Usage Report for Fiscal Year 2019

Project Title:

Theoretical study of interaction between tunneling electrons and individual molecules at surfaces

Name:
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1. Background and purpose of the project, relationship of the project with other projects

During the past decade, computer simulations based on a quantum mechanics have developed an increasingly important impact on solid-state physics and chemistry and on materials science. In field of material science, the surface chemistry is fundamentally important in many areas, such as molecular electronics, heterogeneous catalyst, fuel cell, etc. The adsorption of molecules onto a surface is a necessary prerequisite to any surface mediated chemical process. Understanding the bonding nature between the molecule and the surface on the basis of the electronic structure is therefore one of the most important issues in this field. The computational methods like density functional theory (DFT) have played a prominent role to elucidate the interaction between the molecule and the surface. Combination of DFT calculation and the method based on quantum many-body theory also provides a powerful approach to describe magnetism and dynamics on the surface with a high accuracy and efficiency. In addition, the computational method can be useful to study the details of energy transport and conversion among photon and electrons mediated with adsorbate at solid surfaces in the nanoscale regime. From the theoretical investigation of the adsorbed molecule on surface in combination with scanning tunneling microscopy and spectroscopy (STM/STS) experiment, we could expect the following research goals; 1) the deep understanding of the chemical/physical properties of an adsorbate on the surface not only in ground state but also in excited state, 2) the fine control of the chemistry on the surface. The overall purpose of our theoretical work is closely related with research goal - describing the details of energy transport and conversion at solid surfaces and interfaces in the nanoscale regime - of our laboratory, Surface and Interface Science laboratory.

2. Specific usage status of the system and calculation method

We have been studying the molecular adsorption on the well-defined metal surface using computational method in combination with experimental method. In our studies, first-principles simulations have been carried out using the Vienna Ab-initio Simulation Package (VASP) code and Quantum Espresso code in the density functional level of theory. The pure DFT methods have been mostly used and the inner electrons are replaced by projector augmented wave pseudopotentials (PAW). The climbing image nudged elastic band method (CI-NEB) is used to determine the transition states that are confirmed by imaginary frequency modes. In most of cases, STM image simulations are performed using Tersoff-Hamann approach. The computational results are compared with the available experimental result obtained from STM in our group. For the gas phase molecules, the Gaussian09 and Gaussian16 programs with atomic-orbital basis set are also effectively utilized to obtain stable geometries and corresponding electronic structures.

We also have been studying the many-body phenomena in molecular adsorption system, in particular the Kondo effect. The characteristic electronic state resulting from the Kondo effect, so-called Kondo singlet state appears as a sharp peak structure (Kondo peak) at the Fermi level (EF) in STS. In order to simulate the Kondo peak, we build numerical renormalization group (NRG) code and the STS simulation code based on the Keldysh Green's function method.

Electron-transport and luminescence properties of systems, that consist of a single molecule, substrate and the STM tip, are also our main research target. DFT calculations and the first-principles Green's function methods based on the many-body perturbation theory (MBPT) are used to investigate the basic properties of components, i.e., the adsorption nature of molecules and dielectric properties of the substrate as well as the excited electronic states of molecules with a high accuracy and efficiency. Based on the obtained results, we construct an effective model and investigate electron dynamics in transport and luminescence processes using the Keldysh Green's function method.

３． Result

(1) Molecular adsorption on solid surface: From single molecule to molecular network [Juyeon Park, Ju-Hyung Kim, Sunmi Bak, Kazukuni Tahara, Jaehoon Jung, Maki Kawai, Yoshito Tobe, and Yousoo Kim, Angew. Chem. Int. Ed. 58 (2019) 9611]

We investigated a novel chiral phenomenon on a surface in terms of organizational chirality, i.e., meso-isomerism with a lemniscate-type (∞) molecular arrangement, through the hierarchical formation of 2D supramolecular assemblies of achiral planar hydrocarbon molecules on Ag(111), which was investigated using scanning tunneling microscopy (STM) under ultra-high vacuum (UHV) conditions and density functional theory (DFT) calculation.

High-resolution STM image of a single isolated DBA molecule on the Ag(111) surface clearly reveals that the molecule lies in a planar fashion (Figure 1a). The DBA molecule adsorbs to a three-fold hollow site on the Ag(111) surface, and three rotational symmetry axes in the molecular plane of DBA are displaced from the <112> surface axes by ~20°. In low coverage, the DBA molecules on the Ag(111) surface consequently form four stereoisomers at the single-molecule level (designated "α1", "α2", "β1", and "β2", as presented in Figure 1b), which give rise to two different pairs of DBA/Ag(111) overall (i.e., α1-α2 and β1-β2). As indicated in Figure 1c, all DBA molecules have identical adsorption geometries, which are classified as one of the four stereoisomers of DBA/Ag(111).

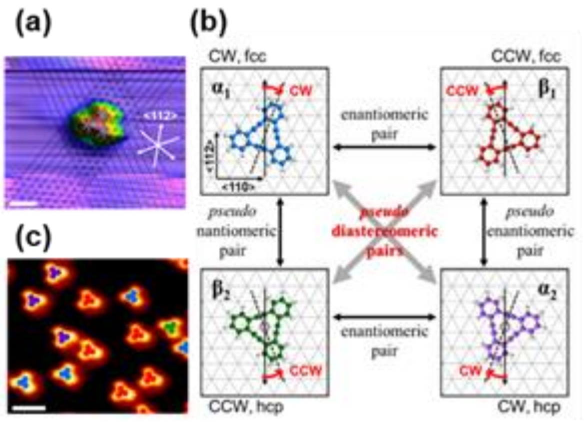

Figure 1. (a) STM image of an isolated DBA molecule on Ag(111) (top and bottom: V_s = 2 mV, I_t = 5.0 nA; middle: V_s = 1000 mV, I_t = 0.5 nA; scale bar (S) = 1.0 nm). (b) 2D isomeric relationship of DBA/Ag(111) according to the <112> and <110> surface axes. Grey circles indicate the second sub-atoms of Ag(111) beneath the adsorbed DBA molecules on the hcp hollow sites. (c) Low-coverage STM image of DBA/Ag(111) (θ = 0.2 ML, V_s = 1900 mV, I_t = 0.6 nA, S = 2 nm). Blue, purple, red, and green symbols represent the four stereoisomers.

