Structure and molecular recognition ability of

thiolated-cyclodextrin monolayer on Au(111) surface

Satoshi Yasuda [1], Iwao Suzuki [2], Jun Sumaoka [3],
Makoto Komiyama [3,*] and Hidemi Shigekawa [1,3,*]

[1] Institute of Applied Physics, CREST, University of Tsukuba, Tsukuba 305-8573, Japan
[2] Graduate School of Pharmaceutical Sciences, Tohoku University,
Aramaki, Aoba-ku, Sendai 980-8578, Japan
[3] Department of Chemistry and Biotechnology, Graduate School of Engineering,
University of Tokyo, Tokyo 113-8656, Japan

* e-mail: hidemi@ims.tsukuba.ac.jp, mkomi@chembio.t.u-tokyo.ac.jp,
World Wide Web: http//dora.ims.tsukuba.ac.jp/

We analyzed the structure and molecular recognition ability of the LP-β-CyD (β-cyclodextrin modified with lipoamide residue) monolayers formed on atomically clean and flat Au(111) surfaces, by using scanning tunneling microscopy (STM) and cyclic voltammetry (CV) measurement. Although the structure of the LP-β-CyD molecules in the adsorbed layer was disorder, formation of the monolayer structure was clearly shown by STM. Immersion time necessary to form a monolayer on the atomically clean and flat Au surface was 1/10 of that previously reported using rough Au surface, despite that the molecular concentration of the LP-β-CyD solution was 1/100. In order to examine the molecular recognition ability of the LP-β-CyD/Au(111) structure, we performed CV measurement using two electroactive makers; ferrocenecarboxylic acid (FCA) and hexacyanoferrate (III) (HCF). FCA molecules can be included into β-CyD cavity, but HCF molecules can not be. Therefore, if the monolayer structure is densely formed with the CyD cavity being perpendicular to the surface, the oxidation-reduction current is expected to be observed only for the case of the FCA molecules, which in fact was clearly shown by our experiment. These results indicate that the LP-β-CyD/Au(111) structure has high potential as a novel molecular recognition sensor with its selective permeability.

Key words: cyclodextrin, molecular recognition, self-assembly, Au(111), STM, cyclic voltammetry

Self-assembled monolayers (SAMs) of organic molecules have been studied extensively to develop the interfacial systems which provide various functional properties on solid surfaces. [1] In particular, from the point of view for the industrial applications, formation of SAMs of thiol and disulfides on Au surface has been an attractive target. Since they easily form stable and highly packed monolayers by simple preparation techniques such as immersion or vapor deposition processes, they are considered to have high potential to fabricate the micro-morphlogy of materials; microcontact printing, [2] lithography with ultraviolet light, and so on. [3] Furthermore, their potential as the functional sensors was shown recently.

From the point of view to develop novel sensors, Rojas et al. analyzed structures of thiolated cyclodextrin (CyD) molecules self-assembled on Au, and revealed, by using the electrochemical method, that the structure

