Conformational Contrast of Surface-Mediated Molecular Switches Yields Ångstrom-Scale Spatial Resolution in Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy

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ABSTRACT: Tip-enhanced Raman spectroscopy (TERS) combines the ability of scanning probe microscopy (SPM) to resolve atomic-scale surface features with the single-molecule chemical sensitivity of surface-enhanced Raman spectroscopy (SERS). Here, we report additional insights into the nature of the conformational dynamics of a free-base porphyrin at room temperature adsorbed on a metal surface. We have interrogated the conformational switch between two metastable surface-mediated isomers of meso-tetrakis(3,5-diteriarybutylphenyl)-porphyrin (H$_2$TBPP) on a Cu(111) surface. At room temperature, the barrier between the porphyrin ring buckled up/down conformations of the H$_2$TBPP-Cu(111) system is easily overcome, and a 2.6 Å lateral resolution by simultaneous TERS and STM analysis is achieved under ultrahigh vacuum (UHV) conditions. This work demonstrates the first UHV-TERS on Cu(111) and shows TERS can unambiguously distinguish the conformational differences between neighboring molecules with Ångstrom-scale spatial resolution, thereby establishing it as a leading method for the study of metal–adsorbate interactions.

KEYWORDS: Ultrahigh vacuum, tip-enhanced Raman spectroscopy, conformational isomers, nanoscale chemical imaging, single molecule spectroscopy

Understanding the nature of molecule–surface interactions at the Ångstrom scale is essential to the development of molecular self-assembly, site-specific chemical reactions, and nanoscale electronic and photonic devices. Surface-bound porphyrins have been extensively interrogated for the aforementioned applications due to their distinct electronic, photonic, and catalytic properties.† Ultra-high vacuum (UHV) scanning tunneling microscopy (STM) is the most widely used technique for studying the absorption of porphyrins on noble metal surfaces (e.g., Ag, Au, and Cu). In contrast to Ag or Au surfaces, Cu has a stronger surface interaction with adsorbed metal-free porphyrin molecules, which results in deformation$^{3,4}$ of the porphyrin ring or even self-metalation with the surface atoms at room or elevated temperatures.$^{5–7}$

While UHV-STM can resolve individual molecules on conductive surfaces,$^{8–10}$ it does not provide direct chemical information except when using inelastic electron tunneling spectroscopy at liquid helium temperatures for small molecules.$^{11}$ On other hand, tip-enhanced Raman spectroscopy (TERS) integrates the single-molecule chemical sensitivity of surface-enhanced Raman spectroscopy (SERS)$^{12}$ by utilizing plasmonic metals as the STM tip material.$^{13–16}$ TERS has been utilized for the study of photochemistry$^{17}$ and electrochemistry$^{18–20}$ at the nanoscale. Under UHV conditions, TERS has been further employed to assess the binding geometries of molecular adsorbates,$^{21,22}$ low-dimensional carbon materials$^{23,24}$ and single-molecule isomerization.$^{25}$ Furthermore, three distinct surface-bound molecular systems have been demonstrated with correlated STM and TERS imaging: isolated molecules,$^{26,27}$ distinct, adjacent adsorbates,$^{28}$ and dynamic molecular phase boundaries.$^{29}$

Here, we report an alternative approach for obtaining contrast in TERS imaging that is based on the spectral shifts from two neighboring surface-mediated conformational isomers. Specifically, we have interrogated the conformational change of meso-
tetakis(3,5-ditertiarybutylphenyl)-porphyrin (H₄TBPP) on a Cu(111) surface with simultaneous STM and UHV-TERS analysis, resulting in 2.6 Å lateral resolution at room temperature. This submolecular lateral resolution of TERS allows us to unambiguously obtain spectroscopic information on the neighboring surface-bound isomers. In combination with time-dependent density functional theory (TDDFT) simulations, we assess the role of the H₂TBPP–Cu interaction with respect to the vibrational normal modes that are directly responsible for the formation of these conformational isomers.

In this study, imaging and spectroscopy were performed with a home-built, two-chamber optical UHV-STM with all optical elements located outside the UHV chamber (base pressure of ∼2 × 10⁻¹¹ Torr). A 561 nm continuous wave laser (LASOS DPSSL) was used as the excitation source. A laser power stabilizer (Brockton Electro-Optics Corp.) maintains the excitation power at 1.00 mW. The excitation polarization was rotated by a half-wave plate to be parallel to the tip axis before entering the UHV chamber. The laser beam was then focused at the tip-sample junction at an angle of incidence of roughly 75° with respect to the Cu(111) surface normal. The TERS signal was collected at the same angle through a viewport on the opposite side of the chamber, which was then focused onto a 100 μm slit of a spectrograph (Princeton Instruments SCT 320) equipped with a thermoelectrically cooled CCD (Princeton Instruments Pixis 400BR).

