

Photoswitching Behavior of a Novel Single Molecular Tip for Noncontact Atomic Force Microscopy Designed for Chemical Identification

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A tripod molecule with an azobenzene arm was designed as a single molecular tip for noncontact atomic force microscopy (NC-AFM). The azobenzene moiety showed photoisomerization that enabled measurements of the same position of the sample by different tip apexes with different interactions. Photoswitching behavior of the molecule synthesized and adsorbed on Au surfaces was examined and reversible switching between the trans- and cis forms was successfully confirmed by NC-AFM measurements.

Identification of chemical species and specific ligands on the submolecular scale is one of the key methods for the elucidation of dynamic surface chemical processes and developing functional mesoscopic molecules. Although scanning probe microscopies (SPM) have revealed high spatial resolution, the most conventional method of scanning tunneling microscopy (STM), which easily achieves atomic scale resolution, cannot identify chemical species, except for the special case of vibrational-mode detection for molecules adsorbed on metal surfaces.¹ Spectroscopic methods using light are the most established means of chemical identification, but these methods cannot be used for single-molecule imaging. The resolution of scanning near field optical microscopy (SNOM) or tip-enhanced Raman spectroscopy has been improved,² but is still far from the submolecular scale.

Noncovalent molecular interaction can be used for the chemical identification. Friction force microscopy (FFM) measurements by chemically modified cantilever tips have succeeded in identifying chemical domains at the μm scale by detecting different magnitude of friction between the molecules.^{3,4} However, considerable improvement of the spatial resolution is difficult due to two reasons. First, a principle problem of FFM is that it demands multisite interaction to obtain a detectable magnitude of signal, where the tip pushes and deforms the sample surface. Second, the tip modification by self-assembled monolayers (SAMs) can achieve organized molecular structure by increasing the density of molecular packing, thereby increasing the effective radius of the tip but giving lower spatial resolution.

In the present paper, we report a novel molecule to be adopted as a tip for SPM that gives a smaller radius and has potential for chemical identification in submolecular resolution. It can be used in combination with noncontact atomic force micros-

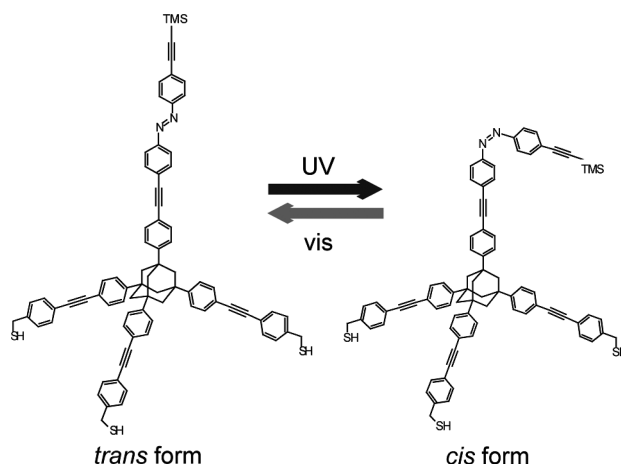


Figure 1. Molecular structure of trans and cis azobenzene derivative molecules (AZO-SH).

copy (NC-AFM), which can achieve molecular and atomic scale imaging using weak attractive forces.^{5,6}

We have designed a molecule (AZO-SH) shown in Figure 1 that is suitable as a molecular tip for NC-AFM. It consists of a rigid adamantane core, three linear legs with thiols at the end, and a tip part that includes an azobenzene arm for photoswitching of the tip apex structure. The AZO-SH molecule is expected to be adsorbed on Au surfaces by formation of three Au-S bonds. Similar tripodal molecules have been reported by Keana and co-workers.⁷ The sharp molecular shape of the AZO-SH molecule has an advantage for reducing van der Waals forces that operate as a background force against chemical interaction at short range. Azobenzene and its derivatives are widely used for photoresponding systems because of its reversible isomerization to the cis form by UV light (ca. 350 nm) and the trans form by visible light (ca. 450 nm) irradiation.⁸ As illustrated in Figure 1, it is expected that photoisomerization will regulate the change of the tip apex, and moieties substituted for the trimethylsilyl (TMS) group can interact with the surface species

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Figure 2. 3D view of an NC-AFM image ($350 \times 350 \text{ nm}^2$, $\Delta f = -10 \text{ Hz}$) of isolated AZO-SH molecules adsorbed on Au(111) substrate. Two kinds of adsorbates were observed with apparent heights of $3.7 \pm 0.3 \text{ nm}$ (solid circles) and less than 2.5 nm (dotted circles), respectively.

in the trans form. Sugawara and co-workers have demonstrated that NC-AFM images drastically changed depending on the atom species picked up from the surface on the tip apex.⁹ Our molecule enables switching the tip apex by photoirradiation. We have synthesized and characterized AZO-SAc molecules, and details will be reported elsewhere.¹⁰

