

論文の内容の要旨

Dissertation Abstract

Controlling Interfacial Interactions of π -Conjugated Molecules on Noble Metal Surfaces (π 電子系分子と不活性金属の界面における相互作用の制御)

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Conjugated molecules are receiving much attention as promising materials with high charge-carrier mobility and environmental stability for molecule-based electronics.^[1] These include not only organic thin-film devices (i.e., organic light emitting diodes (OLED), organic thin-film transistors (OTFT), and organic photovoltaic (OPV)) as well as molecular devices based on a single molecule. Using π -conjugated molecules in electronic devices is also expected to offer excellent controllability in geometric and electronic structures of active components which play a critical role in determining device functionality.^[2]

It is now recognized that interfacial contacts between π -conjugated molecules and metal electrodes play roles as important as the molecules themselves in molecule-based electronics. As shown in **Figure 1**, the interfaces between molecules and metal electrodes are where charge transfers between active components and electrodes occur in organic thin-film devices, and such interfacial contacts are also present in any persuasive model for molecular devices.^[2] In addition, various interactions at the interfaces between molecules and metal electrodes (i.e., surface-molecule and intermolecular interactions) are of great importance in organic epitaxy and the architecture of nanostructures or molecular networks in reference to size and structural control of the system,^[3-5] and the registry of a molecule on a metal surface governed by interfacial interactions has strong correlation with the subsequent film growth and its electronic structure.^[6,7] Thus, how to understand and control interfacial interactions is one of today's challenging issues not only in the field of surface science, but also in various other fields of science and engineering.

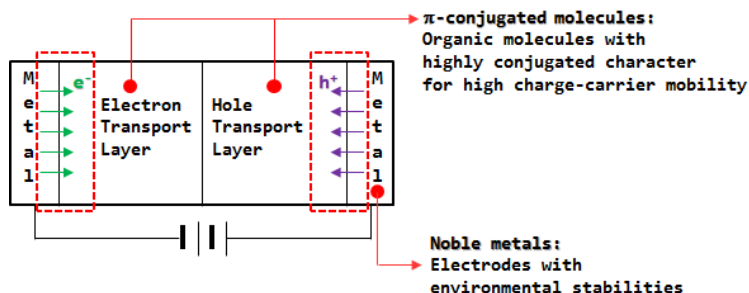


Figure 1. Schematic illustration of charge-injection in organic thin-film devices.

Throughout my doctoral studies, I investigated “*how to understand and control various interfacial interactions between π -conjugated molecules and noble metal surfaces*” with well-designed model systems by means of scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and density functional theory (DFT) calculations. Noble metals have been widely used as electrodes for molecule-based devices owing to their chemical inertness, differently from other transition metals which cause oxidation or instability.^[1,8] The use of noble metal substrates makes it possible to control surface-molecule interactions corresponding to the

work-function of metal, surface lattices and surface templating. Moreover, since π -conjugated molecules normally lie flat on noble metal surfaces, tuning interfacial interactions can be achieved by careful design of the molecules. Here, the geometric and electronic structures of π -conjugated molecules on noble metal surfaces were probed by STM and STS measurements, and DFT calculations also performed to elucidate the experimental results and to describe interfacial interactions in detail.

The Most Intrinsic Interfacial Interactions in Weak Adsorption System of a π -Conjugated Molecule on the Noblest Metal Surface

A well-controlled model system of a π -conjugated molecule on the noblest Au(111) surface was studied to investigate the most intrinsic interfacial interactions between a π -conjugated molecule and the noblest metal surface. Frontier orbitals of molecular adsorbates play a crucial role in the adsorption process when it involves chemical interactions via orbital hybridization. However, in the case of “weak” non-bonding adsorption (so-called physisorption) of a π -conjugated molecule on the noblest Au surface, it is controversial as to whether orbital interaction still contributes to determining adsorption geometry and structure. Most difficulties involved in probing this issue arise mainly from the chemical inertness of the Au surface^[8] when added to the practical problems in the assignment of exact adsorption geometries of weakly adsorbed species at the single-molecule level caused by a lower activation barrier for diffusion. Thus far van der Waals (vdW) interaction has been considered the principal way of describing such a weak adsorption system. The possibility of orbital interaction has been excluded thus far due to such difficulties, and vdW interaction with a shallow potential minimum has been the main consideration in describing the adsorption geometry and structure of a π -conjugated molecule on the Au surface. To disentangle the difficulties in studying such weak adsorption, a well-defined system of dehydrobenzo[12]annulene (DBA) on the Au(111) surface was used. DBA has a well-matched three-fold symmetry with the Au(111) surface as well as a planar π -conjugated framework without any functional groups that might chemically interact with the surface Au atoms.

