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Exploring near-field single-molecule spectroscopy by STM

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The scanning tunneling microscope (STM) is a versatile and powerful tool for investigating and controlling the chemistry of individual molecules on solid surfaces, mainly due to its extremely high spatial resolution. When irradiated on a metal nanoscale structure, light can be squeezed in an extremely small region of several nm, far beyond the diffraction limit of visible light due to the localized surface plasmon (LSP) resonance. We have achieved spectroscopic measurements and controlled photochemical reactions of individual molecules that are spatially fixed on solid surfaces at low temperatures by using the tiny near-field light localized at an STM tip junction, which enables us to access both electronic and optical quantum states of a single molecule. Described here are our recent achievements focusing on single-molecule spectroscopy based on molecular excitation by LSP at the STM junction.

1. Introduction

Nanoplasmonics has been rapidly gaining attention in recent decades. It deals with collective oscillations of electrons of the metallic nanoparticles and nanostructures. Thus, it appears at the junction of nanotechnology, quantum mechanics, photonics, solid-state physics, chemistry, and biology. Because of the diffraction limit, light propagating through space can be collected only half the light wavelength (a few hundred nm in the case of visible light). However, irradiation of light to the metal nanostructure causes group vibration of the metal nanoparticle's free electrons (plasmon), followed by the creation of an electromagnetic field, *i.e.*, localized surface plasmon (LSP), localized in the area of several nm near the nanostructure. The LSP has a characteristic interaction with matter, which has been actively utilized in applied studies, such as near-field photochemistry, near-field light microscopy, and surface-enhanced Raman spectroscopy. Further development and application

of LSP science require a fundamental scientific perspective about its interaction with matter. However, to closely examine the LSP itself, it is necessary to use a microscope with a spatial resolution of an atomic scale (~ 0.1 nm) sufficiently smaller than the size of the LSP.

The scanning tunneling microscope (STM) is a versatile and powerful tool for investigating and controlling the chemistry of individual molecules on solid surfaces. The study of single molecules provides deep insights into a bonding nature and underlying quantum mechanics concerning chemical and physical properties. We have developed an optical STM that combines the STM with light irradiation and detection systems to explore molecular energetic processes, such as energy transfer, conversion, and dissipation. Since the STM has an extremely high (sub-atomic) spatial resolution, it allows us to achieve pioneering research in single-molecule chemistry and spectroscopy using LSP at the STM tip junction.

Molecular spectroscopy deals with the spectra arising from the interaction of the target molecule with the excitation source. As the excitation source of the molecule, we employed near-field photons from the LPS generated at the STM tip either by injecting tunneling electrons or by laser irradiation (Fig.1).

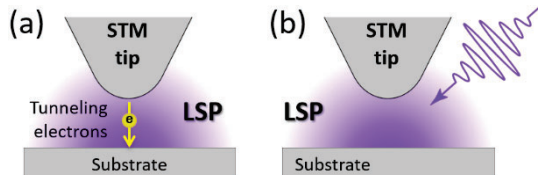


Fig. 1. Schematics of LSP generation at the STM tip (a) by injecting tunneling electrons and (b) by laser irradiation

We then measured specific signals, such as irradiated photons (even with Raman scattering signals) and conductance change, from the target molecule to construct single-molecule spectra that contain characteristic information about the molecular quantum states.

Some of the examples of representative single-molecule molecule spectroscopy developed based on LSP will be described below.

2. Single-molecule absorption spectroscopy [1]

Absorption spectroscopy is a powerful tool to observe excited molecular states; its combination with emission spectroscopy that deals with deexcitation processes effectively investigates the energy dynamics at excited molecular states. Single-molecule luminescence detection has recently shown rapid progress and has become indispensable in various research fields, such as quantum physics, physical chemistry, and biophysics. However, despite considerable effort and progress, single-molecule absorption spectroscopy has been developing relatively slowly due to an inherent problem regarding the light source that excites target molecules. A difficulty lies in the difference between the diffraction limit of excitation light and the absorption cross-section of a single molecule. It has been known that the LSP is generated near the STM tip surface when a bias voltage is applied. The generated localized electric field has been extensively utilized for near-field optical spectroscopies, high-efficiency solar cell devices, and photocatalysis.

