

Surface-Enhanced Raman Spectroscopy to Probe Reversibly Photoswitchable Azobenzene in Controlled Nanoscale Environments

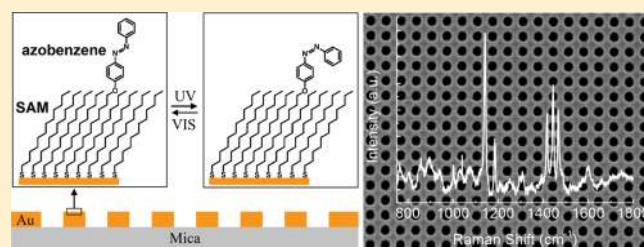
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ABSTRACT: We apply in situ surface-enhanced Raman spectroscopy (SERS) to probe the reversible photoswitching of azobenzene-functionalized molecules inserted in self-assembled monolayers that serve as controlled nanoscale environments. Nanohole arrays are fabricated in Au thin films to enable SERS measurements associated with excitation of surface plasmons. A series of SERS spectra are recorded for azobenzene upon cycling exposure to UV (365 nm) and blue (450 nm) light. Experimental spectra match theoretical calculations. On the basis of both the simulations and the experimental data analysis, SERS provides quantitative information on the reversible photoswitching of azobenzene in controlled nanoscale environments.

KEYWORDS: Surface-enhanced Raman spectroscopy, photoisomerization, azobenzene, nanohole arrays, self-assembled monolayers, surface plasmons



Molecular machines, which experience precise molecular-scale mechanical motions upon external stimuli, have elicited great interest for understanding the fundamental limit at the nanoscale and for a broad range of applications from information processing, nanoelectromechanical systems, energy, biology, to medicine.^{1–21} Of the various molecular machines studied, photoswitchable molecules have attracted the most attention because light, as their trigger, is noninvasive, high speed, and directed.^{17,22–34} Since the first report of its *trans–cis* photoisomeration, azobenzene has arguably been the most studied photoswitchable molecular machine due to its simple molecular structure and spectra.³⁵ The applicability of azobenzenes and other molecular machines in various functional devices depends largely on our capabilities in probing and controlling the interactions and mechanical motions of the molecules once transferred from solution to solid-state substrates.^{13,35–40} Since its discovery by van Duyne and Creighton, surface-enhanced Raman spectroscopy (SERS), which is based on enhanced interactions of light with molecular vibrations, has played an important role in the study of molecular structure and conformation due to its noninvasiveness, single-molecule sensitivity, and fingerprint signatures.^{41–47} Unfortunately, SERS studies of azobenzene on solid-state substrates have not previously succeeded in observing the reversible photoswitching of the molecules.^{35,48–54} This is because the evidence of photoswitching of molecules on the metal substrates used in SERS is often complicated by multiple factors such as surface quenching, steric hindrance, and non-photoinduced switching.^{28,55,56} Herein, we develop an approach to minimize these multiple factors related to molecular switching by inserting azobenzene in self-assembled monolayers (SAMs)

of alkanethiol molecules on Au{111}. As a result, functioning as controlled nanoscale environments,^{57–64} the SAM matrix improves our control of the reversible photoswitching of azobenzene. Likewise, it has been difficult to study functional molecules inserted in two-dimensional SAM matrices spectroscopically because of their low numbers and varied environments.^{38,39,57,64–66} By applying SERS to the inserted functionalized azobenzene in the SAM matrix, we have successfully monitored reversible *trans–cis* photoisomerization at dilute coverage.

Figure 1a is a cross-sectional view of azobenzene-functionalized molecules inserted in a thiolate matrix on an epitaxial Au thin film with a nanohole array. The Au thin films grown on mica substrates have a thickness of 150 nm and the atomically flat terraces on the Au surfaces provide high-quality substrates for SAMs. Azobenzene-functionalized molecules, 4-(1-mercapto-6-hexyloxy)-azobenzene (**1**, purchased from ProChimia Surfaces, Poland, and shown as the thiolate) chemisorbed within domains of dodecanethiolate (**C12**, purchased from Sigma-Aldrich and also shown as the thiolate) SAM on Au surfaces around the nanoholes.^{64,65,67–69}