To observe the immobilization of synthesized AZO-SAc molecules on an Au surface and their trans-cis conversion at the azobenzene moiety by light irradiation, the AZO-SAc molecules were dispersively adsorbed on an Au(111) surface¹¹ and subjected to imaging by NC-AFM using a normal Si cantilever.¹² An in situ base-promoted deprotection method¹³ was adopted for the adsorption, in which AZO-SAc was transformed to AZO-SH in the reaction solution and immersion of the Au(111) substrate to the solution led to binding of the AZO-SH molecule to the Au surface by formation of three Au-S bonds.¹⁴ Figure 2 shows a typical NC-AFM image of the AZO-SH molecules adsorbed on Au(111). Dispersed bright protrusions were observed on the terrace, and their line profile analyses revealed that there were two species with different apparent heights. The major one (solid circles) had an apparent height of $3.7 \pm 0.3 \text{ nm}$ and the minor one (dotted circles) shown was less than 2.5 nm . From the molecular structure in Figure 1, one can expect that physical topography of a *trans*-AZO-SH standing on the Au surface by three S-Au bonds would be approximately 3.9 nm , which is in good agreement with the observed height for the major species. As pointed out by Onishi et al.,¹⁵ the apparent height of a tall isolated molecule tends to be slightly reduced in NC-AFM measurements. This is because the sum of van der Waals forces between the tip and the substrate surface, which has a considerable contribution to the total attractive force, is reduced by increased separation when the tip traces the tall molecule. Although the apparent diameters of the bright protrusions were much larger than that expected from the size of the molecule, the lateral size of the protrusions in SPM images is always enlarged as a result of convolution of the tip shape with a typical effective apex radius of 10 nm .¹⁶ Thus, we assigned the major bright protrusion in Figure 2 to be the isolated *trans*-AZO-SH molecule, which is thermodynamically more stable than the *cis*-form at room temperature. Importantly, they were tightly bound to the Au(111) substrate, even at room temperature, and no apparent migration was observed.

Photoisomerization of the adsorbed AZO-SH molecules was examined as follows.¹⁷ After obtaining the topography of an AZO-SH molecule by NC-AFM (Figure 3a), the surface was irradiated by ultraviolet light (UV; $360 \pm 10 \text{ nm}$) for 10 min while the tip was retracted from the surface by approximately $1.0 \mu\text{m}$ and then the same molecule was observed by NC-AFM again (Figure 3b). This experiment revealed that the apparent height of the molecule was reduced by ca. 0.9 nm . The apparent

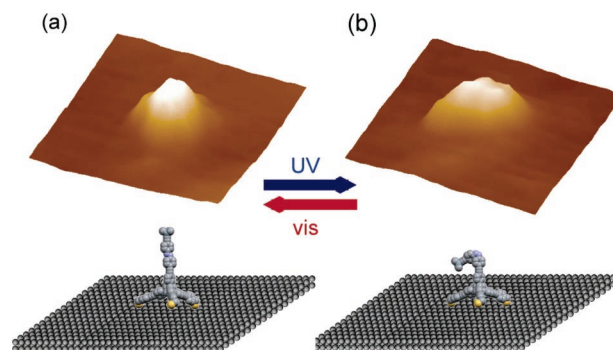


Figure 3. 3D view of typical NC-AFM images ($50 \times 50 \text{ nm}^2$, $\Delta f = -55 \text{ Hz}$) of an AZO-SH adsorbed on Au(111) (a) in the trans form (after visible light ($450 \pm 10 \text{ nm}$) irradiation) and (b) in the cis form (after UV light ($360 \pm 10 \text{ nm}$) irradiation). Corresponding molecular structures of AZO-SH are shown at the bottom.

height of the molecule was recovered to the initial value (4.0 nm), showing the same molecular image as Figure 3a by irradiation of visible light (vis; $450 \pm 10 \text{ nm}$) for 10 min, indicating that trans-cis conformational change was reversible depending on the selection of the wavelength of light. The same cyclic behavior was observed on other molecules whose apparent heights were $3.7 \pm 0.3 \text{ nm}$ prior to light irradiation.¹⁰ The difference of apparent height can be attributed to the change of physical topography between *trans*-AZO-SH and *cis*-AZO-SH, which is calculated to be ca. 1.0 nm . Crude calculations of the frequency shift due to van der Waals forces between the tip and sample (the Au substrate + an AZO-SH molecule) as a function of their separation correlated with a height difference of 1.0 nm between *trans*-AZO-SH and *cis*-AZO-SH in constant-frequency-shift topography. Shigekawa and co-workers have reported on STM observations of reversible photoisomerization of an azobenzene derivative molecule embedded at the boundary of thiol SAMs¹⁸ and found a stochastic height change of the molecule induced by electric field and tunneling current flow. In our case, such stochastic behavior has not been observed and both the trans and cis forms can be stabilized under illumination at the appropriate wavelength. The minor species, which showed an apparent height less than 2.5 nm in Figure 2 (dotted circle), did not change in height by light irradiation. We can tentatively assign these low height protrusions to the AZO-SH laying on the Au surface bound through one or two S-Au bonds, possibly due to insufficient conversion from AZO-SAc to AZO-SH during the adsorption process.¹⁴