Based on the experimental observation, we performed periodic van der Waals density functional (vdW-DF) calculations to investigate the adsorption geometries of DBA on Ag(111) at both fcc and hcp hollow sites. The optimized molecular orientations with respect to the <112> surface axes for the fcc and hcp sites are 19.1° and 20.0°, respectively, which are in good agreement with the experimental observations (i.e., the rotational symmetry axes of DBA are displaced from the <112> surface axes by ~20°). The evaluated adsorption energies (Eads) for DBA adsorbed at the fcc and hcp hollow sites of Ag(111) are -2.47 and -2.45 eV, respectively, and thus lead to a subtle difference in Eads (0.02 eV). Also, the optimized adsorption distances (dads) for the fcc and hcp sites are also identical (3.09 Å). Thus, nearly equal adsorption priority for the two hollow sites, as expected from the computational results, reasonably explain the experimental observations as a random distribution of the four stereoisomers. We further examined the potential energy surfaces for the rotation of a DBA molecule about the surface normal at the fcc and hcp hollow sites of Ag(111) using the optimized geometries, respectively, where the molecule was rotated by 5° increments from -60° to +60° with respect to the <112> surface axes (see Figure 2). Two kinds of local minima were identically observed at ±20° (less-symmetric C_3 configuration) and ±60° (highly-symmetric C_{3v} configuration) for the rotation of DBA about the surface normal at both the fcc and hcp sites, respectively. The global minimum with the C_3 configuration shows the highest Eads of 2.47 (2.45) eV and is more stable than the C_{3v} configuration by 0.12 (0.11) eV at the fcc (hcp) hollow site. Therefore, our calculations confirm that the experimentally observed adsorption geometry corresponds to a global minimum in the potential energy surface according to the rotation of a single isolated DBA molecule on a hollow site of Ag(111), and well demonstrate the two distinguishable enantiomeric pairs of DBA/Ag(111) (i.e., α1-β1 and α2-β2) at the single molecule level as shown in Figure 1b.

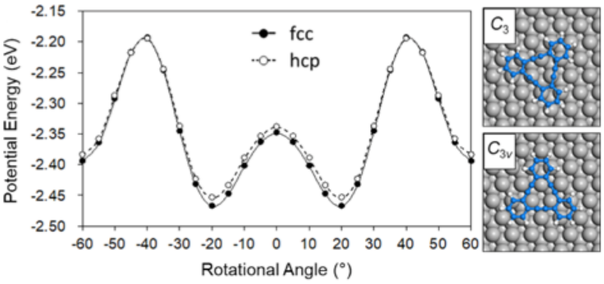

Figure 2. Potential energies due to the rotation of DBA about the surface normal at the fcc (solid line) and hcp (dotted line) hollow sites of Ag(111) with respect to the <112> surface axes. Geometries of both C3 (±20°) and C3v (±60°) configurations at the fcc site are also presented.

To gain deeper insight into the interfacial interactions of DBA/Ag(111), the projected density of states (PDOS) of two local minimum points (i.e., C$_3$ and C$_{3v}$ adsorption configurations) at both the fcc and hcp hollow sites were investigated as shown in Figure S3. The two most distinguishable occupied π-states of the DBA molecule (i.e., highest occupied molecular orbitals, HOMO and HOMO-1 states) are located at approximately -1.6 and -2.3 eV, respectively. Peak alignments between C 2p$_z$ and Ag 4d_(z^2) states and accompanied broadening of the molecular π-states (in particular, for the HOMO states) in the PDOS diagrams imply that an interfacial electronic coupling for the C$_3$ configuration is larger than that for the C$_{3v}$ configuration at both the fcc and hcp hollow sites. Therefore, the experimentally observed formation of surface chirality due to the adsorption of an individual DBA molecule on Ag(111) can be explained by the interfacial electronic structure resulting from orbital interactions between the z-components of molecular π and Ag d states according to the Newns-Anderson scheme.

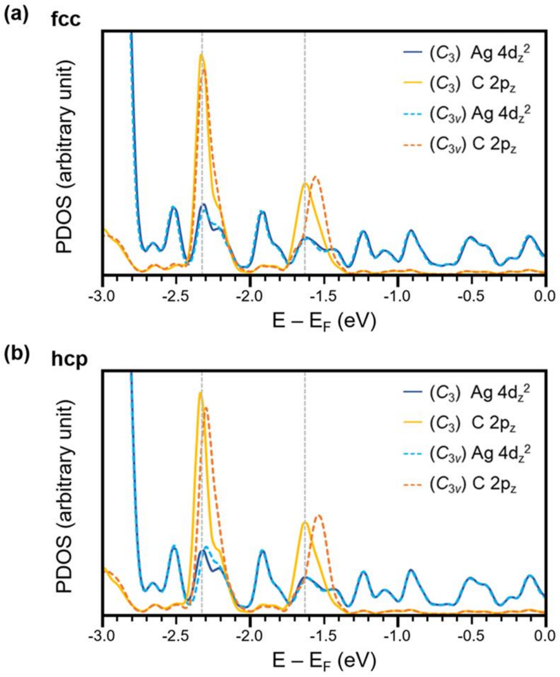

Figure 3. PDOS diagrams for the occupied π-states (C 2p$_z$), the HOMO and the doubly degenerated HOMO-1 states, of both C$_3$ and C$_{3v}$ geometry local minima with the 4d_(z^2) state of Ag(111) on fcc (a) and hcp (b) hollow sites.

This substrate-molecule interactions determine the adsorption geometry at the single-molecule level, which defines a unique diastereomeric conformation of DBA/Ag(111) in consideration of the second sublayer of Ag(111). The hierarchical evolution of organizational chirality spontaneously occurs via coverage-driven phase transitions; the subtle balance between substrate-molecule and intermolecular interactions results in the formation of a highly uniform 2D molecular network at each phase as follows.