Cylindrical nanoholes in square arrays were fabricated into the Au thin films with focused ion beam (FIB) lithography (Nova 600 NanoLab, FEI Company, Hillsboro, OR, USA). The nanoholes have a diameter of 175 nm; the array period is varied within a range from 280 to 450 nm to tune the plasmon resonances to the excitation laser wavelength for maximizing the enhancement

Received: June 6, 2011

Revised: July 5, 2011

Published: July 12, 2011

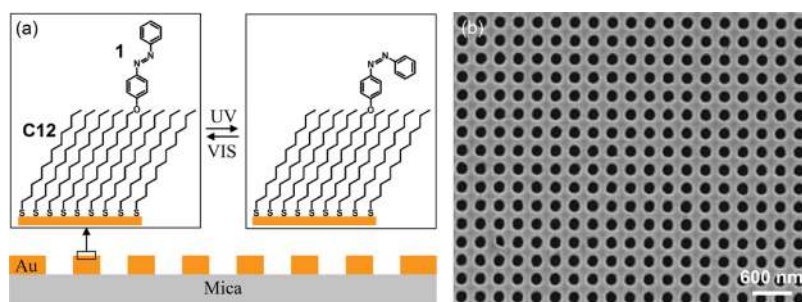


Figure 1. (a) A cross-sectional view of a single azobenzene molecule **1** inserted in a self-assembled monolayer of dodecanethiolate (**C12**) on a Au film with a nanohole array. The azobenzene is reversibly photoisomerized between *trans* and *cis* conformations by cycling exposure to UV (365 nm) and blue (450 nm) light. (b) A representative scanning electron microscopy (SEM) image of the nanohole arrays on Au thin films.

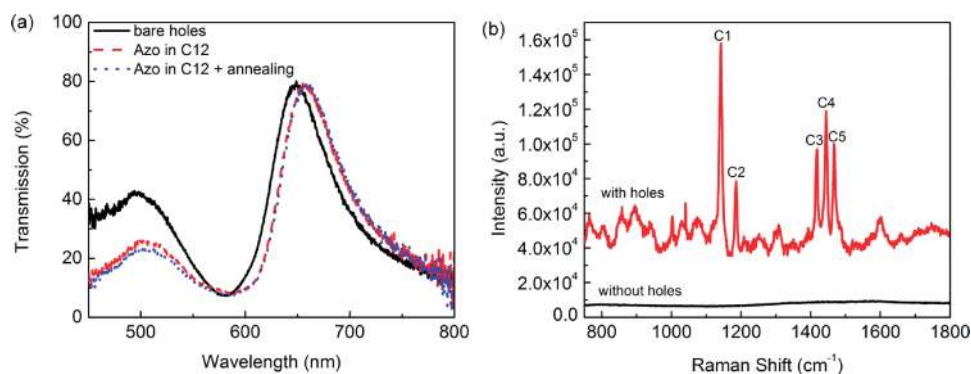


Figure 2. (a) Transmission spectra recorded from the same sample at three different processing stages, that is, the bare Au nanohole arrays after flaming annealing, the Au nanohole arrays with SAM after solution incubation, and the Au nanohole arrays with SAM after vapor annealing. (b) Raman spectra of azobenzenes in a thiolate matrix recorded from the substrate regimes with nanoholes (red) and without nanoholes (black), respectively.

of azobenzene Raman signals.^{70–74} Figure 1b shows a representative scanning electron microscopy (SEM) image of a nanohole array with hole diameters of 175 nm and a period of 300 nm. An ethanolic mixture of **1** and **C12** were coadsorbed with a total thiol concentration of 1 mM and a molar ratio of 1:4, respectively, for 24 h under a nitrogen atmosphere. The samples were then annealed in **C12** vapor for 2 h at 80 °C to add **C12** for increased packing and order of the matrix.⁶⁷ Azobenzene molecules in the matrix were reversibly photoisomerized between *trans* and *cis* conformations by cycling exposure to UV (365 nm) and blue (450 nm) light.³⁶

