nm^2$) and high-resolution (15×15 $nm^2$) STM images of an array of **1** formed on Au(111) and obtained at 0.77 V versus a reversible hydrogen electrode (RHE) in 0.05 M $HClO_4$. Tip potentials and tunneling currents were 0.22 V versus RHE and a) 0.10 nA and b) 0.13 nA. c) Proposed model of adlayer of **1** on Au(111).

shape is almost identical to those reported previously for $Cu^{II}$ phthalocyanine (CuPc)[16a] and $Zn^{II}$ phthalocyanine (ZnPc).[16b] Furthermore, as reported in previous publications, two-dimensional two-component adlayers consisting of $Co^{II}$ phthalocyanine (CoPc) and metalloporphyrins such as $Cu^{II}$ tetraphenylporphyrin (CuTPP) and $Cu^{II}$ octaethylporphyrin (CuOEP) were clearly distinguished by STM imaging in situ.[16d–f] On this basis, we can derive insights about the internal structure of **1** when it attached with the TPP side onto the Au(111) surface in the adlayer, as shown in Figure 2c. Careful inspection of the STM images reveals that the topmost CRPc ligand adopts several different molecular orientations. The intermolecular distance between the nearest-neighbour **1** molecules was found, on the basis of cross-sectional profiles, to be 2.6–2.8 nm. These distances are larger than that of the CoCRPc ($p(8\times4\sqrt{3}R-30^\circ)$; $p$ = primitive, $R$ = rotation) adlattice owing to the random alignment of the CRPc moieties or rotation of the middle layer. Also, the height of one molecule of **1** was estimated to be approximately 0.40 nm based on the defect site (see Figure S1 in the Supporting Information).

When the modification was carried out under a prolonged immersion time of 15 s, interestingly, quite different well-ordered domains were also found in the adlayer of **1** (Figure 3a) and were alternately composed of bright and dark spots in a 1:1 ratio. The terrace was covered with several ordered domains that are even located near a step edge. A close-up view of the ordered structure is shown in Figure 3b.