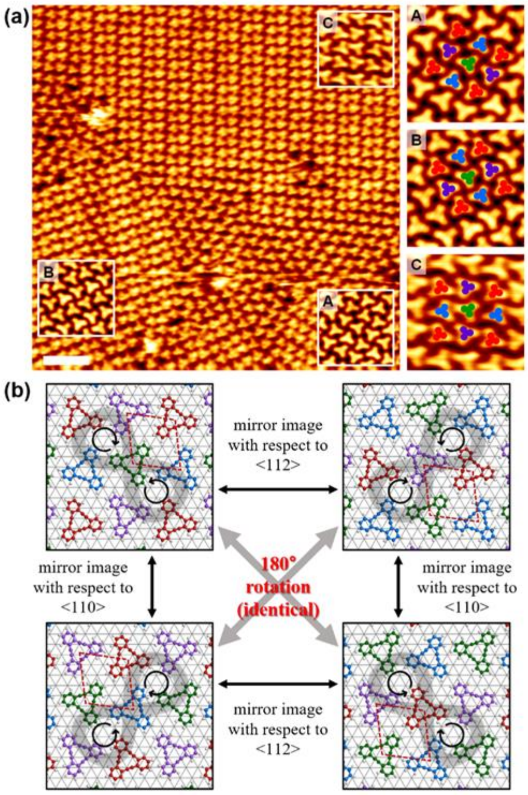

Figure 4. Emergence of a novel meso-isomeric configuration of DBA/Ag(111). (a) STM image of the elongated-square phase of DBA/Ag(111) at θ = ~1.0 ML (V_s = 1000 mA, I_t = 0.5 nA, S = 5 nm), representing three distinct directional domains with respect to Ag(111). (b) 2D isomeric relationship of the elongated-square phase of DBA/Ag(111) with a lemniscate-type (∞) configuration: reflecting through mirror planes along the <110> and <112> surface axes and rotating by 180°. The red dashed parallelograms indicate identical molecular arrangements.

At a coverage of ~0.4 ML, a quasi-three-fold hexagonally scattered phase of DBA/Ag(111) forms with a regular intermolecular center-to-center distance (dc-c = ~18.0 Å) between neighboring molecules, of which the quasi-ordered arrangement can be attributed to substrate-mediated long-range intermolecular repulsions via partial charge transfer between DBA and Ag(111). At a coverage of ~0.7 ML, a six-fold well-ordered porous honeycomb phase of DBA/Ag(111) forms through short-range intermolecular interactions such as vdW and –CH···π intermolecular attractions in balance with electrostatic intermolecular repulsions, leading to an interdigitating pattern and domain-specific organizational chirality. At a saturated one-monolayer coverage of DBA (~1.0 ML), the spontaneous transition to an elongated-square phase occurs and gives rise to a drastic change in the chiral characteristics of the molecular domains (from enantiomeric to meso-isomeric), which is induced by the optimization of –CH···π intermolecular interactions. (Figure 4)

(2) Magnetism of nanostructure on solid surface [H. Isshiki, K. Kondou, S. Takizawa, K. Shimose, T. Kawabe, E. Minamitani, N. Yamaguchi, F. Ishii, A. Shiotari, Y. Sugimoto, S. Miwa, Y. Otani, Nano Lett. 10 (2019) 7119]

An interface of molecule and metal has attracted much attention in the research field of nano-electronics because of their high degree of design freedom. Here we focus on spin-to-charge current conversion, inverse Edelstein effect (IEE), at Cu(111) surface covered by a single layer of lead (II) phthalocyanine molecules. The IEE originates from Rashba spin splitting of electronic band structure. Thud, it is negligible at clean Cu(111). However, the measurable electric voltage due to the spin pumping induced spin to charge conversion at a Cu/PbPc interface. The conversion coefficient, inverse Edelstein length, is estimated to be 0.40±0.06 nm, comparable with the largest Rashba spin splitting of interfaces with heavy metals. Interestingly, the Edelstein length strongly depends on the thickness of the molecule and takes a maximum value when a single layer of molecules is formed on the Cu surface. Comparative analysis between scanning probe microscopy and first-principles calculations reveal that the formation of interface state with Rashba spin splitting causes the inverse Edelstein effect. The thickness dependence would be due to the sensitivity of the Rashba spin-splitting at the interfacial state on the adsorption configuration of the molecules.

(3) Phonon and Electron-phonon coupling in semiconducting/2D materials [E. Minamitani, M. Ogura, S. Watanabe, Appl. Phys. Express, 12 (2019) 095001]

Heat generation in semiconducting materials has become a critical problem in modern nanoscale electronics. As the size of electric devices decreases, the power density and device temperature increase, which is one of the major factors contributing to the degradation of device performance and reliability.

The main carrier of heat in semiconductors is the phonon, which is a quantum of lattice vibration. Current theoretical frameworks require accurate prediction of the interatomic force in the solid. Density functional theory (DFT) calculation is one of the most well-established techniques for accurate force prediction, including the effect of changes in the electronic state with atomic displacement. However, the high computational cost limits the application of DFT calculation in thermal conductivity simulations.

Here we apply the high-dimensional neural network potential (HDNNP). We found that training procedure based on force makes the root mean square error between the forces predicted by HDNNP and DFT less than 40 meV/Å. As typical examples, we present the results of Si and GaN bulk crystals. The deviation from the thermal conductivity calculated using DFT is within 1% at 200 to 500 K for Si and within 5.4% at 200 to 1000 K for GaN.

(4) Raman spectra of self-assembled monolayers on gold electrode

We are developing new experimental technique, tip-enhanced Raman spectroscopy (TERS) in liquid environment, to achieve nanoscale Raman signal mapping of organic molecules on metal electrodes with local structural properties. While a gold tip enhances the incident electric filed as much as 100, TERS measurements still reacquire the highly Raman active molecules to be studied because the long accumulation of the Raman signal is hampered by instrumental instability. It is thus prerequisite to systematically study the Raman intensity as well as the vibrational energy for the various kinds of organic molecules (self-assembled monolayers (SAMs) on gold electrode). In this study, we have succeeded in obtaining Raman spectra of terphenylthiol (Ph_3SH) adsorbed on gold clusters (Fig. 5a)). We found that the simple gold dimer model is enough to reproduce the experimental Raman spectrum (Fig. 5(b)).