All sample preparation was performed under UHV conditions. In particular, the Cu(111) single crystal (Princeton Scientific Corp.) was cleaned by repeated cycles of Ar⁺ ion sputtering and annealing at 820 K. H₂TBPP molecules were thermally sublimed at ∼575 K onto the resulting clean Cu(111). Electrochemically etched Ag tips were cleaned by Ar⁺ ion sputtering preceding all experiments.

Figure 1a shows a typical surface molecular assembly of H₂TBPP on Cu(111) at room temperature. The molecules appear as alternating bright and dark spots in the STM image. In contrast to previously reported results on Ag(111), high-resolution STM images show that H₂TBPP adsorbs on Cu(111) in two distinct configurations: “bowl-down” with the porphyrin ring close to the surface and “bowl-up” with the porphyrin ring further away from the surface due to the strong molecule–surface interaction on Cu(111). The bright spots in Figure 1c are due to the bowl-up H₂TBPP molecules, whereas the dark spots between the alternating bright rows are due to the bowl-down structures.

The optimized geometries for the “bowl-down” and “bowl-up” configurations of H₂TBPP adsorbed on Cu(111) are presented in Figure 1b (top-view of the molecular structures are shown in Figure S1). The separation distances between the center of porphyrin macrocycle and the Cu surface are 2.9 and 6.6 Å for the bowl-down and bowl-up configurations, respectively. The gas phase structure of H₂TBPP is characterized by a flat geometry where the di-tert-butylphenyl groups are perpendicular to the porphyrin ring. We find that the di-tert-butylphenyl groups tilt upward out of the plane of the porphyrin macrocycle by roughly 30° in the bowl-down isomer.

As demonstrated by Marbach et al., the energy barrier for the transition between the bowl-up and bowl-down isomers is readily overcome at room temperature. The molecules randomly flip their conformations over time (Supporting Information, Video 1). Figure 2a shows a high-resolution STM image acquired with constant current mode (0.75 V, 550 pA) in the area of interest before the TERS measurements. The half-bright and half-dark molecules are those that flipped conformation from one STM line scan to another. The lifetime of the isomers is of the order of tens of seconds to minutes, which enables TERS characterization. We also note that the local heating effect in a typical TERS junction is in the order of 10 K, which may alter the flipping dynamics between the two conformational isomers. Therefore, simultaneous STM and TERS measurement is essential to confirm the conformational status of the molecule during TERS line scans.

A TERS line scan (0.25 nm per step, 30 s acquisition per TERS spectrum) was performed over a group of four molecules as indicated by the green dotted lines in Figure 2a. A top-down waterfall plot shows the UHV-TERS spectrum from 750 to 1650 cm⁻¹ acquired along the dotted line (Figure 2b). The figure shows that the most intense vibrational mode (∼1502 cm⁻¹) has a red shift of 15 cm⁻¹, which shifts back to 1502 cm⁻¹ as the STM tip is scanned across the molecules. The simultaneously acquired STM line scan (middle panel, Figure 2c) reveals the status of the molecules during the TERS line scan which shows bowl-down, bowl-up, bowl-up, and bowl-down conformations (top panel, Figure 2c). These results indicate that some molecules on the green dotted lines in Figure 2a have already flipped their conformations before starting the TERS line scan. Therefore, simultaneous STM and TERS analysis is required to accurately characterize this dynamic switching system. Furthermore, the TERS line scan of the numerically integrated 1502 cm⁻¹ mode (bottom panel, Figure 2c) shows that the bowl-down conformations have a higher intensity in the 1502 cm⁻¹ mode than the bowl-up conformations. We analyzed the line spread function of the second step in the TERS line scan as described in a previous publication, which indicates a 2.56 Å lateral resolution, ~2X higher resolution than previously demonstrated by Dong et al. on both molecular systems and carbon nanotubes. Additional STM/TERS line scans are shown in Figure S2 which shows exactly the same correlation as in
Averaging over four neighboring H$_2$TBPP pairs, the average lateral resolution is 3.59 Å ± 1.28 Å. Even though the detailed mechanism of this extraordinary TERS spatial resolution remains under investigation by theoreticians,$^{37-39}$ one possible hypothesis is that the atomic sharpness of the STM tip is essential for achieving the high spatial resolution in TERS. Previous work has demonstrated that atomically sharp plasmonic junctions can provide the subnanometer field localization needed for high resolution.$^{40}$ The submolecular resolution of the TERS line scan allows us to reconstruct the single-molecule TERS spectra from an ensemble of submolecular TERS spectra for individual and neighboring bowl-up and bowl-down conformational isomers. In order to interrogate the detailed spectral differences in the TERS spectra of the two different conformational isomers, we accumulated all TERS spectra in our TERS line scan (15 each) that were associated with bowl-up or bowl-down conformational states based on the STM line scan in Figure 2c to achieve spectra exhibiting better signal-to-noise ratio than individually collected point TERS spectra. In particular, the blue spectrum in Figure 3 represents the TERS spectrum originating from the bowl-up conformation, while the red spectrum originates from the bowl-down conformation.