In this study, we precisely described the near-field interaction between a localized plasmon and a single molecule, which provides novel single-molecule absorption spectroscopy. The gap plasmon localized in the STM junction was used as a spatially controllable plasmonic probe, and detailed spectroscopic measurements in the proximity of a free-base phthalocyanine (H_2Pc) molecule (Fig. 2(a)) were performed on a 3-ML thick NaCl film grown on an Ag(111) surface as shown in Fig. 2(b). The tunneling current excited the LSP, which then interacted with the molecule through the plasmon-exciton coupling, and the emitted photons were detected. Fig. 2(c) illustrates the experimental scheme.

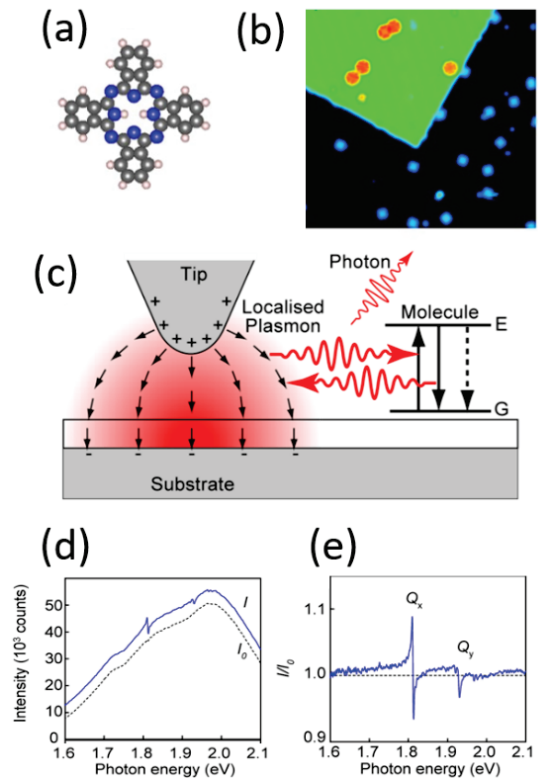


Fig. 2. (a) An H_2Pc molecule (b) An STM image of H_2Pc molecules on a 3-ML thick NaCl film grown on Ag(111) surface ($40 \times 40 \text{ nm}^2$, $V_s = -2.5 \text{ V}$ and $I_t = 2 \text{ pA}$). (c) An illustration of the experimental scheme. (d) STL spectra measured with the tip placed close to (upper) and far from (lower) a single H_2Pc molecule. (e) An I/I_0 spectrum generated from the two curves in (d).

Fig. 2(d) shows two representative STL spectra measured with tip positions far from and close to the molecule. We defined the STL spectrum measured with the tip located far from the molecule as the excitation source spectrum I_0 , and that measured

close to the molecule as I. As shown in Fig. 2(e), the ratio spectrum I/I_0 clearly reveals the change in the spectral shape resulting from the plasmon-exciton coupling. The origin of the dip structures is the absorption of the LSP energy by the molecule through the plasmon-exciton coupling, which leads to the dip structures at 1.81 and 1.92 eV.

Further, by combining single-molecule luminescence spectroscopy and absorption spectroscopy, we have visualized the energy transfer between two different molecules [2].

In this study, we have revealed the detailed energy dynamics in a single molecule coupled to the localized plasmon, which is a coupled plasmon-exciton-vibron system. Our findings pave the way for establishing an absorption/emission spectroscopy with the ultimate sensitivity and spatial resolution, expanding our perception of fundamental energetic processes at the single-molecule level.