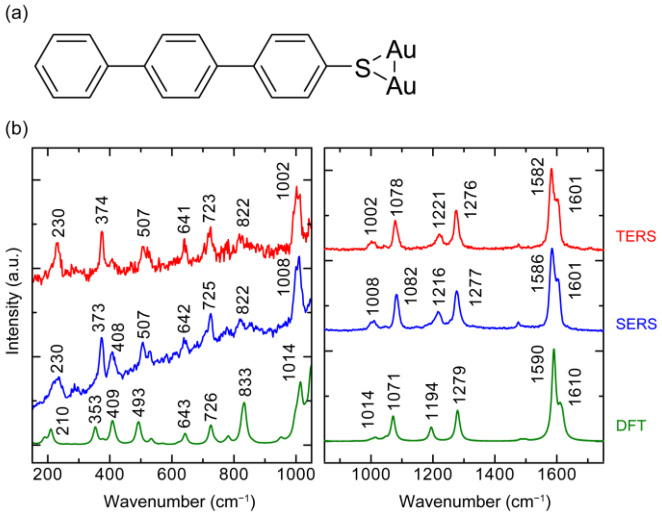

Fig. 5 (a) Molecules calculated in this study. (b) Experimental and calculated Raman spectra of Ph_3SH SAM.

(5) On-surface photo-induced reactions and syntheses [C. Zhang, E. Kazuma and Y. Kim, Angew. Chem. Int. Ed., 58, 17736 (2019); S. Chaunchaiyakul, C. Zhang, H. Imada, E. Kazuma, F. Ishiwari, Y. Shoji, T. Fukushima and Y. Kim, J. Phys. Chem. C, 123, 31272 (2019)]

Dehalogenative cycloaddition reaction is a powerful strategy to generate new ring scaffolds with π-conjugated features on a surface, and thus holds great promise toward atomically precise electronic devices or nanomaterials. The ortho-dihalo substitution provides a good strategy to realize cycloaddition. However, the limited understanding of intermediate states involved (including the selection and competition rules among surface-stabilized radicals and organometallic intermediates, cf. Fig. 6) hinders mechanistic exploration for further precise design and optimization of reaction products.

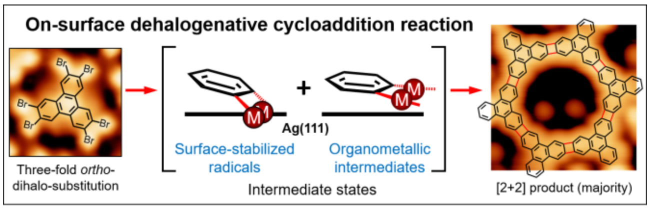

Fig. 6 Schematic illustration of the metal-mediated dehalogenative cycloaddition reaction pathway of the 2,3,6,7,10,11-hexabromotriphenylene (HBTP) molecule on Ag(111).

In this study, we clarified a metal-mediated dehalogenative cycloaddition reaction pathway by visualizing the step-by-step evolution of stable local minima (competing surface-stabilized radicals and organometallic intermediates) toward cycloaddition products from real-space STM observations. We chose the HBTP molecule as the precursor with threefold ortho-dibromo substitutions for possible dehalogenative cycloaddition into two dimensions on Ag(111).

Based on the experimental observations, we further calculated the adsorption configurations of the molecular precursor, intermediate states, final covalent-bonded nanostructures and the corresponding self-assembled structures on Ag(111). We also revealed the primary intermolecular interactions involved in these structures. Direct comparisons of the DFT-simulated STM images and the STM data have been gained to further confirm the rationality of hypothesis.

Finally, at higher temperature 2D covalent networks are formed after several competing intermediate states. Four elementary components, i.e., dominant di-TP, also cis-BTP and trans-BTP, and one minor tris-TP, are found to be involved in the covalent networks (Fig. 7). The corresponding chemical structures and STM morphologies are displayed in Fig. 7a,b. The well-resolved phenyl rings indicate direct correlations between them and also different connection modes. This assignment is further evidenced by DFT-simulated STM images (Fig. 7c) based on the corresponding models on Ag(111) (Fig. 7d) with good consistence in dimension and topography. Besides, the ability in the nice interpretation of long-range polymers based on the elementary components further provides solid evidence to support the assignment of different bonding modes.

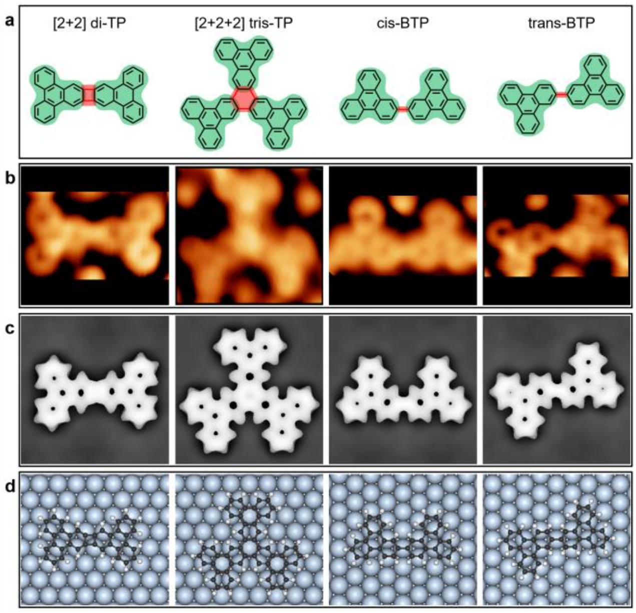

Fig. 7 Four elementary components involved in the formed covalent networks by cycloaddition. (a) Chemical structures of four elementary components (with contours). (b) Submolecularly resolved STM images. (c) Corresponding STM simulations and (d) DFT-optimized structural models on Ag(111).