For large signal enhancement, SERS requires significant overlap between the wavelength of the excitation laser and that of plasmon resonances of the substrates.⁴¹ To probe the surface plasmon resonances on the Au thin films with nanohole arrays, we recorded transmission spectra of the samples using an UV–vis–IR spectrometer (USB4000, Ocean Optics Inc., Dunedin, Florida). The transmission measurements were made with normal incidence for the probe light. Figure 2a shows the transmission spectra of a bare Au nanohole array immediately after flame annealing, the sample after its incubation in an ethanolic mixture of **1** and **C12** followed by blowing dry with N₂, and the same sample after vapor annealing, respectively. All three spectra exhibit two transmission peaks in the wavelength range of interest. The peak at the shorter wavelength is due to the bulk Au film transparency at the threshold of interband sp-d transition.⁷⁵ The longer wavelength peak arises from the surface plasmon resonances.^{70,72} Formation of SAMs caused a redshift of

the resonance peak from 648 to 658 nm due to the increase of the refractive index surrounding the nanohole arrays. Insertion of **C12** after vapor annealing caused a slight further redshift of the resonance peak.

With knowledge of the resonant wavelength of the Au substrates, we chose a 632.8 nm He–Ne laser as the Raman excitation source. Raman analysis was performed in a back-scattering geometry in a confocal configuration at room temperature with polarized light using a Renishaw inVia Raman system (Renishaw Inc., Illinois). Laser power and beam diameter were approximately 17 mW and 1 μm, respectively, while the integration time was set to 150 s. The area intensities of the peaks were estimated by curve fitting done using Wire 3.2 software (Renishaw Inc., Illinois). Figure 2b shows the Raman spectra of azobenzene in the **C12** matrix recorded at areas with and without nanoholes, respectively. No obvious Raman signal appears in the spectra recorded from the areas without nanoholes. In contrast, a strong Raman signal with five peaks was obtained for the azobenzene in the area of nanoholes. We assign the five peaks as C1, C2, C3, C4, and C5 modes and discuss them in detail below in the context of associated calculations of this system.

To follow reversible *trans*–*cis* photoisomerization of tethered azobenzene in the matrix and to test the capability of SERS to probe photoswitching of small numbers of molecules, we recorded a series of SERS spectra while cycling exposure of the sample to UV (365 nm) and blue (450 nm) light. The time-dependent spectra upon irradiation of UV and blue light are shown in Figure 3a and 3b, respectively. The duration (in minutes) of

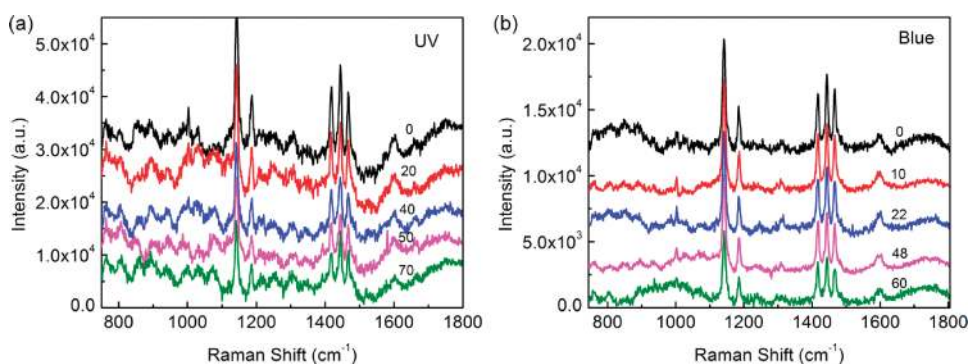


Figure 3. A series of time-dependent SERS spectra after alternating exposure of the samples to (a) UV (365 nm) and (b) blue (450 nm) light. The exposure time (in minutes) is indicated as a number near the corresponding spectra. The background signals are subtracted from the original spectra, and vertical offsets of the spectra are used for clarity.