works as a selective molecular receptor. [4] CyDs have a donut-shaped structure consisting of several glucopyranose units, and are able to include various guest molecules in their cavities as shown in Fig. 1(a). [5] Since thiolated CyDs are adsorbed onto Au surface by the chemical bonding between sulfur atoms in thiols and Au, CyDs are considered to sit on the Au surface with their cavity axis aligned perpendicular to the surface. The conformation gives a function as a recognition sensor to the CyD/Au system. Using CyDs modified by lipoamide residue, Suzuki et al. demonstrated that the redox signal of the ferrocene carboxylic acid changed with the concentration of the guest molecules in the solution. [6,7] Namely, inclusion of the guest molecules prevents the electromarker from reaching the Au surface through the cavity (Fig. 1(c)). These results indicate that CyD monolayer was formed on Au surface with the CyD cavity axis aligned
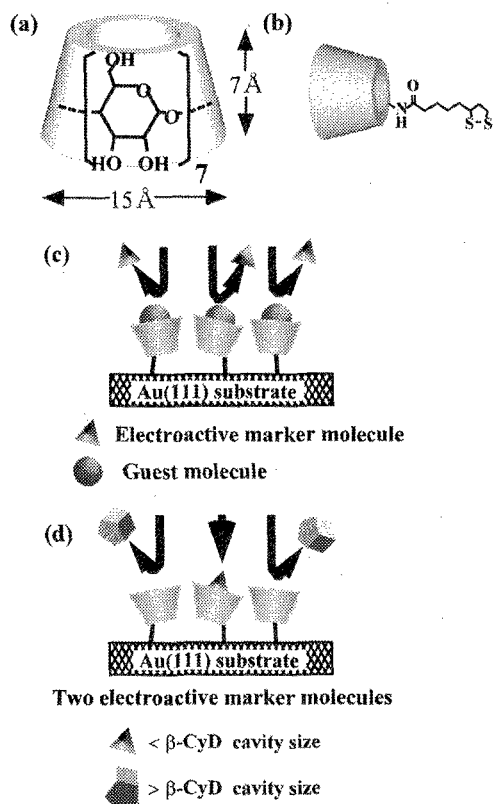
Fig. 1 Schematic structures of (a) β-cyclodextrin (b-CyD), (b) β-CyD modified with lipoamide residue (LP-β-CyD), and molecular recognition mechanism by LP-β-CyD monolayer with (c) and without (d) guest compounds.

perpendicular to the surface, and the existence of guest molecules could be identified by the reduction in the measured current.

Studies of the thiolated CyD monolayers have been performed not only on their molecular recognition ability,[6, 7, 8] but also on their structures and growth processes.[9, 10, 11] M. Weisser et al. investigated the growth process of the thiolated CyDs on Au system by using the plasmon surface polariton spectroscopy (PSPS),[9] and reported that the growth process could be explained by the Elovich mechanism based on the repulsive interaction between adsorbed molecules. However, since CyDs contain many hydroxyl groups (Fig. 1(a)), attractive interaction between CyDs due to the hydrogen bonds is considered to be more probable. On the other hand, in order to explain the change in the dielectric constant obtained by the PSPS measurement, J. Qien et al proposed a structural model; CyDs with thiol groups form monolayer, but when long spacers exist between CyD and thiol groups as shown in Fig. 1(b), they form a quasi-doublelayer structure.[11] For further development as a recognition sensor, it is very

important whether the adsorbed layer is a monolayer or a quasi-doublelayer.

In our recent study by using scanning tunneling microscopy (STM),[12] we analyzed the growth process of the β-CyD molecules modified with lipoamide residue (LP-β-CyD) on Au(111) surface, and revealed that the LP-β-CyD molecules formed a monolayer instead of the quasi-doublelayer structure. In addition, the monolayer was formed through the island formation process, which is based on the attractive interaction between adsorbed molecules. These results show a strong contrast compared to the previous results obtained by such as PSPS technique. This difference is considered to be due to the uncertainty of the macroscopic analyses. As is well known, since the results obtained by macroscopic analyses give the information averaged over the surface, the results sometimes differ from the real microscopic structures. In addition, Au surface condition must critically influences on the structure of the adsorbed layers and their growth processes. In our STM observation, we used extremely flat and clean Au(111) surface prepared by vapor deposition on clean mica. However, all previous studies on the thiolated CyDs on Au surface have been performed by using Au wires or films, without confirming the quality of their surface structures.

In this study, we analyzed the molecular recognition ability of the LP-β-CyD on Au(111) system by measuring the cyclic voltammetry for the samples prepared by Au(111) substrate characterized by STM on an atomic scale.

Fig. 1 shows the schematic structures of (a) β-CyD (consisting of seven glucopyranose units), (b) LP-β-CyD, which is modified with a lipoylamide residue chemically added onto the primary hydroxyl side.