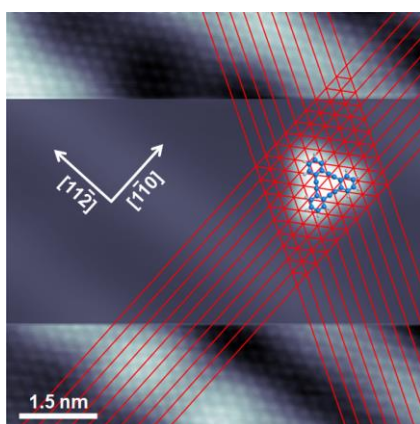


Figure 2. Experimentally determined adsorption geometry of DBA/Au(111). Top and bottom regions were obtained with a sample bias (V_s) of -2 mV and tunneling current (I_t) of 9.0 nA, whereas the middle region was obtained at V_s of -500 mV and I_t of 0.4 nA.

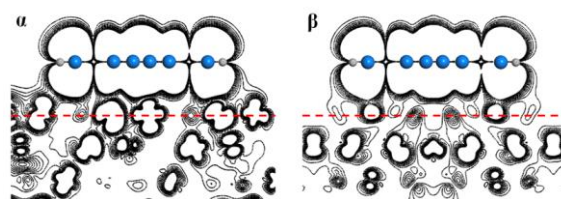


Figure 3. PCD distributions for two local minimum states. The experimentally determined adsorption structure (designated “ α ”) is most favorable, followed by a second local minimum structure (designated “ β ”). Dashed line indicates a center of the first layer of Au(111), and the positions of six carbon atoms of DBA are depicted by dots.

Because low coverage deposition at room temperature prevents lateral interaction between adsorbates and enables reliable detection of the proper geometry of DBA at the single-molecule level, and since the Au atoms in the vicinity of DBA may be observed by varying the tunneling conditions and DBA appears as an easily distinguishable triangular shape, it is feasible to accurately determine the adsorption geometry of DBA/Au(111), which adsorbs to a hollow site as shown in **Figure 2**. Based on the experimentally determined adsorption structure, DFT calculations were performed to elucidate interplay between DBA and the Au(111) surface in weak adsorption. By comparison of inequivalent local minimum structures, it has been clearly shown that structural stability of the system originates mainly from the electronic structures at the molecule-surface interface. Energy alignment between the π state of DBA and the Au $5d_{z^2}$ states gives rise to a difference in the interaction strength corresponding to molecular orientation, which is related to the degree of overlap between the molecular orbital states of DBA and the Au d states. The variation in the strength of orbital interaction corresponding to the adsorption geometries is well explained by a qualitative comparison of the partial charge density (PCD)

distributions as shown in **Figure 3**, and the optimal interfacial distance is also closely related to the energy level alignment between the π components of DBA and the Au d states. Further experiments to probe the orbital interaction of a π -conjugated molecule on the noblest Au surface showed that it can play a critical role even in elementary surface processes (i.e., lateral manipulation of a single molecule, and further two-dimensional (2D) molecular assembly).

