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Takako Iizuka-sakano [a], Katsuhiko Fujita [a b], Takashi Isoshima [a c], Tatsuo Wada [a c] & Hiroyuki Sasabe [a c d]

[a] Frontier Research Program (FRP), The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako, Saitama, 351-0198, Japan

[b] Department of Applied Science for Electronics and Materials, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, 816-8580, Japan

[c] Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Co. (JST), 2-1 Hirosawa, Wako, Saitama, 351-0198, Japan

[d] Chitose Institute of Science and Technology (CIST), 758-65, Bibi, Chitose, Hokkaido, 066-8655, Japan

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TAKAKO IIZUKA-SAKANO[a], KATSUHIKO FUJITA[ab], TAKASHI ISOSHIMA[ac], TATSUO WADA[ac] and HIROYUKI SASABE[acd]

[a]*Frontier Research Program (FRP), The Institute of Physical and Chemical Research (RIKEN), 2–1 Hirosawa, Wako, Saitama 351–0198, Japan,* [b]*Department of Applied Science for Electronics and Materials, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816–8580, Japan,* [c]*Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Co. (JST), 2–1 Hirosawa, Wako, Saitama 351–0198, Japan and* [d]*Chitose Institute of Science and Technology (CIST), 758–65, Bibi, Chitose, Hokkaido 066–8655, Japan*

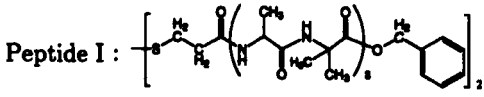
We numerically investigate molecular arrangement and orientation in the self-assembled peptide monolayer adsorbed on gold considering dipoles of each amide group in peptides and a dipole due to the Au-S bond at the chemisorption site. We investigate a single peptide adsorbed on gold and SAM of two dimensional crystal. Comparing their results with that of ignoring Au-S dipole, we show that molecules can take an orientation standing normal to the surface by Au-S dipole.

Keywords: self-assembled monolayer; helical peptide; Au-S bond; dipole-dipole interaction; molecular arrangement

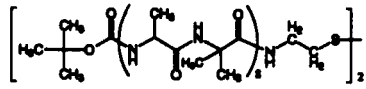
INTRODUCTION

To study the formation of monolayers by self-assembly is important not only to understand the nature of self-assembly itself but also to

design and control their structure. Organosulfer helical peptides,

Peptide I : 

and

Peptide II :  ,

form a self-assembled monolayer (SAM)[1] adsorbed on gold surface [2]. They possess molecular dipole moments of 55 D which are in opposite sense to each other on the gold surface. Such large dipole moments provide significant dipole-dipole interactions playing an important role in the molecular arrangement. We have discussed molecular arrangement of the SAM numerically with multiple dipole model in which we consider the dipoles of amide groups and exactly treat dipole-dipole interaction between them[3]. Meanwhile it is experimentally reported that the SAM of Peptide I shows larger thickness than that composed of Peptide II[2]. This suggests a factor which affects the molecular arrangement: dipole due to the Au–S bond at the chemisorption site. In this paper, we modify multiple dipole model considering dipole due to the Au–S bond at the chemisorption site and discuss the influence of it.

MODEL

In Peptides I and II, 16 amide groups predominantly contribute to the molecular dipole. We regard the dipole of each amide group as the same : 3.4 D (= 55 D/16) parallel to the helix axis[3]. Figure 1 shows Peptide II, and Peptide I has the dipole in opposite sense. We also consider the dipole (p_{SAu}) due to Au–S bond at the chemisorption site as shown in Figure 1. The senses of p_{SAu} in Peptide I and II are the same.

In the calculation, we neglect the dispersion force and employ a hard core potential in order to avoid overlap between molecules.

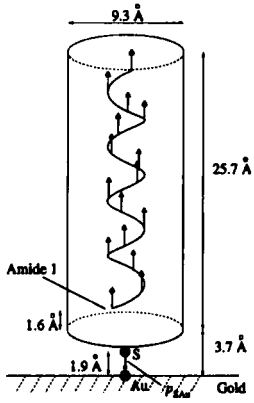


FIGURE 1
Model of Peptide II

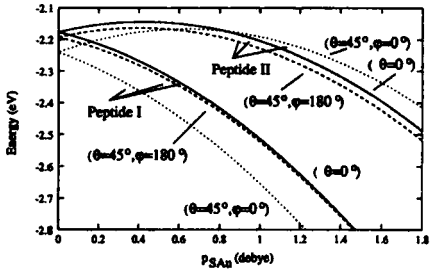


FIGURE 2: energy change depending on p_{SAu} when only one Peptide I or II is adsorbed on gold.

We exactly include the dipole-dipole interaction between molecules separated by less than the cut-off distance of 9.98Å×16. We treat the electric potential due to the metal surface with the method of images.

We calculate energy of a molecule with various orientation and discuss stable molecular orientation.

RESULTS AND DISCUSSION

First, we investigate what orientation is stable when only one peptide is adsorbed on gold. Figure 2 shows the energy change depending on p_{SAu} when a molecule tilts at an angle θ of 0° and 45° from the surface normal and when its projection to the surface forms an angle φ of 0° and 180° from the direction of Amide 1, the amide group closest to the binding site. We can see the following features: 1) Peptide I has less energy than Peptide II at $p_{SAu} \neq 0$. This shows there is a possibility that Peptide I is adsorbed faster than Peptide II. 2) The gradient in Peptide I is larger than Peptide II. This shows Peptide I is easier to tilt than Peptide II. Then, the SAM of Peptide I is

thinner than that of Peptide II. This result is, however, inconsistent with the experimental results.

The experimental results can be qualitatively elucidated by considering the influence of neighboring Au–S dipoles. An interaction between a molecule and the neighboring Au–S dipoles becomes negative (positive) when Peptide I (II) is adsorbed normal to the surface because the direction of the molecular dipole is parallel (antiparallel) to the neighboring Au–S dipoles. Then, Peptide I tends to stand normal to the surface and the SAM can take large thickness as in the experimental results.

Next, we investigate the SAM, assuming that it forms a crystal with hexagonal two dimensional lattice. We find there are two kinds of (meta-) stable orientations : tilting and standing normal to the surface in each crystal arrangements. Although the tilting orientation is more stable at $p_{SAu} = 0$, the standing orientation becomes more stable when p_{SAu} is large.

As a conclusion, the Au–S dipole presents a significant influence to orientation and arrangement of helical peptide SAM : it makes Peptide I stand and the thickness of the SAM large. These numerical results are consistent with the experimental results.

Acknowledgments

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