The Au(111) substrates were prepared by the vapor deposition of about 75-nm-thick Au films onto freshly cleaved mica sheets. During Au deposition, temperature of the mica substrates was kept at 450°C. The deposition rate was 0.3∼1.0 Å/s, and base pressure was kept under 1.0×10^{-7} Torr. Following the deposition, they were annealed at 550°C for 2 h. After cooling under vacuum for approximately 12 hours, these substrates were stored in a chamber with N_2 gas flow. Before each experiment, each substrate was briefly annealed in H_2 flame, and immediately immersed into the 0.01mM EtOH solution containing LP-β-CyD molecules for an hour at room temperature. They were repeatedly rinsed with EtOH and dried with N_2 gas flow. According to previous studies, physisorbed molecules can be clearly removed by the rinsing process, and only chemisorbed molecules remain on the surface.[9]

All STM observations were performed in constant current mode in air at room temperature using Pt/Ir tips.

Cyclic voltammetry was performed using three-electrode potentiostat. The bare Au(111) substrate or LP-β-CyD modified Au(111) substrate was used as the working electrode, respectively. Pt wire and Ag/AgCl (3M KCl) were used as the counter and reference electrodes, respectively. The sweep rate was 100mV/s. Ferrocencarboxylic acid (FCA) and hexacyanoferrate (III) (HCF) were used as electroactive markers. Since FCA has low solubility in the electrolyte, 0.01M FCA was solved in *N, N*-dimethylformamide (DMF) solution first, and poured into the electrolyte solution. The amount of DMF solution was kept lower than 1% (v/v) in the total electrolyte solution.

Fig. 2(a) is a typical STM image of the Au(111) substrate used in this study. The Au(111)-22×$\sqrt{3}$ herringbone structure, which is known to appear on the clean and flat Au(111) surface,[13] was confirmed by STM before each experiment.

Fig. 2(b) shows a typical STM image of LP-β-CyD molecular layer self-assembled on a Au(111) substrate. As shown in Fig. 2(b), LP-β-CyD molecules are densely adsorbed on all over the Au(111) surface. In the analysis of the electrochemical measurement, Suzuki et al. reported that 12 h immersion time was necessary to form a monolayer on a rough Au surface in the 1mM EtOH solution of LP-β-CyD.[6] However, we confirmed that the monolayer on Au(111) surface shown in Fig. 2(b) was obtained by 1 h immersion time in 0.01mM EtOH solution of LP-β-CyD. These results strongly indicate the importance of the quality of the Au surface as expected.

A magnification of Fig. 2(b) is shown in Fig. 2(c). The LP-β-CyD monolayer on Au(111) surface forms a disorder structure as shown in Fig. 2(c). On the other hand, from recent reports, n-alkanethiols are known to form the order structures on Au(111) surface. For n>9, the molecules form ($\sqrt{3} \times \sqrt{3}$)R30° structure[14] and for shorter chains, a $p \times \sqrt{3}$ ($8 \leq p \leq 10$) lattice and two-dimensional liquid phase were formed.[15] In

addition, the aromatic thiols such as 4-mercaptopyridine, was also observed to form an ordered lader-like structure on Au(111) surface.[16] In the self-assembled monolayers, their molecular structures are governed by the interactions such as the chemisorption of the thiol groups with Au surface, nonbonded interaction (e. g., van der Waals, electrostatic one) between molecules, and the spatial structure of the adsorbed molecules.[17] The symmetry of LP-β-CyD molecule is lower compared to those of the n-alkanethiol and aromatic molecules without CyD, as shown Fig. 1, and CyD molecules are rather rigid. Therefore, the uniformity of nonbonded interaction between molecules is considered to become poorer due to the lower density of the thiol groups of lipoylamide residue on Au(111) surface, and resulting in the observed disordering in the arrangement on the surface.

Fig. 3(a) shows the typical cyclic voltammogram of Au(111) substrate used for this study in the aqueous of 0.1M H_2SO_4 solutions. The anodic wave in the voltammogram of Au(111) begins at 1.1V and shows two peaks corresponding to the well known electrochemical oxidation process of the clean Au(111) surface.