With the intention of accurately detecting small band shifts, a Raman difference spectrum of the two isomers is plotted in Figure 3. The difference spectrum reveals that the 1502 cm$^{-1}$ mode in the bowl-down conformation is unambiguously red-shifted to 1517 cm$^{-1}$ for the bowl-up conformation. Additionally, we note that the vibrational mode at ~1425 cm$^{-1}$ appears to be shifted as well. However, the signal-to-noise ratio is not high enough to conclude that the shift is significant in the difference spectrum.

In order to understand the origin of the observed spectral shifts, we used TDDFT to simulate the resonance Raman spectra of the two conformations. The geometries and vibrational frequencies of H$_2$TBPP on the Cu(111) surface were obtained using the discrete interaction model-quantum mechanics (DIM/QM) method$^{41-43}$ as implemented in the ADF program.$^{44,45}$

The calculations were performed at the BP86/DZP level. The molecular force-field parameters needed for the DIM/QM optimization were taken from the AMBER force field.$^{46}$ For the Cu atoms, we used the following parameters $\sigma = 2.3125$ kcal mol$^{-1}$ and $R = 1.5058$ Å. These values were obtained by parametrizing the binding of benzene to the Cu surface.

The resonant Raman scattering of H$_2$TBPP adsorbed on the Cu(111) surface was calculated using a time-dependent wave packet formalism.$^{47}$ The excited-state properties were obtained using the DIM/QM method, but only the image field effects were included in the simulations. We applied a three-point numerical differentiation with respect to mass-weighted normal modes to calculate the excited-state energy and transition dipole derivatives needed with respect to the mass-weighted normal mode in order to evaluate the Franck–Condon factors and Herzberg–Teller contributions. All simulated Raman spectra were broadened by Lorentzians with full width at half maxima of 7 cm$^{-1}$. The vibrational frequencies were scaled by a factor of 0.983 to match the experimental results. The DIM/QM model
accounts for the dispersion and image field interactions with the surface. To test the model, we also considered a different configuration, “flat structure” of H$_2$TBPP adsorbed on the Cu(111) facet (Figure S3). This configuration has previously been studied at the DFT level on Ag(111) surface. Our results are in good agreement with the previous DFT results showing that the DIM/QM model can provide reasonable absorption geometries.

The resonance Raman scattering spectra were generated by using the lowest excitation energy that corresponds to excitation into the $Q_x(0,0)$ band of H$_2$TBPP. Figure 4a shows the resonance Raman scattering spectra. The strongest Raman modes are 1502 cm$^{-1}$ for the bowl-down and 1517 cm$^{-1}$ for the bowl-up conformations. A small shoulder adjacent to the most intense mode is also observed for both configurations. Another important pair of active Raman modes are 1458 and 1466 cm$^{-1}$ for bowl-down and bowl-up, respectively, which are comparable to a pair of frequencies appearing around 1425 cm$^{-1}$ in the experimental spectra.

We further visualized the active normal modes corresponding to the important pairs of Raman signals in Figure 4b with movies illustrating the normal mode motion being included in the Supporting Information. The normal modes are overall characterized by in-plane skeletal porphyrin vibrations. Normal modes at 1502 and 1517 cm$^{-1}$ show similar porphyrin in-plane vibration, but differ in their motion of the center N–H bonds. For the bowl-up conformation, the N–H bond vibration is restricted, whereas it displays a rocking motion for the bowl-down conformation. Similar normal modes are found in isolated H$_2$TBPP molecules where the corresponding mode frequencies are 1558 and 1511 cm$^{-1}$, respectively. The stronger interaction with the Cu surface in the down configuration leads to the down shift of this vibrational frequency. The other aforementioned pair of normal modes (residing at 1458 and 1466 cm$^{-1}$) are found to be identical in the simulations. The slight difference in the frequencies may be ascribed to the deformation of the porphyrin structure. The attraction from the surface is weak in the bowl-up configuration leading to a slightly less bent porphyrin ring in comparison to the bowl-down configuration.