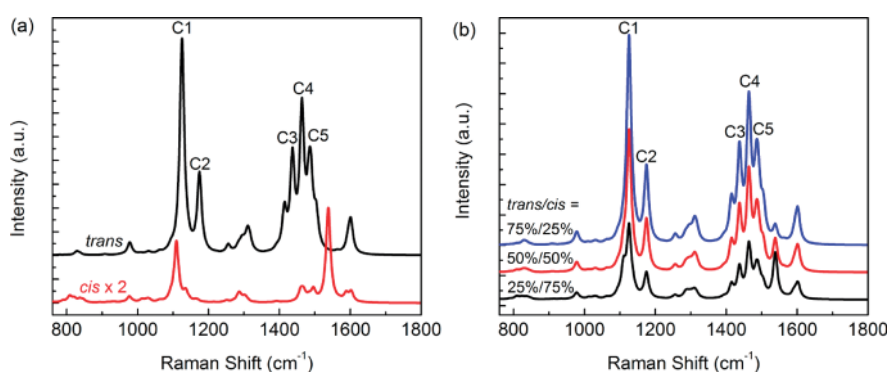


Figure 4. Simulated (B3LYP/6-31G*) Raman spectra of (a) the *trans* and *cis* isomers of 4-(1-mercapto-6-hexyloxy)-azobenzene, and (b) the various convoluted mole fractions of the two spectra. The spectrum intensity of the *cis* isomer is amplified by $2\times$ to have a better view of the modes.

the light irradiation is indicated near the corresponding Raman spectra.

To gain further insight into the modes observed in the SERS spectra and their correlation with *trans*–*cis* photoisomerization of azobenzene, we have performed B3LYP/6-31G* calculations⁷⁶ of the Raman spectra (Figure 4a) for the two isomers of the azobenzene, 4-(1-mercapto-6-hexyloxy)-azobenzene, used in the experimental studies and have examined the dependence of the spectrum on the mole fractions of the two isomers. The calculations were done using the NWChem program package.⁷⁷ The calculated frequencies were scaled by 0.9614 to correct for anharmonicity, and the intensities were plotted as Lorentzian curves.⁷⁸ The *cis* spectrum is an order of magnitude weaker than the *trans* spectrum. The C3 peak for the *cis* spectrum nearly vanishes while the other four major peaks have some contributions from the *cis* isomer. The intensity drop for the *cis* spectrum can be attributed to loss of conjugation of the *cis* isomer and the consequent reduced polarizability and Raman intensity. Figure 4b shows the spectra with various mole fractions of the *trans* and *cis* spectra convoluted. The experimental (Figure 3) and simulated (Figure 4b) spectra are in good agreement. We assign the C1–C5 peaks to the azobenzene unit with minimal coupling to the alkyl chain (see Figure 5). As shown in the figure, C1 and C2 are predominately CN stretches coupled with ring breathing modes. C3 is mainly an in-plane ring bending mode with minor coupling to the NN stretch. C4 is similar to C3 with the addition of alkyl HCH bending. C5 is a mixture of the three moderately intense modes combining the NN stretch,

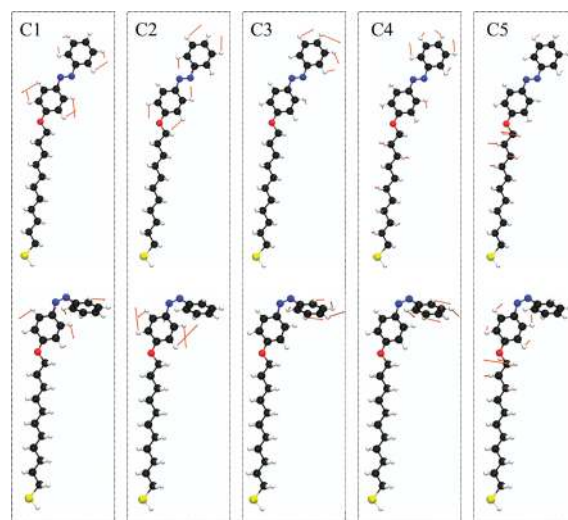


Figure 5. Schematic of C1–C5 modes for *trans* and *cis* isomers.

minor in-plane ring modes, and alkyl HCH bending. These assignments are in agreement with other reports of azobenzene spectra.⁷⁹

To have temporal information on the SERS modes for probing the switching kinetics of azobenzene, we analyze the experimental spectra (Figure 3) as follows: first, we calculate the ratios between the peak areas of each pair of modes for each spectrum