On the basis of the structural models, the CI-NEB has been used to find the transition states, and subsequently, the possible reaction pathways with the corresponding reaction barriers have been discovered from the point of theoretical calculations. Based on both experimental and theoretical indications, the underlying mechanisms of the on-surface dehalogenative cycloaddition reaction process have been revealed to provide an atomic-scale understanding of the overall reaction process. We thus established the stepwise metal-mediated cycloaddition pathway on Ag(111). A key insight is the clarification of essential incorporation of metal substrate and adatoms in the evolution process, which determines the selection between competing radicals and organometallic intermediates and can be generalized to other halogen-based on-surface reactions.

On the other hand, understanding the basic rules involved in molecular self-assembly processes is also important for further investigation in on-surface synthesis and also functionalization of on-surface nanostructures. Here, we also investigated the self-assembly of one three-dimensional tripod molecule on Ag(111) and explored the intermolecular interactions involved.

Upright orientation of a molecular adsorbate is one of the most practical keys for controlling surface functionalities by using self-assembled monolayers. However, lateral interactions between the upright molecules become more complex than planar molecules since they are not confined in a single plane. In this work, we studied TMMT molecule self-assembled on Ag(111) (cf. Fig. 8).

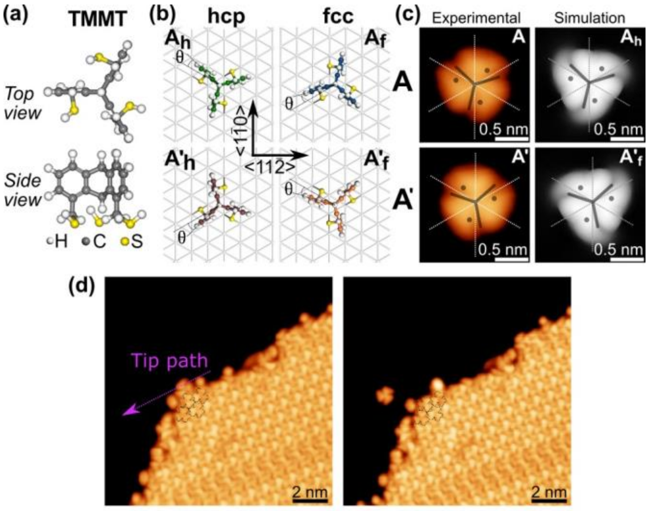

Fig. 8 (a) Chemical structure of pristine 1,8,13-tris(mercaptomethyl)-triptycenes (TMMT). (b) Calculated adsorption geometries of the two possible adsorption sites (hollow hcp and fcc) of the two chiralities (A and A') of a single TMMT on Ag(111). (c) STM images of isolated (A)- and (A')-TMMT adsorbed on Ag(111) and simulated STM images of single (Ah)- and (A'f)-TMMT on Ag(111). (d) Before and after isolating an individual TMMT from the netwoek by using the STM tip.

Through combined analysis of experimental and theoretical results of individual TMMTs, we verified their upright orientation on Ag(111). DFT calculations further show a weak C-H···π intermolecular interaction between the triptycene units and a strong S-Ag molecule-substrate interaction. Our results provide a fundamental insight into the formation of upright-oriented molecular assemblies in which the stabilizing forces are not confined two-dimensionally. We reveal that the S atoms, methylene groups, and the triptycene unit of the TMMT molecules play different roles in the self-assembly process. Such fundamental understanding is of important consideration in the design of precursor molecules to achieve precisely-aligned functional surfaces and therefore to establish three-dimensional molecular architectures.

(6) Selective formation of triplet excited state of single molecule driven by scanning tunneling microscopy [K. Kimura, K. Miwa, H. Imada, M. Imai-Imada, S. Kawahara, J. Takeya, M. Kawai, M. Galperin, and Y. Kim, Nature 570 (2019) 210]

The formation of electron-hole pair (exciton) in organic molecules induced by charge injection is an essential process in organic light emitting diodes (OLEDs). The charge injection leads to excitons with singlet spin multiplicity (S_1) and triplet spin multiplicity (T_1) in a 1:3 ratio owing to the spin statistics. Effective use of T_1 exciton is the main strategy for improving the quantum efficiency of OLEDs, and extensive investigations have been conducted to develop the T_1-based OLEDs.

T_1 exciton has lower energy than S_1 exciton due to the exchange interaction between electrons in the molecule. In principle, this energy difference allows the selective formation of T_1 exciton at low voltage. Such selective T_1 formation could enable the realization of low operating voltage OLEDs, which could improve device lifetimes and reduce power consumption. Demonstration of selective formation of T_1 exciton and clarification of the underlying dynamics of exciton physics could result in the realization of novel T_1-based OLEDs. In order to achieve this, the detailed investigation of both optical and charge-transport processes in a well-defined molecular system using high precise microscopic spectroscopy is required.

In this work, we demonstrate selective formation of T_1 exciton by charge injection from the metal and unveil the exciton formation mechanism at the level of single molecule using a scanning tunneling microscope (STM) combined with an optical detection system. Single-molecule electroluminescence and its bias voltage dependence were measured for a 3,4,9,10-perylenetetracarboxylicdianhydride molecule adsorbed on a three-monolayer thick NaCl film grown on a silver surface. The experimental results demonstrated that only phosphorescence (luminescence from T_1 exciton) occurs at low applied voltage, which indicates the selective formation of T_1 exciton without the formation of S_1 exciton.

To analyze the detailed mechanism, we conducted the theoretical analyses on the luminescence processes. W formulated the current and photon flux using Hubbard nonequiribrium Green function (NEGF) method, which has been developed by us recently. In this technique, the molecule-electrode coupling and molecule-radiative field coupling are taken into account within proper diagrammatic perturbation series expansion, which enables to analyze the dynamics of system beyond the Markov approximation. In the previous studies, it has been demonstrated that the technique is appreciable over the wide range of parameters. To conduct the system specific analysis, we performed first-principles calculations based on the density function theory (DFT) and time-dependent DFT (TDDFT) to extract the information of electronic and vibrational structure of the molecule. Other necessary parameters were quantitatively estimated based on the previous literatures.