3. Single-molecule resonance tip-enhanced Raman spectroscopy [3]

Raman spectroscopy is commonly used to study the vibrations of molecules, but its resolution is limited by the wavelength of the light used to irradiate the sample. This becomes problematic for the study of very small systems such as single molecules. Tip-enhanced Raman spectroscopy (TERS) overcomes this problem by using the STM tip to enhance the resolution. However, this method has its own limitations concerning chemical and physical interaction between the molecule and the local electric field at the LSP generated at the STM junction. In our work, we preserve the intrinsic properties of the target molecule by introducing an ultrathin insulating film between the molecule and metal substrate, which allows us to perform resonance TERS on a single molecule.

Fig. 3(a) shows the experimental configuration in our work. We deposit the copper naphthalocyanine (CuNc) molecule on the 3-ML thick NaCl film grown on Ag(111) surface at a cryogenic temperature, which provides isolated CuNc molecules on both the Ag(111) and NaCl surface as shown in Fig. 3(b). In previous STM-TERS works, the molecule is directly adsorbed on the metal

surface[4,5]. CuNc is hybridized with the metal substrate. Fig. 3(c) shows the STS spectra of the molecules adsorbed on an NaCl film and directly on the metal, where the HOMO and LUMO peaks are clearly measured only on the NaCl film. This confirms that the NaCl film makes the molecule electronically decoupled from the metal substrate and thus keeps it in its original electronic state.

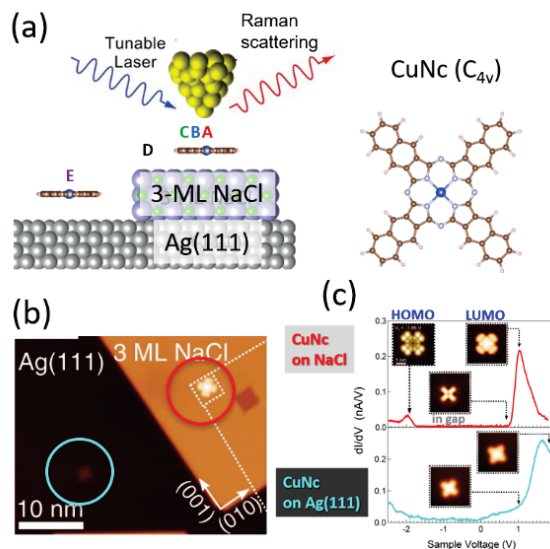


Fig. 3. (a) The experimental configuration. We use a CuNc adsorbed on NaCl surface supported by Ag(111). The incident light comes from a tuneable laser for resonance Raman spectroscopy. The Raman signal is enhanced by using an electrochemically fabricated gold tip. (b) STM image of the molecule on NaCl and Ag(111). (c) STS spectra of the molecule adsorbed on the Ag(111) (top) and the NaCl (bottom). Insets show the STM topographic images on the bias voltage indicated by the arrows.

Owing to the decoupling of the CuNc molecule from the metal surface, we can measure the single-molecule absorption via the single-molecule absorption spectroscopy we originally developed. The red curve in Fig. 4(b) shows the absorption spectrum showing an absorption dip at around 738 nm. This feature was found to correspond to the absorption of the molecule obtained using UV-Vis measurements in ambient conditions, which suggests that this feature is the 0-0 transition of the molecule. We then performed STM-TERS on the CuNc molecule with careful tuning of the incident light to perform resonance TERS measurements. Fig. 4(a) shows the resonance STM-TERS spectra for the molecule on NaCl and the metal surface. As observed, the signals are only present when the tip is on a molecular lobe and when the tip is placed

laterally away while keeping the tunneling feedback, all signals disappear. Moreover, no TERS signal appears when the tip is placed near a molecule on the Ag(111). This confirms that the TERS enhancement is governed by direct molecular resonance. Lastly, we tuned the laser around the absorption dip. As shown in Fig. 4(b), the Raman intensity of three representative peaks monotonously decreases as the wavelength increases, but a sudden jump was observed at around 738 nm. Moreover, the peak in the Raman excitation spectra corresponds well to the dip in the STM absorption spectra [1]. This behavior is clear proof of the single-molecule resonance Raman effect [3].