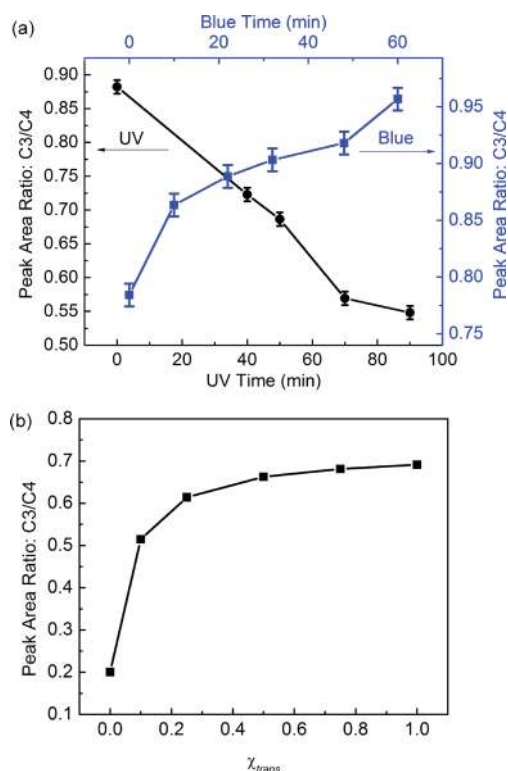


Figure 6. (a) The experimental peak area ratio (C3/C4) of the Raman modes C3 and C4 as a function of UV (black) and blue (blue) light exposure time. (b) The simulated (B3LYP/6-31G*) peak area ratio (C3/C4) of the Raman modes C3 and C4 as a function of mole fraction (χ_{trans}) of the *trans* isomer.

for each light exposure time. As a result, a set of data points ($C_i/C_j, t$) was obtained, where C_i and C_j are the peak areas for the i^{th} and j^{th} modes, respectively; i and j range from 1 to 5; and t is the exposure time. Second, for each pair of i and j , a plot of C_i/C_j as a function of t is plotted with y and x axes as C_i/C_j and t , respectively. The plots for UV and blue light exposure are separated. Finally, among these plots, we identify one group of plots ($C3/C4$ as a function of t), shown in Figure 6a, that exhibits monotonic and reversible trends upon cycling exposure between UV and blue light. The error bars are determined by the standard deviations of the peak area ratios in four sets of measurements.

In the same way, we analyze data for the calculated Raman spectra (Figure 4). In this case, the ratios of the peak areas of each pair of modes are derived from

$$\frac{C_i}{C_j} = \frac{\chi_{trans}^{trans} C_i^{trans} + (1 - \chi_{trans}^{trans}) C_i^{cis}}{\chi_{trans}^{trans} C_j^{trans} + (1 - \chi_{trans}^{trans}) C_j^{cis}}$$

where χ_{trans}^{trans} is the mole fraction of the *trans* isomer, and C_i^{trans} and C_i^{cis} are the i^{th} peak areas for the *trans* and *cis* isomer, respectively. If there were no contribution from the *cis* isomer ($C_i^{cis} = 0$), the ratio would be unity and the corresponding plots would result in a flat line. The extracted plot of the experimental ratio (Figure 6a) is not flat and matches the calculated ratio with contributions from both *cis* and *trans* isomers (Figure 6b), reflecting the photo-switching of azobenzene. Specifically, UV light transforms the azobenzenes from *trans* to *cis*, leading to a decrease of the peak area ratio (C3/C4); blue light switches azobenzene back from *cis* to *trans*, leading to an increase in C3/C4.

In summary, we have succeeded in probing the reversible photoswitching of azobenzene with SERS. This success is, first of all, attributed to the high sensitivity of SERS in distinguishing the fingerprint of the *trans* and *cis* isomers of azobenzene. Also, by inserting the tethered azobenzene in alkanethiolate SAMs, we provide controlled nanoscale environments for the molecular machines to enhance their photoswitching.³⁶ This enhanced photoswitching facilitates the observation of the reversible *trans*–*cis* photoisomerization by monitoring the peak area ratios as a function of light exposure time. The experimental observations and vibrational peak assignments are supported by theoretical calculations. We believe that SERS with its ability to probe the reversible photoisomerization of azobenzene will enable molecular-level understanding and engineering of the azobenzene-based functional devices. Eventually, such a combination of advanced molecular self-assembly methods with spectroscopic tools may enable all-optical molecular devices where powering, writing, and detecting are all based on light.^{17,25,80}

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ACKNOWLEDGMENT

We thank the Department of Energy (Grant DE-FG02-07ER15877), the NSF-supported Center for Nanoscale Science (MRSEC), and the Kavli Foundation for support of the work described here. The Raman simulations were supported through the instrumentation funded by the NSF (Grant OCI-0821527) and CAREER program of the NSF (Grant CHE-0955689). The substrates were fabricated at the California NanoSystems Institute.

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