Based on TDDFT calculation, triplet and singlet excitation energies of this molecule are shown as 1.18 and 2.49 eV, respectively. Figure 9 shows the simulated luminescence spectra where both phosphorescence and fluorescence appear. In the analysis of voltage dependence of phosphorescence shows the threshold around -2.0 V. In the case of fluorescence, the threshold is found about -3.5V. Therefore, when we tune the bias voltage in the range from -2.0 V to -3.5 V, only phosphorescence occurs. The computational results reproduce the experimental results (Fig 9). In addition, the dependence of calculated luminescence intensity on the bias voltage corresponds to the measured results well. Thus, we concluded that the considering exchange interaction plays an important role in the molecular electroluminescence processes, and our findings would potentially lead to the realization of OLED operating with a low voltage.

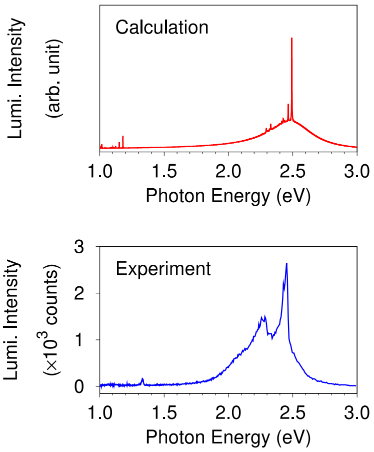

Fig. 9. Computational (upper) and measured (lower) results of luminescence spectra.

4. Conclusion

We have tried to examine a variety of molecular behaviors on the surface in FY2019. Our theoretical studies combined with experiments in FY2019 provide deep insight into a variety of chemical and physical phenomena on solid surface: (1) Photochemistry and plasmon-induced chemical reactions, (2) Electron-phonon coupling at surface and interfaces, (3) Raman spectra of self-assembled monolayers on gold electrode, (4) Single molecule electroluminescence induced by the metal-molecule charge transfer. We expect that our results can provide new perspective to develop a potential strategy for controlling electronic properties of molecular adsorbates on the surface.

５． Schedule and prospect for the future

(1) Controlling chemical reactivity of ultrathin oxide film

Ultrathin oxide film grown on metal substrate has been a subject of great interest not only as a supporting material for chemically active nanoparticles but also as a catalyst in the field of heterogeneous catalysis, where it provides various ways to control the properties of adsorbates via following factors: (i) charge transfer between adsorbates and oxide-metal interface, which is closely correlated with the electronic affinity (EA) of adsorbate and workfunction reduction, (ii) adhesion between oxide and metal layers with strong polaronic distortion, (iii) film thickness, and (iv) the chemical composition of oxide surface. Therefore, we will continue our work to find the way for controlling the chemical reactivity using theoretical and experimental studies. In FY2020, we will extend our study into dissociation of CH_3OH and O_2 on MgO/Ag(100) using combined STM and DFT methodology. The influence from solvent medium on the chemical reactions occurring on surface will be studied in order to provide insights into the electrochemical reactions. In particular, regarding the CH_3OH dissociation on MgO/Ag(100), we will try to find a way to selectively dissociate a bond in CH_3OH, e.g., C-H, O-H, and C-O, using an ionic species on MgO film surface which is introduced through charge transfer between the oxide surface and oxide-metal interface (Fig. 2). For the for O_2 dissociation on MgO/Ag(100), we should consider an influence from the charge redistribution between the oxide-metal interface and the adsorbate, because of O_2 has much higher EA than that of H2O molecule. The other branch of our study is exploring the single atom catalyst on ultrathin oxide film, which is now widely studied due to its prominent importance in heterogeneous catalyst. Therefore, we will introduce single atom catalyst to oxide film and will study how to control its catalytic activity and selectivity. In addition, we are extending our model system to other ultrathin oxide film systems, such as titania and ceria. In FY2020, the study on titania will be intensively performed to find a proper supporting substrate to efficiently realize ultrathin titania film. We believe that our study provides not only profound insight into the chemical reactivity control of ultrathin oxide film but also an impetus for investigating ultrathin oxide films for a wider range of applications.

(2) Molecular adsorption on solid surface: From single molecule to molecular network, and their optical properties

The controllable fabrication of molecular architectures is a topic of great importance not only as a fundamental subject in surface science but also for realizing molecular-scale electronic devices. Computational techniques can provide the underlying mechanisms for the formation of various molecular architectures experimentally observed by STM as well as single molecule adsorption. For the adsorption of single molecules on metal substrate, we suggested the origin of adsorption-induced stability reversal of photochromic DAE on metal surfaces and revealed that the interfacial orbital interaction originated from the weak electronic coupling between the molecular π-state and the electronic states of the Au surface can play a decisive role in constraining adsorption geometry even in the archetypal vdW adsorption system. For one-dimensional (1-D) systems, we have explained (i) the formation mechanism of 1D zipper-type architecture of azobenzene derivatives with the balanced non-bonding interactions, H-bonding and vdW interactions, between adjacent molecules and (ii) the dispersive electronic feature due to the π-orbitals stacking in 1-D molecular lines fabricated on the Si(001)-(2×1)-H. For 2D systems, we contributed to unveil the adsorption geometry of 2D molecular films composed of fluorinated fullerene ($C_{60}F_{36}$), which is strongly related to the distribution of frontier molecular orbitals and thus the n-type character of molecular film. In addition, we revealed the novel formation mechanism of supramolecular assembly using photochromic diarylethene derivative, which is the first report on molecular architectures formed by ion-dipole interaction on solid surface. Very recently, the electronic structures of dimethyl disulfide (DMDS) adsorbed on Ag(111) and Cu(111) were also investigated for studying its photodissociation and plasmon induced chemical reaction on the surface. Our results provide not only deeper insight into the molecular adsorption process, but also a general basis for designing the architectures of molecular electronics with desired electronic properties. In FY2020, we will continue the research not only for a variety of molecular assemblies but also isolated molecule on the surfaces as follows: (1) the formation mechanism of van der Waals interface between π-conjugated molecule and novel metal substrate, and (2) optical property of adsorbate on solid surface, especially, O_2 dissociation on Ag(110) is now actively being studied.