In order to clarify the molecular recognition ability of the CyD/Au monolayer, we performed CV measurements using two electroactive marker; ferrocenecarboxylic acid (FCA) and hexacyanoferrate (III) (HCF). Both molecules are known to show reduction and oxidation response on Au surface, namely, redox response. However, FCA molecules can be included into β-CyD cavity, but HCF molecules can not be. Therefore, if the monolayer structure is formed with the CyD cavity being perpendicular to the surface, the oxidation-reduction current is expected to be observed only for the case of the FCA molecules (Fig. 1(d)).

Fig. 3(b) shows the cyclic voltammograms of the 1mM HCF for the bare Au(111) substrate (solid line) and LP-β-CyD/Au(111) structure (dotted line),
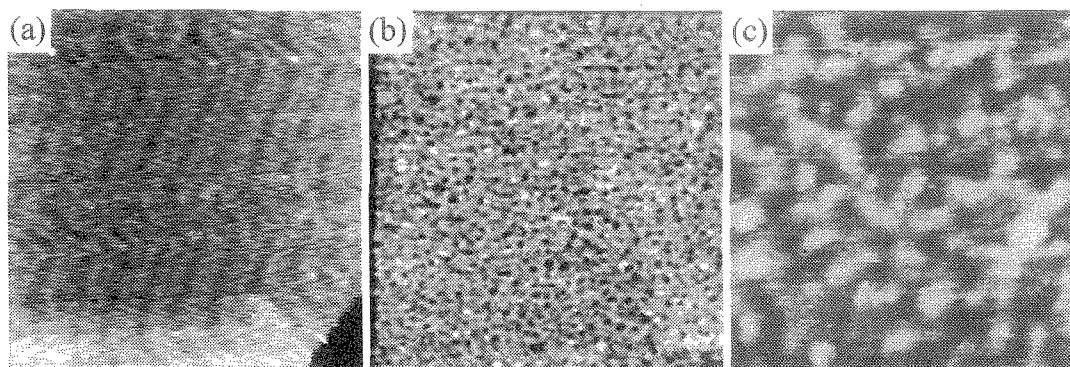

Fig. 2. STM images of (a) Au(111)-22×$\sqrt{3}$ herringbone structure (75nm × 75nm, Vt = 0.3V, Is = 1.5nA) (b)LP-β-CyD/Au(111) surface (150nm × 150nm, Vt = 0.75V, Is = 150pA). (c) magnification of (b) (30nm × 30nm, Vt = 1V, Is = 500pA).
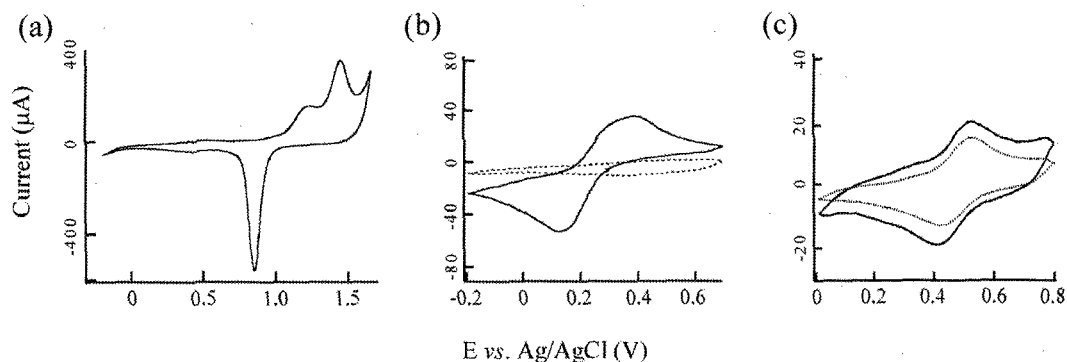
(a)   (b)   (c)

E vs. Ag/AgCl (V)

Fig. 3 Cyclic voltammograms of Au(111) surfaces measured in (a) 0.1M H_2SO_4, (b) 0.1M H_2SO_4+1mM HCF, and (c) 0.1M Na_2SO_4+0.1mM FCA . Solid and dotted lines show the results obtained for the bare Au(111) surface and LP-β-CyD / Au(111) surface, respectively.

respectively. Redox response was clearly observed for the bare Au(111) substrate, however, for the case of the LP-β-CyD monolayer on Au(111) substrate, almost no redox response appeared, as expected.

On the other hand, Fig. 3(c) shows the cyclic voltammograms of the 0.1mM FCA for the bare Au(111) substrate (solid line) and LP-β-CyD/Au(111) structure (dotted line), respectively. In both cases, redox response was observed. The result indicates that the FCA molecules penetrate the β-CyD cavity, and redox reaction appeared.

Redox reaction is almost completely blocked for the case of HCF molecule (Fig. 3(b)). On the other hand, in the case of FCA marker, the observed redox response is quite similar for the both cases with or without LP-β-CyD molecules on the Au surface (Fig. 3(c)). Since the redox currents are proportional to the electrode area, the obtained results strongly indicate that, (1) LP-β-CyD molecules form almost the perfect monolayer on Au(111) surface, which corresponds well with the STM image in Fig. 2. (2) LP-β-CyD molecules are adsorbed on Au(111) with their cavity axis aligned perpendicular to the surface.

Conclusively, we observed by STM the formation of the LP-β-CyD monolayer structure on the atomically clean and flat Au(111) surface. Immersion time necessary to form the monolayer was 1/10 of that previously reported using a rough Au surface, despite that the molecular concentration of the LP-β-CyD solution was 1/100. From the results of the cyclic voltammetry measurements using two electroactive marker; HCF and FCA molecules, selective permeability was shown clearly, indicating that the LP-β-CyD monolayer is formed and the molecules are adsorbed on the Au(111) surface with their cavity axis aligned perpendicular to the surface. High potential of the LP-β-CyD/Au structure as a novel molecular recognition sensor was clearly demonstrated.

Reference

1) A. Ulman, An Introduction to Ultrathin Organic Films, Academic Press, Boston, MA, 1991.
2) A. Kumar, et al., Acc. Chem. Res., 28, 219 (1995).
3) R. C. Tiberio, et al., Appl. Phys. Lett., 62, 476 (1993).
4) M. T. Rojas, R. Königer, J. F. Stoddart and A. E. Kaifer, J. Am. Chem. Soc. 117, 336 (1995).
5) J. Szejtli. Comprehensive Supramolecular Chemistry, ed. J.-M. Lehn (Pergamon, London, 1996) 1ˢ ed., Vol. 3, Chap. 2, p.5.
6) I. Suzuki, K. Murakami, J. Anzai, T. Osa and P. He, Mat. Sci. and Engineering. C6, 19 (1998).
7) P. He, et al., Anal. Chim. Acta. 337, 217 (1997).
8) J-Y. Lee, et al., J. Phy. Chem. B. 102, 9940 (1998).
9) M. Weisser, G. Nelles, P. Wohlfart, G. Wenz and S. M-Neher, J. Phys. Chem. 100, 17893 (1996).
10) G. Nelles, et al., J. Am. Chem. Soc. 118, 5039 (1996).
11) J. Quian, et al., Langmuir, 13, 7092 (1997).
12) S. Yasuda, I. Suzuki, T. Nakamura, M. Matsumoto, M. Komiyama and H. Shigekawa, Appl. Phys. Lett, 76, 643 (2000)
13) D. D. Chambliss, R. J. Wilson, and S. Chiang, Phys. Rev. Lett. 66, 1721 (1991).
14) C.A. Widrig, C. A. Alves and M. D. Porter, J. Am. Chem. Soc. 113, 2805 (1991)
15) G. E. Poirier, et al., Langmuir 10, 2853 (1994)
16) T. Sawaguchi, et al., Langmuir 14, 3565 (1998)
17) H. Sellers, A. Ulman, Y. Shnidman and J. E. Eilers, J. Am. Chem. Soc. 115, 9389 (1993)
18) W. Sheen, et al., Appl. Phys. Lett., 62, 476 (1993).