Control of Various Interactions at the Interface between π -Conjugated Molecules and Noble Metal Surfaces

Molecular ordering and the structure of π -conjugated molecules on a noble metal surface are normally governed by a complex process that operates through various surface-molecule and intermolecular interactions (e.g., covalent bonding, hydrogen bonding, dipole-dipole interaction, metal-ligand coordination, vdW interaction, and surface templating) at the interface between molecules and surfaces.^[4, 5] The numerous factors involved in the prediction and control of molecular structures make systematic study and sophisticated molecule design essential to the achievement of desired structures. The control of variables for this research topic is mainly achieved by careful selection of the metal substrate and chemical tuning of the molecule.

First, to exclude the surface templating effect in the molecular ordering of DBA on noble metal surfaces, the Ag(111) surface was used for comparison with the Au(111) surface. As there is no surface templating effect on Ag(111), the molecular ordering of the DBA molecules is widely uniform on the Ag(111) surface as opposed to the chain-like structure of DBA along the face-centered-cubic (fcc) domain of Au(111). The intrinsic interfacial interaction between the molecule and the surface (i.e., the interaction between the π components of the molecule and the d states of the noble metal) is still maintained even though the strength of the interaction locally differs due to a change in the metal work-function. In addition, the transition of molecular ordering corresponding to coverage of the molecule was easily achieved on the Ag(111) surface, because intermolecular interaction is more strongly reflected on surfaces not involved in surface templating.

Second, controllable molecular ordering on the Au(111) surface has been demonstrated through the chemical tuning (alkoxy substitution) of DBA. Fine-tuning the subtle balance between molecule-molecule and surface-molecule interactions by changing the primary intermolecular interaction through modification of the alkoxy group promises to permit control of the formation of molecular ordering. The π -conjugated triangular core of each alkoxyated DBA derivative is locked on a specific site on the Au(111) surface by the interaction between -O- and the Au surface atoms. Under this precondition, the intermolecular interactions have been tuned from the hydrogen bonding interaction to the chain-chain vdW interaction by substituting alkoxy groups (see **Figure 4**). Such tunable intermolecular interactions enable control of molecular ordering, i.e., restricting the number of polymorphs, and the introduction of domain-specific chirality.

Finally, more complex system was studied using bis([1,2,5]thiadiazolo)-tetracyanoquinodimethane (BTDA-TCNQ). By comparison of molecular ordering on various noble metal surfaces (i.e., Au(111), Ag(111), and Cu(111)), different growth mechanisms were investigated aimed at achieving the formation of widely uniform geometric and electronic structures. In addition to STM measurements, STS and STS mapping techniques were used to elucidate the electronic structures in combination with DFT calculations. Although data

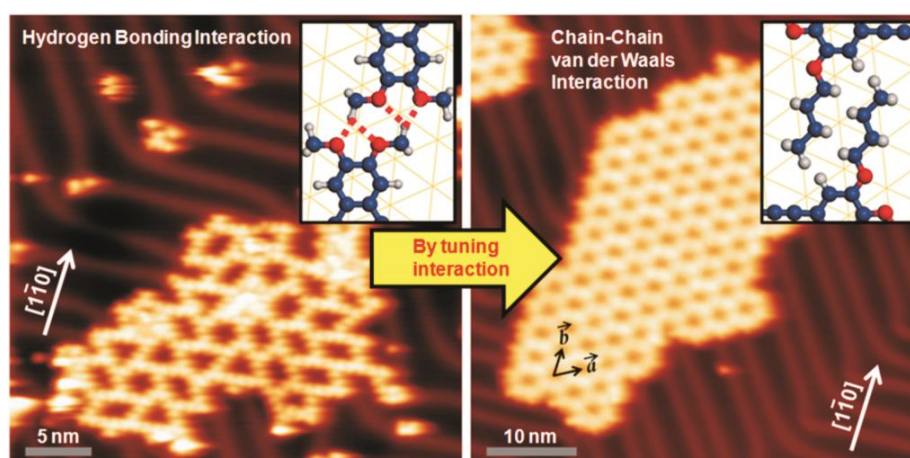


Figure 4. STM images of 2D molecular network formed by alkoxyated derivatives of DBA ($V_s = 2.0$ V, $I_t = 0.2$ nA).

analysis is still ongoing, it is expected that the study will demonstrate anisotropic electron confinement owing to strong intermolecular interaction well-balanced with surface-molecule interaction.^[9] For potential applications, molecular structures on amorphous Au and the vicinal Au(788) surfaces have been demonstrated on the basis of the result on Au(111).

