Surface and Interface Science Laboratory（2024）
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(0) Research fields

CPR Subcommittee**:** Chemistry

Keywords: surface and interface, scanning tunneling microscopy,
Single-molecule spectroscopy and chemistry, energy conversion and transfer,

(1) Long-term goal of laboratory and research background

Quantum-state excitations of molecules at solid surfaces and interfaces govern fundamental processes such as chemical reactions, energy transfer, light emission, and catalysis. However, direct observation and control of these processes at the single-molecule level remain challenging with conventional ensemble-based spectroscopies. We address this challenge by using the scanning tunneling microscope (STM) as both an atomic-resolution probe and a localized source of quantum excitations. Through the development of photon-STM–based single-molecule spectroscopies, we enable real-space, quantitative analysis of energy conversion at molecular interfaces. Our goal is to elucidate reaction mechanisms and energy conversion principles with atomic precision, providing foundations for quantum-controlled molecular functionalities and next-generation energy and optoelectronic devices.

(2) Current research activities (FY2024) and plan

(A-1) Electron-Excitation–Driven Single-Molecule Reactions on Metal Surfaces

In this study, we performed a detailed analysis of reaction processes induced by tunneling-electron injection using a scanning tunneling microscope (STM) on single diarylethene (DAE) molecules adsorbed on a Cu(111) surface. As a result, we discovered a novel reaction pathway fundamentally distinct from conventional photoinduced isomerization, in which ring-opening and dehydrogenation of the methyl group at the 2-position of the thiophene ring proceed simultaneously. STM observations enabled the identification of two adsorption structures (α, β) corresponding to primary dehydrogenation products, as well as a secondary dehydrogenation product (γ), thereby demonstrating the irreversible nature of the reaction and the formation of strong chemical bonds with the substrate. Furthermore, comparison with density functional theory (DFT) calculations and STM simulations quantitatively clarified a sequential reaction mechanism driven by LUMO excitation, presenting a new framework for controlling single-molecule reactions on metal surfaces.

Future plan, Building on the concept of “tunneling-electron–induced molecular skeletal transformation” established in this study, we will pursue a systematic understanding of reaction selectivity through molecular design, substrate choice, and local electronic-state control. In particular, we will extend the target systems to other photoresponsive and π-conjugated molecules, clarifying the branching conditions between reversible and irreversible reactions from the perspectives of electronic structure and adsorption geometry. By introducing time-resolved STM and combined excitation with optical and terahertz fields, we aim to elucidate early-stage reaction processes and intermediate-state dynamics, ultimately establishing design principles for highly stable and durable single-molecule switches and molecular functional devices operating on solid surfaces.

(A-2) Atomic-Scale Visualization of Frontier Molecular Orbitals in Multiple-Resonance TADF Molecules

We successfully achieved direct visualization of frontier molecular orbitals (HOMO and LUMO) at the single-molecule level for the thermally activated delayed fluorescence (TADF) molecule DABNA-1, which exploits the multiple-resonance (MR) effect, using scanning tunneling microscopy and spectroscopy (STM/STS). By employing a monolayer NaCl insulating film formed on an Au(111) substrate, the molecular electronic states were effectively decoupled from the metal substrate, and the introduction of a Cl-terminated STM tip dramatically enhanced atomic resolution. As a result, the orbital separation characteristic of MR-TADF molecules—previously inferred mainly from theoretical calculations or ensemble-averaged measurements—was clearly observed in real space. In particular, we experimentally demonstrated that the HOMO and LUMO are spatially separated due to heteroatom arrangement and are strongly localized around the para positions, revealing the electronic-state origin of high oscillator strength and narrowband emission based on the MR effect at the single-molecule scale.

Future plan, Based on the single-molecule STM methodology established in this study, we will expand our research to next-generation MR-TADF molecules with different heteroatom configurations and fused-

ring structures. We aim to systematically elucidate how the spatial symmetry of HOMO–LUMO separation, orbital overlap, and interfacial interactions influence exciton formation and reverse intersystem crossing (RISC) processes. Furthermore, by integrating optical-excitation STM and time-resolved spectroscopy, we will directly probe excited-state dynamics and interface-induced electronic-state modulation. Through these efforts, we seek to establish quantum-mechanical design principles for ultra-high-efficiency and highly stable organic light-emitting materials by linking molecular design with real-space electronic structure.

(A-3) Elucidation of Single-Molecule Reaction Selectivity via Molecular Orientation Control
Using scanning tunneling microscopy (STM), we demonstrated at the single-molecule level that identical molecules adsorbed on a Cu(111) surface exhibit drastically different tunneling-electron–induced reaction selectivity depending on their adsorption orientation. By precisely controlling molecular orientation through STM manipulation and statistically comparing reaction probabilities and products for each configuration, we showed that reaction pathways strongly depend on the local electron-injection site and molecular geometry. Comparison with first-principles calculations further revealed that symmetry breaking in the molecular skeleton modulates the local electronic-state distribution, concentrating reactivity at specific bonding sites. This work demonstrates that single-molecule reactions on metal surfaces can be actively controlled not only by intrinsic molecular chemistry but also by the geometric degree of freedom associated with adsorption orientation, thereby introducing a new concept for interfacial chemical reaction control.

Future plan, We will further develop the concept of “adsorption-orientation–based single-molecule reaction control” by extending our studies to more complex multifunctional and π-conjugated molecular systems. In particular, we will systematically investigate correlations between adsorption degrees of freedom—such as rotation, inversion, and translation—and the position and energy of tunneling-electron injection, aiming to generalize the governing factors that determine reaction selectivity. By introducing combined stimuli such as optical excitation and localized electromagnetic fields, we will explore new reaction-control schemes in which electronic excitation and steric effects act cooperatively. These studies will establish fundamental principles for single-molecule synthesis, molecular-function writing, and the design of nanoscale reaction networks on surfaces.