We have examined the photoswitching behavior of the AZO-SH molecule fixed on an Au-coated cantilever tip.¹⁹ Although the AZO-SH molecule can be dispersively adsorbed on the Au-coated tip as on Au(111), adsorption at the tip apex was expected to be a stochastic event. As a result, we have succeeded in obtaining the photoswitching behavior of the AZO-SH on the tip. A clean Au(111) surface was scanned by an AZO-SH-adsorbed tip in NC-AFM mode, and in the middle of scanning the tip was stopped at the position indicated by arrow in Figure 4a and irradiated by UV light ($360 \pm 10 \text{ nm}$) for several minutes, then scanning was restarted. As clearly indicated by the line profile A-B in Figure 4a, a virtual step of ca. 0.8 nm high was observed at the scanning line, where UV irradiation starts. It can be attributed to the photoisomerization from the *trans*-AZO-SH to the *cis*-AZO-SH, as schematically shown in Figure 4a. We also confirmed the reverse process by irradiation with visible light ($450 \pm 10 \text{ nm}$) to the *cis*-AZO-SH tip, where the apparent height increased at the virtual step by ca. 0.6 nm (Figure 4b). These results are

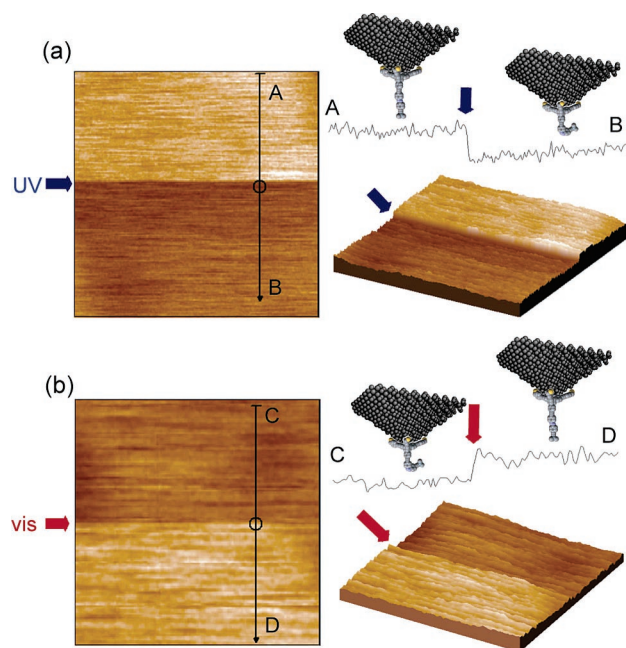


Figure 4. Switching behavior of the AZO-SH fixed on the apex of an Au-coated cantilever tip while NC-AFM imaging of an Au(111) surface. (a) UV light (360 ± 10 nm) irradiation at the point indicated by an arrow transformed the AZO-SH from the trans form to the cis form, resulting in a virtual step in the NC-AFM image of a Au(111) surface. 50×50 nm², $\Delta f = -19$ Hz. (b) Visible light (450 ± 10 nm) irradiation at the point indicated by an arrow transformed the AZO-SH from the cis form to the trans form. 30×30 nm², $\Delta f = -19$ Hz.

consistent with photoswitching behavior of AZO-SH on Au(111) (Figure 3). We can conclude that a newly designed AZO-SH molecule can act as a photoswitching tip that enables observation of the same area with different tips with different structures.

If the TMS protecting ligand is removed from the AZO-SH and terminated with H, a very sharp tip suitable for high-resolution NC-AFM imaging should be realized. We have also started the synthesis of a different tip-part molecule that enables temporal hydrogen-bonding with the surface ligands in its trans form and chemical mapping should be possible.

In summary, it has been demonstrated that our newly designed AZO-SH molecule can be strongly fixed on the Au surface in isolated form and photoswitching between the trans and cis forms can be possible by UV (360 nm) and visible (450 nm) light irradiation. Such photoswitching enables in-situ change of the tip apexes with different interaction with the sample, leading to novel chemical analysis on submolecular scale as well as high-resolution topographic imaging on the same area by NC-AFM.

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- (11) Au(111) substrates were prepared by vacuum evaporation of gold onto freshly cleaved mica and annealing in a butane flame. Such pretreatments always gave a flat Au(111) surface with terraces of 100–200 nm wide.
- (12) NC-AFM measurements were performed in an ultrahigh vacuum (UHV) AFM (JEOL JSPM-4610A) at room temperature. Stiff and conductive Si cantilevers ($f_0 \sim 315$ kHz, $k \sim 48$ N/m) (MicroMasch) were used as force sensors. The peak-to-peak amplitude of vibration of the cantilever was set at approximately 12 nm.
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- (14) Molecules' adsorption processes were performed in a glove-box exchanged with dry N₂ gas. In a dilute THF (Aldrich, Ltd., HPLC-grade) solution of AZO-SAc in a vial, NH₄OH (28% NH₃ in water, Ald Ltd) was added and the mixture was incubated for a few minutes in the dark condition to provide AZO-SH. The clean Au(111) substrate or the clean Au-coated cantilever was deposited in the reaction solution for less than 3 min and immediately rinsed with pure THF solvent and Milli-Q water (Nihon Millipore).
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