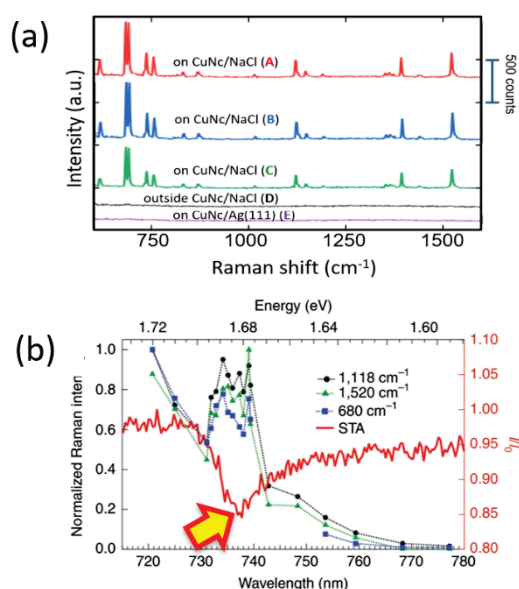


Fig. 4. (a) STM-TERS spectra of the molecule adsorbed on NaCl and Ag(111) surface. The inset shows the location of the tip during measurements. (b) Raman peak intensity of three representative peaks as a function of incident wavelength plotted together with single molecule absorption observed using single-molecule absorption spectroscopy.

In conclusion, we demonstrated single-molecule STM-TERS under direct molecular resonance conditions. Our results demonstrate that by placing the molecule on a NaCl surface instead of directly on the metal, the intrinsic properties of the molecule are preserved. This allows for various measurements, including STS, absorption spectroscopy, and resonance Raman measurements, to be performed on a pristine sample. Our technique provides a truly non-invasive probe for

investigating the intrinsic properties of single molecules, which can be further applied to various molecular systems.

4. Single-molecule photoluminescence spectroscopy [6]

Measurement of electroluminescence (EL) induced by the tunneling current of an STM (STM-EL) has been developing rapidly in recent years. In addition to morphological and electronic characterization by STM, the photon signals provide fruitful information on charge and excitation dynamics. Although STM-EL is a unique and powerful technique for investigating electronic excitations, one critical drawback is the low state selectivity during excitation. In contrast to tunable lasers used in optical spectroscopy, the energy of the tunneling electrons is not well defined nor monochromatic, which makes it particularly difficult to selectively excite only one quantum state by the electrons in STM. This problem has hindered the elucidation of the intrinsic characteristics of individual excited states (energy level, line width, etc.) and detailed state-to-state descriptions of the subsequent dynamic processes.

This study combines a narrow-line tunable laser with STM to achieve high state-selectivity in nanoscale excitation and precisely characterize single-molecule electronic and vibrational states with μeV energy resolution. As illustrated in Fig. 5(a), nanocavity plasmons formed between the STM tip and the metal substrate are driven at a well-defined frequency by an externally irradiated laser field, which then excites the molecule to induce photoluminescence (PL). For the demonstration of precise STM-PL spectroscopy, H_2Pc and its deuterated compound were deposited on NaCl-film/Ag(111) (Fig. 5(b)). Fig. 5(c) shows the STM-PL spectra measured at four STM tip positions of different distances from the molecule center. The STM-PL spectrum shows almost no photon signal when the tip is more than 5 nm away. As the tip approaches the molecule, the photon signal rapidly grows to show a clear luminescence signal from vibronic transitions. The line shape of the resonance is more precisely investigated by PL excitation (PLE) spectroscopy, where the excitation laser

energy is swept while monitoring the intensity of the red-shifted luminescence (Fig. 5(d)). Fig. 5(e) shows a single-molecule PLE spectrum of the H₂Pc, which reveals an intensive resonance at 1817.4 meV with a peak width of 0.5 meV and a small resonance on the higher energy side. Since the initial state of the excitation is determined to be the vibrational ground state of S₀ at 4.5 K, the lowest-energy transition at 1817.4 meV is unambiguously assigned to the 0-0 transition from S₀ to S₁. This result proves that a tunable monochromatic probe is essential for characterizing individual quantum states in a plasmonic nanocavity.