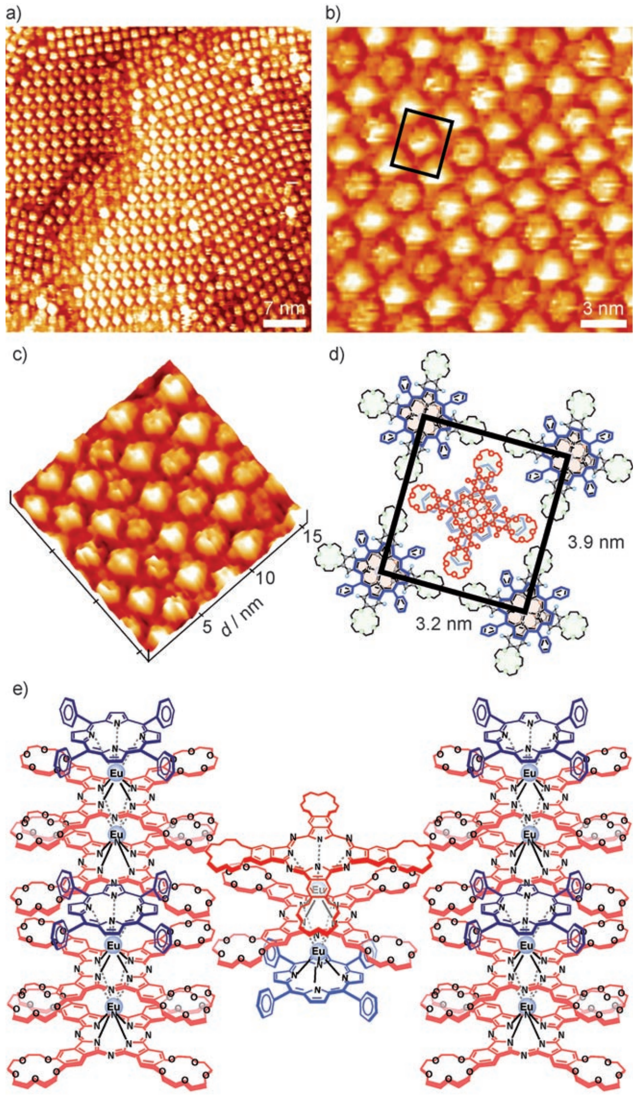

*Figure 3.* a) Large-scale (50×50 $nm^2$) and b) high-resolution (20×20 $nm^2$) STM images of an array of **1** formed on Au(111) acquired at 0.80 V versus RHE in 0.05 M $HClO_4$. c) Height-shaded plot. d, e) Proposed structural models of a superstructure of an adlayer of **1**. Tip potential and tunneling currents were a) 0.22 V versus RHE and 0.14 nA, and b) 0.20 V versus RHE and 0.13 nA.

From the cross-sectional profiles, the adlattice is superimposed as a rectangular unit cell with distances of approximately 3.2 and 3.9 nm as shown in Figure 3b. Analysis of a height-shaded plot (Figure 3c) reveals that the additional bright features probably arise from ligand rotation at an angle of 45°. This feature indicates the topmost (see below) TPP ligand of **1**, that is, the STM image shows both the topmost TPP ligand and the 2nd CRPc ligand. This kind of difference between the first and second layers was also observed by the high-resolution STM image of the supramolecularly assembled open-cage $C_{60}$ derivative molecular layer on the ZnOEP adlayer formed on Au(111) in an acidic solution.[17] On the contrary, the dark features in Figure 3b and c also indicate the topmost ligand of **1**. This is probably a CRPc ligand, as shown in Figure 2b. According to the previous STM and orbital-mediated tunneling study on CoPc and $Co^{II}$ tetraphenylporphyrin (CoTPP) in the alternate binary array, phthalocyanines always appear as brighter spots than porphyrins under the same experimental condition,[18] thereby making it possible to differentiate between the two compounds. Thus, if STM images are brighter when the phthalocyanine moiety is adsorbed onto the Au surface, the four bright spots, which correspond to the four corners of a rectangle unit cell in Figure 3b, suggest that in these places the CRPc site of **1** is adsorbed onto the Au surface. In other words, the TPP moiety is facing the bulk solution in these places (a schematic illustration is shown in Figure S2 in the Supporting Information) and the difference in height is approximately 0.15 nm (Figure S3 in the Supporting Information). The well-ordered alternating structure is thus assigned to the adsorption of two different orientations of **1**. Considering this and intermolecular distances and molecular shapes, a structural model for the top view is proposed and depicted in Figure 3d. For molecules of **1** at the corner of the unit cell, the individual CRPc moieties of the middle or bottom layers are arranged in a face-to-face configuration, whereas the topmost TPP moiety alternately sits at 45° (Figure 3d). The central molecule in the unit cell orients as a topmost CRPc ligand facing the solution phase. Differences in brightness, therefore, probably result from changes in the orientation of the topmost TPP and CRPc ligands in the **1** adlayer (see Figure 3e).