(3) Electronic structures of layered materials, such as graphene and dichalcogenide, and of framework materials, such as MOF and COF

Electronic structures of layered materials, such as graphene and dichalcogenide, and of framework materials, such as MOF and COF

Functionalization of layered materials, such as graphene and dichalcogenide, has attracted great scientific interest not only in controlling their physical properties but also in improving chemical adaptability to integrate them as a building block into a variety of functional devices. In particular, we first suggested that the atomic oxidation of graphene grown on a metal substrate results in the formation of graphene enolate, i.e., negatively charged oxygen adsorbed at ontop position on its basal plane, which is strikingly different from the formation of epoxy groups, i.e., adsorption of atomic oxygen at bridge position, on pristine graphene and on graphite (Fig. 5). Whereas the enolate is the transition state between two nearest epoxides both on graphene and on graphite, we revealed that improved interfacial interaction between graphene and metal substrate during atomic oxidation plays a crucial role not only in the formation of graphene enolate as a local minimum but also in stabilizing it over the graphene epoxide. In addition, we recently studied the growth mechanism of covalent organic framework (COF) through photo-excitation. In FY2020, we are going to theoretically investigate (1) our very recent experimental finding of well-ordered graphene functionalization with OH group, in which the formation of graphene enolate would be one of the main driving forces, and (2) the catalytic effect of metal-organic framework (MOF).

(4) Magnetism of nanostructure on solid surface

As the simplest system, we focus on the spin of NO molecules on metallic surfaces. A NO molecule has a single unpaired electron. Whether the magnetic moment from this unpaired electron is persistent on metallic surface or not has been a simple but long-standing problem in the field of surface science. By using first-principle calculation, we will reveal the relationship between various adsorption configuration and molecular spin.

(5) Efficient ab-initio simulation of phonon properties in combination with machine learning technique

We will extend out technique of thermal conductivity simulation using HDNNP to the system with disorder. Especially, we will focus on the amorphous semiconductors. Since the wavevector becomes ill-defined in amorphous semiconductors due to the lackness of translational symmetry, heat is carried by the characteristic vibrational mode called as “propagon” instead of phonon. We plan to find suitable way to generate the training dataset for HDNNP to reproduce such vibrational properties in amorphous systems.

(6) Raman spectra of self-assembled monolayers on gold electrode

As mentioned in the above section, we have established the simulation method of Raman spectra for organic monolayers of metal surfaces. We will try to perform experiments for next half year, and will perform DFT calculation to find next more attractive targets.

(7) On-surface photo-induced reactions and syntheses

As mentioned in the above section, we have explored several molecular systems including on-surface reaction/self-assembly. The next step is to further deeply explore and understand the interaction rules (intermolecular interactions and molecule-substrate interactions) and the reaction rules/mechanisms in the molecular systems. In FY2020, we will continue to investigate some other topics related to the on-surface photo-induced synthesis from the following prospects: (1) adsorption configurations; (2) interaction and functionalization rules (molecule-molecule and molecule-substrate interactions resulting from different functional groups); (3) electronic and magnetic properties; (4) possible reaction pathways and rules.

(8) Photoelectric conversion in single molecule on surface

Our studies on carrier dynamics in energy conversion processes are extended to the research on photoelectric conversion in single molecule. Single molecule luminescence can be induced by the tunneling current of STM, enabling us to investigate the electroluminescence processes of a molecule with submolecular spatial resolution in a well-defined manner. Especially, we focus on electron correlations in electroluminescence processes, e.g., charging of the molecule, formation of single/triplet excitons, radiative and nonradiative decay, and so forth. The key factor in the theoretical analysis is the calculation of (i) excited electronic states of the molecule as well as (ii) nonequilibrium electron dynamics in electroluminescence processes under applied bias. We plan to investigate these points using the method based on first-principles calculations and the nonequilibrium Green’s function (NEGF) methods. Our study would make a contribution for understanding the fundamental nature of molecular electroluminescence and in the designing of novel functional materials for organic (opto)electronic devices.

Usage Report for Fiscal Year 2019

Fiscal Year 2019 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

1. Kensuke Kimura, Kuniyuki Miwa, Hiroshi Imada, Miyabi Imai-Imada, Shota Kawahara, Jun Takeya, Maki Kawai, Michael Galperin, Yousoo Kim, "Selective triplet exciton formation in a single molecule", Nature 570, 210 (June, 2019)

2. Juyeon Park, Ju-Hyung Kim, Sunmi Bak, Kazukuni Tahara, Jaehoon Jung, Maki Kawai, Yoshito Tobe, and Yousoo Kim, "On-surface evolution of meso-isomerism in two-dimensional supramolecular assemblies", Angew. Chem. Int. Ed. 58, 9611 (May, 2019)

3. Chi Zhang, Emiko Kazuma, and Yousoo Kim, "Atomic-scale visualization of the stepwise metal-mediated dehalogenative cycloaddition reaction pathways: competition between radicals and organometallic intermediates", Angew. Chem. Int. Ed. 58, 17736 (October, 2019)

4. Songpol Chaunchaiyakul, Chi Zhang, Hiroshi Imada, Emiko Kazuma, Fumitaka Ishiwari, Yoshiaki Shoji, Takanori Fukushima, and Yousoo Kim, "Self-assembly growth of an upright molecular precursor with a rigid framework", J. Phys. Chem. C 123, 31272 (December, 2019)

5. H. Isshiki, K. Kondou, S. Takizawa, K. Shimose, T. Kawabe, E. Minamitani, N. Yamaguchi, F. Ishii, A. Shiotari, Y. Sugimoto, S. Miwa, Y. Otani, "Realization of Spin-dependent Functionality by Covering a Metal Surface with a Single Layer of Molecules", Nano Lett, 10, 7119 (October, 2019)

6. Emi Minamitani, Masayoshi Ogura, Satoshi Watanabe, "Simulating lattice thermal conductivity in semiconducting materials using high-dimensional neural network potential", Appl. Phys. Express 12, 095001 (August, 2019)

[Oral presentation]