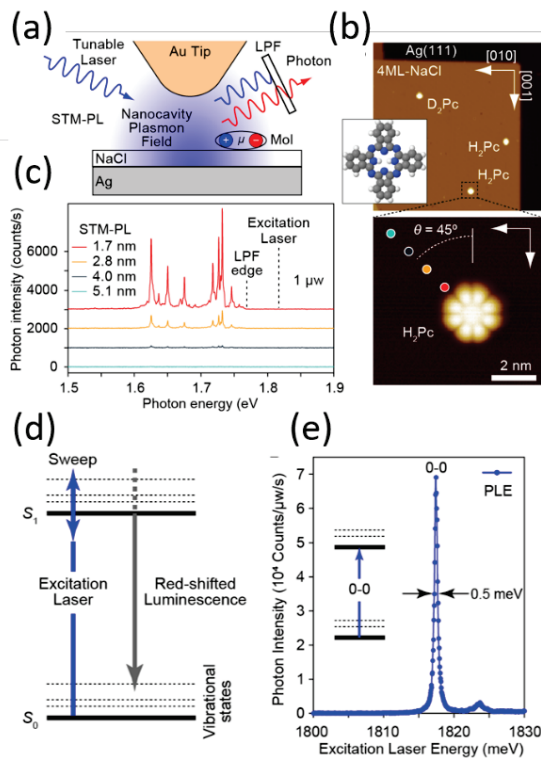


Fig. 5. (a) Schematic illustration of STM-PL from a single molecule adsorbed on NaCl/Ag(111) surface. (b) Molecular structure of H₂Pc and STM images of the sample. (c) STM-PL spectra measured at four different points indicated in (b). (d) Energy diagram for PLE measurement. (e) A PLE spectrum of H₂Pc.

It should be noteworthy that our experimental setup can be readily modified to realize a time-resolved nanospectroscopy by using a pulsed laser instead of the continuous one. We foresee that complementary nanospectroscopy of high energy- and time-resolution opens the door to better understanding and efficient exploitation of energy conversion dynamics.

5. Single-molecule photocurrent imaging [7]

Given its central role in various light energy conversion systems, photoinduced electron transfer (PET) from photoexcited molecules has been widely studied using optical spectroscopy and photocurrent measurement. Detailed insights into this process as an initial process of photocurrent generation have been obtained using microscopic techniques that combine STM and optical systems. These techniques have allowed photocurrent generation efficiency to be related to local molecular morphology on the nanoscale, far below the diffraction limit. However, their spatial resolution remains insufficient to distinguish individual molecules, and observed PET signals from the photoexcited molecule are often obscured by ensemble averaging over inhomogeneous local structures. Since electron transfer between two substances depends on the direct overlap of their electron wavefunctions, atomic-scale geometric changes can profoundly affect the efficiency of the process. Consequently, developing a photocurrent measurement technique with an atomic spatial resolution that could reveal the fundamental physics governing the PET process would be highly desirable.

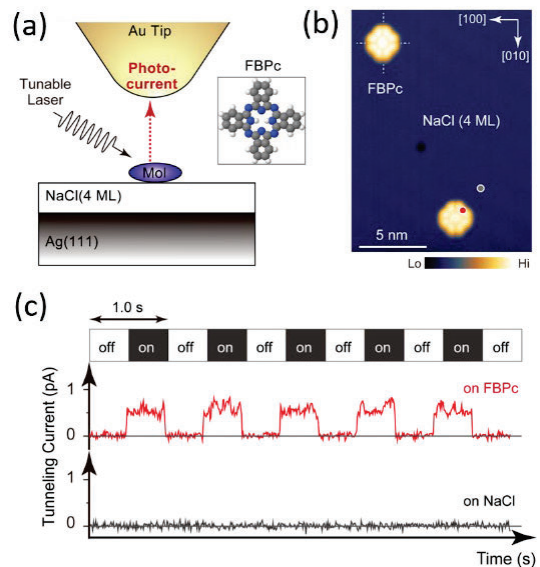


Fig. 6. (a) A schematic illustration of the experiment. The inset is a structure of a FBPc. (b) An STM image of a FBPc/NaCl/Ag(111). (c) Current trace on a FBPc (red) and NaCl (gray). A laser was tuned on and off at 1 Hz using a laser shutter. The tip positions are indicated in (b).