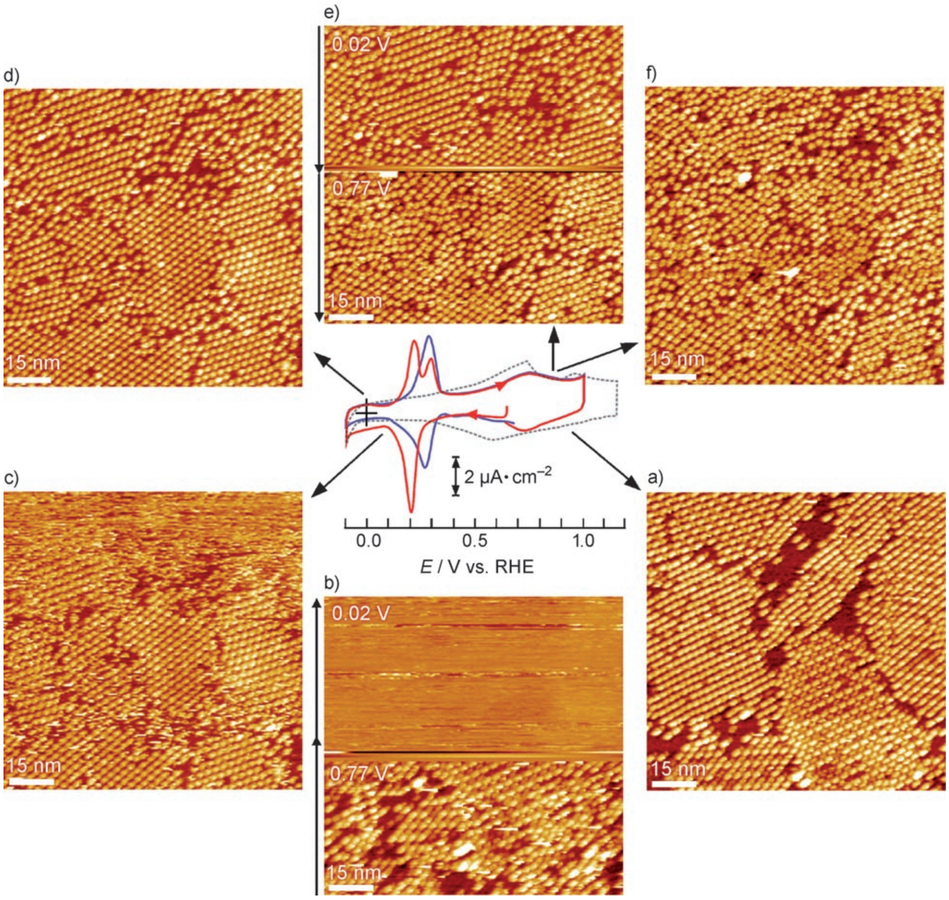

***Figure 4.*** Cyclic voltammograms of clean Au(111) (dotted line) and **1**-modified Au(111) electrode (red line: first scan; blue line: continuous scan) recorded at a scan rate of 20 mV s$^{-1}$. Relative large-scale (100×100 nm$^2$) STM images of an array of **1** on Au(111) obtained at a) 0.85 V, b) 0.02 V stepping from 0.77 V, c) 0.02 V after 1 min of (b), d) 0 V, e) 0.77 V stepping from 0.02 V, and f) 0.77 V after 3 min of (e) in 0.05 M HClO$_4$. The tip potential and tunneling current were 0.20 V versus RHE and 0.13 nA, respectively.

Electrochemical characterization of an adlayer of **1** was performed through cyclic voltammetry (CV) in 0.05 M HClO$_4$. The central part of Figure 4 shows typical cyclic voltammograms of a well-defined Au(111) (dotted line) and a **1**-modified Au(111) electrode (red and blue lines) in 0.05 M HClO$_4$ recorded at a scan rate of 20 mV s$^{-1}$. The voltammogram for bare Au(111) in the double-layer potential region is identical to that reported previously,[16a–c] indicating that a well-defined Au(111) surface was exposed to the solution. A characteristic redox couple is observed at 0.20 V for the first scan of the **1**-modified Au(111) electrode (red line) with a much broader redox couple observed between 0.50 and 0.90 V. The transferred electronic charge is estimated to be approximately 0.39 µC cm$^{-2}$ based on the peak area at 0.20 V, indicating that the redox couple is not related to the presence of Eu$^{III}$. Notably, the CV of **1** is very similar to that recently reported for $Y^{3+}Pc_2$ on Au(111).[8] The 0.20 V redox couple can therefore be attributed primarily to a charge-transfer reaction involving the Pc and/or TPP dianions and radical anions. Note that continuous potential cycling between 1.00 and −0.10 V resulted in a change in the curve, as shown by the blue line. The potential of the redox couple shifted slightly to the positive side, at 0.25 V, and two anodic peaks became one peak observed at 0.28 V.

To investigate the redox reactions of the CV profile in detail, potential-dependent STM images of the adlayer of **1** were obtained at various potentials and at the same location. As shown in Figure 4a, an as-prepared adlayer of **1** was confirmed at 0.85 V. Several domains such as squarely arranged (central upper and left portions) and alternately arranged molecules of **1** (other portions) were found on the terrace. The identical structure was observed in the potential range between 0.90 and 0.40 V. After observing the well-defined structure, the potential was stepped to 0.02 V. The composite STM image of the potential step from 0.77 to 0.02 V showed that the adlayer of **1** immediately becomes disordered (Figure 4b). After 1 min, several domains consisting of hexagonally arranged molecules of **1** began to appear on the terrace, as shown in Figure 4c, indicating that the structural change of the adlayer of **1** was caused by the potential step. The hexagonally arranged domains of **1** were stable, even at 0 V (see Figure 4d). Notably, the internal structure of **1** was unclear at or near 0 V in the high-resolution STM image under the present experimental condition. The nearest-neighbor distance of hexagonally arranged molecules of **1** was 2.6–2.7 nm, suggesting that the molecule of **1** rotates its ligand. A disordered phase was formed on the surface and the brightness within each molecule of **1** became almost uniform. Hexagonally arranged arrays of **1** were found in the potential region between −0.10 and 0.50 V. When the potential was returned to 0.77 V from 0.02 V, the adlayer became slightly more disordered again (Figure 4e). The disordered adlayer of **1** can be seen in the STM image obtained 3 min later (Figure 4f). At this potential, an internal structure similar to the STM image of Figure 2b was again observed. The distinctive ordered pattern observed in Figure 4a was not observed. This electrochemical result suggests that the molecular orientation of the topmost TPP ligand of **1** in the well-ordered superstructure is reversed during the electrochemical redox reaction. Because it is known that porphyrin and Pc are electron donating molecules, a charge transfer might take place onto the Au(111) surface owing to the adsorption of **1**. According to a report on the potential of zero charge (pzc) for an Au(111) electrode, the value of pzc of reconstructed Au(111) is 0.32 V versus the saturated calomel electrode (SCE) in 0.01 M $HClO_4$.[19] Because the surface charge of the Au(111) electrode surface is controlled by the variation of electrode potentials, the reverse of the topmost TPP ligand, that is, the electrochemical structural change observed in Figure 4 might be tentatively explained by a subtle difference in charge distribution between TPP and CRPc ligands of **1**. As the structural changes are reversible with potential switching, the redox couple at 0.20 V can clearly be attributed to a charge-transfer reaction with a structural change in the adlayer.

In conclusion, a unique molecular assembly and surface properties of **1** were found as a result of the adsorption orientation and electrochemical potential variation on the Au surface. This finding is applicable to bottom-up nanofabrication of the surface by controlling the molecular orientation and the rotation of the ligands.

## Experimental Section

The TPP/CRPc/CRPc triple-decker molecule, **1**, was used as synthesized previously.[14] Benzene was obtained from Kanto Chemical Co. (Spectroscopy Grade).

Au(111) single-crystal electrodes were prepared by the Clavilier method.[20] The adlayer of **1** was formed by immersing an Au(111) electrode successively into an approximate 10 μM **1** benzene solution for 7–15 s after annealing in a hydrogen flame and air cooling for more than 3 min.[16] The **1**-modified Au(111) electrode was then rinsed with ultrapure water and transferred into an electrochemical STM cell filled with 0.05 M $HClO_4$ (Cica-Merck, ultrapure grade).

Electrochemical STM measurements were performed in 0.05 M $HClO_4$ using a Nanoscope E (Digital Instruments) with a tungsten tip etched in 1 M KOH. To minimize residual Faradaic currents, the tips were coated with nail polish. STM images were recorded in the constant-current mode with a high-resolution scanner (HD-0.5I). All potential values are based on the RHE.

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