(B) Elucidation of Single-Molecule Luminescence Mechanisms at Metal–Electrode Interfaces
We conducted a detailed analysis of the relationship between electronic states and luminescence properties at molecule–electrode interfaces by investigating STM-induced luminescence from single molecules positioned on metal electrode surfaces. Using a molecule–metal decoupling structure incorporating a thin NaCl insulating layer, we successfully obtained highly reproducible luminescence spectra originating from intrinsic molecular excited states. Analysis of bias-voltage dependence and spatial distribution of the luminescence revealed that exciton formation is governed by the cooperative interaction between tunneling-electron injection and electrode-surface plasmons. This approach enables a quantitative understanding of organic molecular luminescence mechanisms from the perspective of a single molecule and a single interface, which had previously been discussed mainly in terms of ensemble-averaged behavior. The results demonstrate that molecular luminescence properties can be actively controlled not only by molecular structure but also by electrode-interface conditions.

Future plan, Building on the STM-induced single-molecule luminescence techniques established in this work, we will systematically investigate how variations in metal electrode materials, insulating-layer thickness, and molecular orientation affect exciton formation and radiative relaxation processes. In particular, we aim to achieve flexible control of emission wavelength, quantum efficiency, and polarization characteristics by tuning the coupling strength between electrode-derived plasmonic fields and molecular excited states. By combining time-resolved STM luminescence spectroscopy with external optical excitation, we will directly observe the dynamics of exciton generation, relaxation, and annihilation. Through these efforts, we seek to establish design principles for molecular-scale light-emitting devices and nanoscale light sources, advancing applications in molecular optoelectronics.

(C) Development of Cryogenic Terahertz Scanning Noise Microscopy and Nanoscale Measurement of Nonequilibrium Hot-Electron Temperature
To quantitatively measure the local temperature of nonequilibrium electrons (hot electrons) at the nanoscale, we developed a cryogenic terahertz scanning noise microscope (Cryo-SNoiM). This instrument employs a dual-cooling architecture consisting of a detection chamber in which the terahertz detector is cooled to approximately 5 K and a measurement chamber that allows independent temperature control of the AFM and sample from room temperature down to about 110 K. This design ensures high stability and

reproducibility under low-temperature conditions while enabling probe selection and optical alignment prior to measurement. As a proof-of-concept experiment, we visualized hot-electron distributions in current-heated nanoscale metal wires at low temperature and successfully derived electron temperatures quantitatively using near-field signal intensity ratios without adjustable parameters. This achievement establishes a new measurement platform for directly observing thermal transport phenomena in cryogenic nonequilibrium electronic systems, which had previously been difficult to access.

Future plan, We will apply Cryo-SNoiM–based cryogenic nanoscale thermal measurements to molecular devices, low-dimensional materials, and quantum transport systems. In particular, we aim to track the generation, diffusion, and dissipation of hot electrons in real space in molecular junctions and two-dimensional materials where electron–phonon nonequilibrium effects are pronounced. By integrating Cryo-SNoiM with STM spectroscopy and optical excitation techniques, we will establish a comprehensive measurement framework for understanding electronic excitation states and energy-conversion processes. These efforts will contribute to elucidating the operational limits of quantum devices and to creating fundamental principles for novel nanoelectronic and molecular devices functioning under low-temperature conditions.

(3) Members

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(4) Representative research achievements

1. Yuzu Kobayashi, Yasuyuki Yokota*, Yoshiaki Shoji, Sanjayan Sajisha, Colin J. Martin, Jun Takeya, Takanori Fukushima*, and Yousoo Kim*, “Fluorescence detection of tetraphenylporphyrin isolated on the Au(111) electrode enabled by tripodal molecules”, **J. Phys. Chem. C** 128 (2024) 15082-15090.
2. Hirokazu Sato, Taehwan Lee, Minhui Lee, Emiko Kazuma, Yousoo Kim, Jaehoon Jung, Kyoung Chul Ko and Tomoko K. Shimizu, “Simultaneous ring-opening and dehydrogenation of diarylethene induced by tunneling electrons”, **Chem. Phys. Chem.** (2025) e202400988.
3. Zewei Yi, Zhaoyu Zhang, Yuan Guo, Yuhong Gao, Rujia Hou, Chi Zhang*, Yousoo Kim*, and Wei Xu*, “Revealing the influence of molecular chemisorption direction on the reaction selectivity of dehalogenative coupling on Au(111): Polymerization versus Cyclization”, **ACS Nano** 18 (2024) 14640-14649.
4. Jaehyun Bae, Miyabi Imai-Imada, Hyung Suk Kim, Minhui Lee, Hiroshi Imada, Youichi Tsuchiya, Takuji Hatakeyama, Chihaya Adachi and Yousoo Kim, “Visualization of multiple-resonance-induced frontier molecular orbitals in a single multiple-resonance thermally activated delayed fluorescence molecule,” **ACS Nano** 18 (2024) 17987-17995.
5. Qianchun Weng*, Weijie Deng, Susumu Komiyama, Toru Sasaki, Hiroshi Imada, Wei Lu, Iwao Hosako, and Yousoo Kim, “Nanoscale thermal imaging of hot electrons by cryogenic terahertz scanning noise microscopy”, **Rev. Sci. Instrum.** 95 (2024) 063705, 1-8.

Supplementary

Laboratory Group Photo (Apr 18, 2025)

Laboratory Homepage
https://www2.riken.jp/Kimlab/index.html