In this study, we report an atomic-scale investigation of photocurrent generation in a single-molecule junction, which is achieved by an STM combined with a narrow-line tuneable laser (Fig. 6 (a)). The experimental setup was carefully designed to optimize the efficiency of molecular excitation; as a result, the excitation laser energy can be tuned to the single-molecule absorption resonance with μeV precision. The experimental technique for resonantly exciting a single molecule using a localized plasmon field driven by a tuneable laser has been established in previous studies [3,6]. We applied this technique for single-molecule photocurrent measurements. Fig. 6(b) shows an STM image of our sample, in which a free-base phthalocyanine (FBPc) molecule is adsorbed on a 4-ML NaCl(100) film grown on the Ag(111) substrate. For the photocurrent measurement, the STM tip was placed on the molecule, and the STM feedback loop was opened, and then the laser was irradiated with the wavelength of 683 nm corresponding to the molecular resonance. Fig. 6(c) (red) shows the trace of tunnel current (I_t) measured on the molecule while the laser was turned on and off at 1 Hz using a shutter. The I_t clearly flows in the laser-on state and stays zero in the laser-off state.

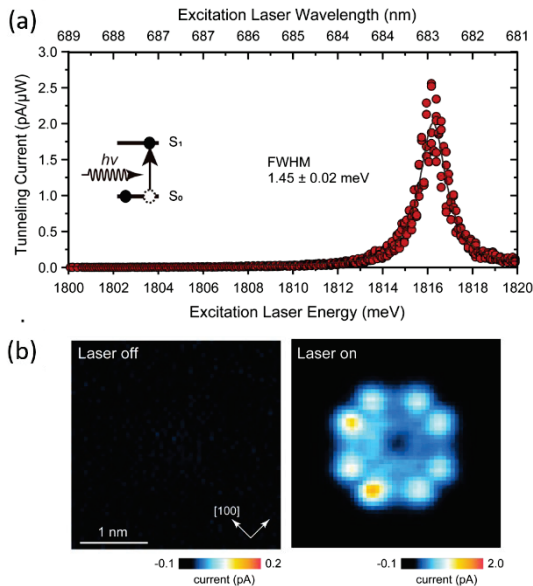


Fig. 7. (a) I_t vs excitation laser energy curve of a FBPc/NaCl(4 ML)/Ag(111). (b) I_t images over the FBPc for the laser-off (left) and laser-on (right) states ($V_s = -2.0$ V).

To elucidate the origin of the excitation, we measured I_t as a function of the laser energy (Fig.

7(a)). The I_t - $h\nu$ curve exhibits a clear peak centered at 1816.24 meV. The peak energy proves that the S_0 - S_1 electronic excitation triggers the photocurrent. Fig. 7(b) shows the I_t images under the laser-off and laser-on conditions. While the observed signals under the laser-off condition were within the margin of error for current measurement, signals far exceeding the noise level were obtained under illumination. The photocurrent image reveals a four-fold symmetric pattern with nodes and lobes similar to the MOs of phthalocyanines that STM has visualized.

In summary, we conducted an atomic-scale investigation of photocurrent generation in a single FBPc molecule using an STM combined with a tuneable laser. The mechanism of photocurrent generation is governed by the frontier MOs in the excited state and their coupling to the metallic electrodes. Based on this understanding, we believe the photocurrent images presented here strongly reflect the characteristic spatial distribution of the molecule's electronic excited states. Our findings provide a new technical basis and perspective for improving energy conversion efficiency by engineering molecular interfaces at the atomic scale.

6. Conclusion

We have been developing new spectroscopic techniques by selective excitation of quantum states in isolated adsorbed molecular systems by taking most of the near-field photons generated at the STM tip junction as the excitation sources for the local quantum states with atomic-scale spatial resolution.

7. References

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