1. Vipin Kumar, Jaehoon Jung, "Theoretical study of structural, electronic, v ibrational, mechanical, and thermoelectric properties with high mobility carrier of ternary c ompounds", Theory meets experiment in low-dimensional structures with correlated electrons, Prague, Czech Republic, Jul (2019)
2. R. Jaculbia, H. Imada, K. Miwa, B. Yang, E. Kazuma, N. Hayazawa, Y. Kim, "Vibrationally resolved imaging of a single molecule using tip-enhanced Resonance Raman spectroscopy", 10th International Conference on Advanced Vibrational Spectroscopy (ICAVS10), Auckland, New Zealand, Jul. (2019)
3. Y. Kim, "Single-molecule chemistry and spectroscopy at surfaces", 2019 RIKEN-NCHU Joint Symposium, Taichung City, Taiwan, Aug. (2019)
4. Y. Yokota, "Novel approaches for microscopic understanding of electrochemical interfaces: in situ and ex situ techniques", 2019 RIKEN-NCHU Joint Symposium, Taichung City, Taiwan, Aug. (2019)
5. Y. Kim, "Single-molecule chemistry and spectroscopy with a photon STM", The Seventh RIKEN-NCTU Symposium on Physical and Chemical Sciences, Hsinchu, Taiwan, Oct. (2019)
6. Y. Kim, "Single-molecule optical spectroscopy", 704.WE-Heraeus-Seminar "Exploring the Limits of Nanoscience with Scanning Probe Methods", Bad Honnef, Germany, Oct. (2019)

7. Y. Kim, “Overview of Surface and Interface Science Laboratory”, IBS-RIKEN Joint Conference, Daejeon, Korea, Oct. (2019)
8. Y. Yokota, “Developments of in-situ and ex-situ techniques for molecular scale understanding of electrochemical interfaces”, IBS-RIKEN Joint Conference, Daejeon, Korea, Oct. (2019)
9. H. Imada, “Atomic-scale study of exciton creation and annihilation in a molecular system”, IBS-RIKEN Joint Conference, Daejeon, Korea, Oct. (2019)
10. R. A. Wong, Y. Yokota, M. Wakisaka, J. Inukai, Y. Kim, “Probing the redox-dependent electronic and interfacial structure in ferrocene-terminated self-assembled monolayers with photoelectron spectroscopy”, 236th ECS Meeting, Atlanta, USA, Oct. (2019)
11. K. Kimura, K. Miwa, H. Imada, M. Imai-Imada, Y. Kim, “Creation of spin singlet and triplet excitons in a single molecule”, International School and Symposium on Nanoscale Transport and phoTonics (ISNTT2019), Kanagawa, Japan, Nov. (2019)
12. H. Imada, “STM study of exciton creation and annihilation in a single molecule”, he 81st Okazaki Conference "Forefront of Measurement Technologies for Surface Chemistry and Physics in Real-Space, k-Space, and Real-Time", Aichi, Japan, Dec. (2019)
13. H. Imada, “Plasmon-exciton coupling at an STM junction: fundamental and applications for spatially-resolved single-molecule spectroscopy”, 27th International Colloquium on Scanning Probe Microscopy (ICSPM27), Shizuoka, Japan, Dec. (2019)
14. R. B. Jaculbia, H. Imada, K. Miwa, T. Iwasa, M. Takenaka, B. Yang, E. Kazuma, N. Hayazawa, T. Taketsugu, Y. Kim, “Single molecule tip-enhanced Resonance Raman spectroscopy in low temperature environments”, Philippine-Japan Conference on Photonics and Optical materials, Quezon, Philippines, Dec. (2019)

[Poster presentation]

1. Youngjoon An, Jaehoon Jung, “Density functional theory study on global aromaticity of carbon nanobelts”, Graphene 2019, Rome, Italy, Jun. (2019)
2. K. Kimura, K. Miwa, H. Imada, M. Imai-Imada, S. Kawahara, J. Takeya, M. Kawai, M. Galperin, Y. Kim, “Investigation of selective triplet exciton formation in a molecule with an STM”, 704.WE-Heraeus-Seminar “Exploring the Limits of Nanoscience with Scanning Probe Methods”, Bad Honnef, Germany, Oct. (2019)
3. M. Hong, Y. Yokota, N. Hayazawa, E. Kazuma, Y. Kim, “Tip-enhanced Raman spectroscopy of aromatic thiol self-assembled monolayers on Au(111)”, 27th International Colloquium on Scanning Probe Microscopy (ICSPM27), Shizuoka, Japan, Dec. (2019)
4. S. Chaunchaiyakul, H. Imada, E. Kazuma, F. Ishiwari, Y. Shoji, T. Fukushima, Y. Kim, “Nonplanar stereochiral intermolecular interactions between upright molecular precursors”, 27th International Colloquium on Scanning Probe Microscopy (ICSPM27), Shizuoka, Japan, Dec. (2019)
5. Y. Yokota, M. Hong, N. Hayazawa, B. Yang, E. Kazuma, F. C. Catalan, Y. Kim, “Experimental verification of deactivation process in atmospheric tip-enhanced Raman spectroscopy (TERS)”, 27th International Colloquium on Scanning Probe Microscopy (ICSPM27), Shizuoka, Japan, Dec. (2019)
6. M. Imai-Imada, H. Imada, K. Kimura, K. Miwa, J. Takeya, Y. Kim, “Visualization of exciton creation and annihilation in a single molecule”, 27th International Colloquium on Scanning Probe Microscopy (ICSPM27), Shizuoka, Japan, Dec. (2019)

7. Prihatno Fajar, Jaehoon Jung, “Dissociation of O2 on ultrathin MgO film : ligand field effect at oxide-metal interface”, The 18th Asian Chemical Congress (ACC) , Taipei, Taiwan, Dec. (2019)
8. Hadiputra Rizky, Jaehoon Jung, “Role of the film thickness on the structural and electronic properties of rutile TiO2 (110) supported by a metal substrate”, The 18th Asian Chemical Congress (ACC) , Taipei, Taiwan, Dec. (2019).

[Others (Book, Press release, etc.)]

1. “単一分子電界発光の機構解明—発光過程における分子内電子間クーロン相互作用が鍵–”，理化学研究所報道発表, March, 2019
2. “有機 EL の新たな発光機構を発見－三重項励起子を低電圧で選択的に形成－”，理化学研究所報道発表, June, 2019