In conclusion, we have obtained vibrational spectra of surface-mediated conformational isomers on Cu(111) using simultaneous UHV-TERS and STM imaging for the first time. With the demonstrated 2.6 Å lateral spatial resolution, single-molecule spectra can be built up from a series of point spectra taken over one adsorbate. TERS can thus unambiguously distinguish the conformational differences between neighboring molecules that originate from subtle differences in metal–adsorbate interactions. TDDFT simulations allow further insight into the chemical information obtained by TERS and provide a direct route for evaluating the conformational isomerization mechanism and the exact structure of the two isomers. The time frame for the actual flipping dynamics is faster than what STM electronics can capture. In order to fully understand the dynamics, a pump–probe experiment with ultrafast lasers combined with UHV-TERS is needed for future studies. Overall, this work advances the understanding of adsorbed single molecules and their reactions at metal surfaces.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.6b03958.

Top view of the optimized geometries for the bowl-up and bowl-down H$_2$TBPP on Cu(111); optimized geometries and simulated resonance Raman spectrum of the “flat” geometries H2TBPP on Cu(111); STM/TERS line scans on two additional neighboring H$_2$TBPP pairs; surface reconstruction and self-metalation of H$_2$TBPP after annealing at 380 K (PDF)

STM movie showing the flipping between bowl-up and bowl-down isomers at room temperature (AVI)

Movie showing the 1458 cm$^{-1}$ normal mode of the bowl-down H$_2$TBPP (AVI)

Movie showing the 1502 cm$^{-1}$ normal mode of the bowl-down H$_2$TBPP (AVI)

Movie showing the 1466 cm$^{-1}$ normal mode of the bowl-up H$_2$TBPP (AVI)

Movie showing the 1517 cm$^{-1}$ normal mode of the bowl-up H$_2$TBPP (AVI)

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The authors declare no competing financial interest.

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Figure S1. Optimized geometries bowl-down (left) and bowl-up (right) configurations of H$_2$TBPP adsorption on Cu(111) facet in sideview (top) and topview (bottom).
Figure S2. (a) STM topographic image probed by a Ag tip (imaging conditions: 0.75 V, 550 pA, 16 nm × 8 nm) before TERS imaging experiments were performed on two different pairs of H$_2$TBPP. The dotted green line indicates the locations where TERS spectra were obtained along Pair 3 and Pair 4. (b) and (c) top: TERS line scan of the integrated 1502 cm$^{-1}$ mode along Pair 3 and Pair 4, bottom: simultaneously acquired STM line scan.

Figure S2 shows two additional neighboring H$_2$TBPP pairs which were probed by simultaneous STM and TERS line scan as described in the main manuscript. The integrated intensity of the 1502 cm$^{-1}$ peak in both TERS line scans were anti-correlated with the STM topographic line scan. This observation is consistent with the line scans with four molecules as shown in Figure 2.
**Figure S3.** Top: optimized geometries bowl-down (left) and bowl-up (right) configurations of the flat H$_2$TBPP adsorption structures on Cu(111) facet in sideview (top) and topview (bottom). Bottom: simulated resonance Raman scattering of bowl-up and bowl-down H$_2$TBPP flat structures and selected active normal modes.

Our results for the Raman spectrum are in good agreement with the previous DFT simulations (Ref. 48 in the main manuscript), but do not agree with the experimental spectra obtained in this work. This indicates that the configuration probed in the TERS measurements are closer to the configuration discussed in the main manuscript.
Upon thermal annealing, two different surface structure is observed as seen in the top panel of Figure S2. Marbach and co-workers have observed a change in structure to a hexagonal closed-pack structure at 330 K and self-metalation at 450 K.\textsuperscript{1} We annealed our sample to 380 K to obtained both configurations. The black line in Figure S2 shows the reconfigured H\textsubscript{2}TBPP molecules which the circle shows the CuTBPP from self-metalation. Our TDDFT simulation also predicted the reconfigured H\textsubscript{2}TBPP as the bowl-flat geometry (slightly different from the bowl-up structrure) in the bottom panel of Figure S2.
References: