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Tip-enhanced Raman spectroscopy of 4,4′-bipyridine and 4,4′-bipyridine *N,N*′-dioxide adsorbed on gold thin films

I.I. Rzeźnicka [a,b,*], H. Horino [c,1], N. Kikkawa [a], S. Sakaguchi [a], A. Morita [a,d], S. Takahashi [e], T. Komeda [e], H. Fukumura [a], T. Yamada [f,2], M. Kawai [f,g]

[a] *Department of Chemistry, Graduate School of Science, Tohoku University, Japan*
[b] *Institute for International Education, Tohoku University, Japan*
[c] *Graduate School of Environmental Studies, Tohoku University, Japan*
[d] *Elements Strategy Initiative for Catalysis and Batteries (ESICB), Kyoto University, Kyoto, Japan*
[e] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan*
[f] *RIKEN, Advanced Science Institute, Wako, Japan*
[g] *Department of Advanced Materials Science, The University of Tokyo, Kashiwa, Japan*

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ABSTRACT

A tip-enhanced Raman spectroscopy (TERS) set-up added on a scanning tunneling microscope (STM) was constructed and was used to study the molecular arrangement of 4,4′-bipyridine (4,4′-BiPy) and 4,4′-bipyridine *N,N*′-dioxide (4,4′-BiPyO_2) adsorbed on Au(111). Over a monolayer of 4,4′-BiPy, in the ambient atmosphere, intense TERS signals were recorded, involving Au – N stretching vibration at 185 cm^{-1}. At the early stage of 4,4′-BiPy adsorption, the Au – N stretching signal was not detected. By the aid of the theoretical calculations of the Raman scattering intensities for each vibrational normal mode, a standing-up, tilted orientation at monolayer coverage and a vertical orientation with the longitudinal molecular axis parallel to the surface at low surface coverage was concluded. Adsorption of 4,4′-BiPyO_2 on Au(111) resulted in formation of a (6×9) adlattice. Moderately intense TERS signals were observed, containing the N – O stretching modes and the in-plane ring vibrational modes. Neither Au – O nor Au – N stretching modes were observed. 4,4′-BiPyO_2 was laid with the longitudinal axis parallel to the surface, and the molecular plane vertical to the surface. These results demonstrate that STM-TERS is an effective method for simultaneous imaging and vibrational analysis, facilitating identification of the adsorbed layers with the nanometer-scale spatial resolution and monolayer sensitivity.

1. Introduction

4,4′-bipyridine (4,4′-BiPy), together with its oxide form, 4,4′-bipyridine *N,N*′-dioxide (4,4′-BiPyO_2), has been used as ligands to design new metal complexes with interesting photochemical properties for application in dye-sensitized solar cells [1], as electroluminescent materials [2], or as components of future molecular electronic devices [3]. Both molecules tend to self-assemble on solid surfaces and can be used as building blocks for 2D and 3D supramolecular lattices [4–7]. Understanding the physicochemical properties of self-assembled monolayers composed of 4,4′-BiPy and 4,4′-BiPyO_2 on solid surfaces is thus of crucial importance for designing new functional interfaces.

Properties of self-assembled monolayers such as electron transport, optical and magnetic properties depend on the orientation of the adsorbed molecules and their arrangement in a two-dimensional lattice. Molecular orientation can be investigated by vibrational spectroscopy and the 2D arrangement can be determined by scanning probe microscopy. Detection of a vibrational signal from monolayers on metal surfaces has been a challenge due to weak signals and opaque character of the substrates. Infrared spectroscopy was one of the first techniques giving information about orientation of molecules adsorbed on metal and semiconductor surfaces [8]. High-resolution electron energy loss spectroscopy (HREELS), restricted to ultra-high vacuum conditions, has been useful to study orientation of molecules in monolayer and submonolayer regimes. Surface-enhanced infrared adsorption spectroscopy (SEIRAS) and surface-enhanced Raman spectroscopy (SERS) have been used to study molecular orientation under less demanding experimental conditions [9,10].

Raman spectroscopy has been combined with either scanning tunneling microscopy (STM), or atomic force microscopy (AFM), in the so-called “tip-enhanced” Raman spectroscopy (TERS) [11–15]. This technique is capable of simultaneous imaging and vibrational spectroscopy of organic monolayers adsorbed on surfaces with the nanometer-scale spatial resolution and a high sensitivity, reaching even, the detection of a single molecule [16]. A nanometer-sized tip,

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[*] Corresponding author at: Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai, 980-0877 Japan. Tel.: +81 22 217 5199; fax: +81 22 217 5371.

E-mail address: irzeznicka@m.tains.tohoku.ac.jp (I.I. Rzeźnicka).

[1] Kyoto University, SACI (Office of Society-Academia Collaboration for Innovation).

[2] School of Engineering, The University of Tokyo.

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usually made of Au or Ag, is illuminated by a laser beam through a high numerical aperture objective lens. The ingoing and outgoing electromagnetic fields are being enhanced by several orders of magnitude due to both antenna effect of the tip and excitation of localized surface plasmon at the tip-surface nano-cavity [17]. TERS has been gaining popularity in various fields of study. It has been so far applied to study composition of cell membranes [18], chemistry of heme proteins [19], carbon nanotubes [20], DNA bases [21], and dye molecules on metal surfaces [16,22]. Ultimate single-molecular sensitivity has also been demonstrated [16]. Given its high spatial resolution and sensitivity, it is reasonable to apply TERS to study the processes of self-assembly, molecular orientation and complexation of organic molecules on metal surfaces.

Adsorption of 4,4′-BiPy on transition metals has been studied using scanning probe microscopy techniques, infrared and Raman spectroscopies [23–25]. On Au(111), no ordered layers have been found upon adsorption from neutral solutions. On the other hand, ordered layers have been reported when adsorption was carried out from acidic solutions [26], or in an electrochemical environment [24,25]. STM works of Umemura [27], and Pinheiro [26], showed formation of extended, one-dimensional molecular chains. Two other groups have employed infrared spectroscopy with in-situ imaging using electrochemical STM. Wandlowski et al. reported three distinctly different 4,4′-BiPy adlayers with changing substrate potential [25,28]. Diao et al. [29] reported formation of ordered layers for a protonated 4,4′-BiPy on a Cu(111) surface and observation of IR-inactive bands.

SERS has been widely employed to study orientation of 4,4′-BiPy in monolayers formed on noble metals surfaces [23,30–33] in connection to the observed enhanced redox reactions of certain biological molecules, such as cytochrome C adsorbed on metal electrodes modified with 4,4′-BiPy [34]. According to a theoretical derivation of SERS surface-selection rules a vertical orientation of 4,4′-BiPy with respect to the surfaces has been proposed [30,35]. Vibrational bands at ~1600 cm^{-1} were the most enhanced.

In this contribution, we report STM and TERS, both operated in the ambient atmosphere, for 4,4′-BiPy and 4,4′-BiPyO_2, adsorbed from neutral solutions onto Au(111) at different immersion periods. The unique feature of the STM-based TERS is its ability to obtain simultaneously molecularly resolved images of the adlayer and its vibrational signals. The orientation of molecules in the adlayers formed on Au(111) was determined by the aid of theoretical calculation of Raman tensor elements and scattering intensities taking into account the incident light polarization and the orientation of the light-scattering molecule with respect to it. Although STM, infrared spectroscopy and Raman scattering have been extensively applied in the study of 4,4′-BiPy adsorbed on gold, the important grafting bond, the Au–N bond has never been observed. We detected this Au–N stretching vibration by TERS.

2. Experimental

2.1. Materials

4,4′-dipyridyl (98%), and 4,4′-dipyridyl *N,N*′-dioxide (98%) were purchased from Aldrich and were used without further purification. The abbreviation for the compounds throughout the text is as follows: 4,4′-BiPy stands for the 4,4′-dipyridyl, and 4,4′-BiPyO_2 for the 4,4′-dipyridyl *N,N*′-dioxide. Ethanol (99.5%) from Wako, Japan was used as solvent.

2.2. Sample preparation

Slides of thin film of Au deposited on mica (SPI Supplies/Structure Probe, Inc., USA) were used as substrates. Prior to immersion into bipyridine solutions, they were flame annealed in a butane flame in order to form clean (111) terraces. The annealed substrates were immediately immersed into a neutral, 1 mM ethanolic solution of 4,4′-BiPy or 4,4′-BiPyO_2 for the period of 30 min to several days.

2.3. Ordinary Raman (OR)

An ordinary Raman spectrometer (Spex 500 M) equipped with a liquid nitrogen-cooled CCD camera detector was used in order to obtain a reference spectra for 4,4-BiPyO_2 in a powder form. The excitation source was a 488-nm Ar^+ laser with an output of 10 mW at the sample.

2.4. Tip-enhanced Raman spectroscopy (TERS)

Our TERS set-up consists of a commercial STM unit (Nanoscope E, Veeco Instruments Inc., USA), a spectrograph (SP-2150i, Roper Scientific, GmbH), and an optical path. The STM has a modified piezo scanner head which allows to install a high numerical aperture objective lens (Mitutoyo, LWD 100X, N.A. = 0.7, WD = 6 mm) in front of the STM tip. The lens was placed at an angle of 60° of the optical axis to the surface normal with the light polarization parallel to the plane of incidence (*p*-polarization). The position of the lens with respect to the STM unit was controlled by an assembly of *XYZ* stages. The same objective lens was used to deliver an excitation laser beam as well as collect the backscattered light from a tip-surface junction.

Fig. 1 depicts the optical pathway used in this study. A red, He-Ne laser beam (632.8 nm, max. output 30 mW, CVI Melles Griot, USA) passes through a band-pass filter (Sigma Koki, Japan, bandwidth = 3 nm) and a polarizer. The transmitted beam is reflected by a mirror, passed through a 45° dichroic beam splitter (RazorEdge, type U, Semrock, USA), and reflected by two other mirrors before being focused on the tip-surface junction by the objective lens.

The backscattered radiation is collected by the same objective lens and reflected by two mirrors before falling on the dichroic beam splitter, which rejects most of the excitation light, allowing only the Raman signal to pass through. The Raman signal impinges on an ultra-steep long-pass edge filter (LPEF) (RazorEdge, type E, Semrock, USA), and is then focused by a lens (diameter = 25 mm, focal length = 100 mm) onto the slit of the spectrograph. The LPEF used in this study has an advantage of having a sharp rising edge, allowing for detection of weak signals close to the laser line (average transmission >93% at 636.9 nm). A total length of the optical pathway for the backscattered light is 22 cm.

A back-illuminated, charge-coupled device (CCD) camera (Spec-10, Princeton Instruments) cooled by liquid nitrogen is used to acquire Raman spectra. The spectrograph has a diffraction grating with 300 g/mm, yielding a spectral resolution of 10 cm^{-1}.

A zoom lens magnifier was utilized to monitor the coarse approaching motion of STM tip and the TERS laser beam spot. All experiments were carried out in ambient conditions with the incident laser power of 0.4 mW, giving a power density of 8×10^7 W/m^2 in the focal region.

Raman signals could not be detected when the STM tip was far away from the surface and when *s*-polarized light was used for the excitation. The STM images and TERS signals were recorded while scanning the surface at a constant current mode with the preset tunneling current of 0.7 nA and bias of 200 mV (sample positive). All TERS spectra were recorded with the acquisition time of 2 s. In order to avoid contamination, experiments were carried out only for a maximum of 2–3 h after placing the sample and the tip in the ambient environment.

2.5. Tip preparation

Gold tips were used in all TERS measurements reported here. They were prepared by electrochemically etching of a gold wire (0.3 mm thick) in a (1:1 by volume) mixture of hydrochloric acid and ethanol using a gold ring (2 cm in diameter) as the cathode. The procedure has been described in details elsewhere [36,37]. The best tips in term