In summary, my doctoral studies are aimed at proposing a better way to understand interfacial contacts between π -conjugated molecules and noble metal surfaces, and methodology to control interfacial interactions. Since interfacial interactions have strong correlation with geometric and electronic structures of the system as well as single adsorption events, I anticipate that this study will provide not only deeper insight into the interfacial contacts between π -conjugated molecules and noble metal surfaces, but also a general basis for designing the architectures of molecule-based electronics.

References

- [1] C. D. Dimitrakopoulos and P. R. L. Malenfant. Organic thin film transistors for large area electronics. *Adv. Mater.* **14**, 99 (2002).
- [2] X. Y. Zhu. Electronic structure and electron dynamics at molecule-metal interfaces: Implications for molecule-based electronics. *Surf. Sci. Rep.* **56**, 1 (2004).
- [3] S. R. Forrest. Ultrathin organic films grown by organic molecular beam deposition and related techniques. *Chem. Rev.* **97**, 1793 (1997).
- [4] J. V. Barth, G. Costantini and K. Kern. Engineering atomic and molecular nanostructures at surfaces. *Nature* **437**, 671 (2005).
- [5] L. Bartels. Tailoring molecular layers at metal surfaces. *Nature Chem.* **2**, 87 (2010).
- [6] H. Ishii, K. Sugiyama, E. Ito and K. Seki. Energy level alignment and interfacial electronic structures at organic/metal and organic/organic interfaces. *Adv. Mater.* **11**, 605 (1999).
- [7] H. Yamane, K. Kanai, Y. Ouchi, N. Ueno and K. Seki. Impact of interface geometric structure on organic-metal interface energetics and subsequent films electronic structure. *J. Electron. Spectrosc. Relat. Phenom.* **174**, 28 (2009).
- [8] B. Hammer and J. K. Nørskov. Why gold is the noblest of all the metals. *Nature* **376**, 238 (1995).
- [9] R. Temirov, S. Soubatch, A. Luican and F. S. Tautz. Free-electron-like dispersion in an organic monolayer film on a metal substrate. *Nature* **444**, 350 (2006).

Publication

4. Ju-Hyung Kim, Jaehoon Jung, Miyabi Imai, Eisuke Ohta, Yuki Suna, Takanori Fukushima, Takuzo Aida, Yousoo Kim and Maki Kawai. Geometric and electronic structures of organic-metal hybrid system: bis([1,2,5]thiadiazolo)-tetracyanoquinodimethane on noble metal surfaces. *in preparation* (2012).
3. Juyeon Park, Ju-Hyung Kim, Jaehoon Jung, Kazukuni Tahara, Yoshito Tobe, Yousoo Kim and Maki Kawai. Steering organic crystalline thin film via cooperative interfacial and π -conjugated molecular interaction. *in preparation* (2012).
2. Ju-Hyung Kim, Jaehoon Jung, Kazukuni Tahara, Yoshito Tobe, Yousoo Kim and Maki Kawai. Orbital interaction in weak adsorption of a π -conjugated molecule on the noblest gold surface. *in preparation* (2012).
1. Ju-Hyung Kim, Kazukuni Tahara, Jaehoon Jung, Steven De Feyter, Yoshito Tobe, Yousoo Kim and Maki Kawai. Ordering of molecules with π -conjugated triangular core by switching hydrogen bonding and van der Waals interactions. *submitted* (2012).

Presentation

2. "How does a pi-conjugated molecule recognize a specific site on the noblest metal surface?" (Oral), Japan Physical Society (JPS) Fall Meeting, Japan, September 2011.
1. "Two dimensional molecular networks of triangular dehydrobenzo[12]annulene and its derivatives on the Au(111) surface" (Oral), Asian Conference on Nanoscience and Nanotechnology 2010 (AsiaNANO2010), Japan, November 2010.