Visualizing On-Surface Decomposition Chemistry at the Nanoscale Using Tip-Enhanced Raman Spectroscopy

Zhen-Feng Cai, Timon Käser, Naresh Kumar, and Renato Zenobi*

Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 3, Zurich CH-8093, Switzerland.

ABSTRACT: Chemical imaging of molecular decomposition processes at solid-liquid interfaces is a long-standing problem in achieving mechanistic understanding. Conventional analytical tools fail to meet this challenge due to the lack of required chemical sensitivity and specificity at the nanometer scale. In this work, we demonstrate that high-resolution hyperspectral tip-enhanced Raman spectroscopy (TERS) imaging can be a powerful analytical tool to study on-surface decomposition chemistry at the nanoscale. Specifically, we present a TERS based hyperspectral approach to visualize the on-surface decomposition process of a pyridine-4-thiol (4-PyS) self-assembled monolayer on atomically flat Au(111) surfaces under ambient conditions. Reactive intermediates involved in the degradation process are spectroscopically detected with 5 nm spatial resolution. With supporting density functional theory simulations, a key species could be assigned to the disulfide reaction intermediate. This work opens a new application area of studying on-surface decomposition chemistry and related dynamics quantitatively at solid-liquid interfaces with nanometer spatial resolution.

Molecular degradation is an important and intricate process in the chemical, biological and materials sciences. For functional materials and devices, high stability against structural and chemical degradation is often a key requirement for successful applications. It has been reported that degradation processes often occur heterogeneous, for example, proceeding more rapidly at solid/liquid interfaces than in bulk. Thus, it is of great importance to obtain a clear picture of the spatial variation of the interfacial degradation processes at the molecular level. On-surface decomposition of organic layers can serve as a model to obtain nanoscale mechanistic insights into material degradation processes. Spatially resolved investigation of the decomposed sites and reactive intermediates involved at interfaces is crucial to the clear elucidation of the degradation mechanism. In order to achieve this, both high spatial resolution and chemical selectivity are required for characterization, which is still challenging for conventional analytical techniques used to study on-surface degradation chemistry. For instance, scanning tunneling microscopy (STM) and atomic force microscopy can provide nanometer-scale structural information of on-surface assemblies, but they are blind to the chemical nature of the adsorbed species. X-ray photoelectron spectroscopy is often used for studying on-surface chemical composition, but the ensemble averaging of this technique does not afford spatial molecular information and cannot distinguish site-resolved phenomena. Electrochemical methods like reductive desorption have also been applied to establish the surface coverage of organic molecules but again no spatially resolved information can be obtained.

Tip-enhanced Raman spectroscopy (TERS) has been proven to be a powerful nano-spectroscopic technique that can provide spatially well-resolved chemical fingerprints of on-surface species at the nanometer scale. TERS allows for unambiguous chemical identification and very high spatial resolution, which makes it a promising tool for visualizing on-surface chemical transformations. Notably, spatially-resolved chemical analysis cannot be achieved using surface-enhanced Raman spectroscopy or shell-isolated nanoparticle enhanced Raman spectroscopy. For instance, our group utilized two-dimensional (2D) TERS imaging to monitor a plasmon-induced [4+4]-cycloaddition polymerization on a Au(111) surface. In addition, photocatalytic conversion of 4-nitrothiophenol to dimercaptoazobenzene was extensively investigated using TERS to reveal the reaction dynamics and mechanism. Such unique capabilities of nanoscale spatial resolution and ultra-high molecular sensitivity and specificity suggest that TERS could be an ideal tool for studying the on-surface decomposition processes of functional organic adlayers at the nanoscale under ambient conditions.

Here, we demonstrate the application of high-resolution TERS imaging to study on-surface decomposition chemistry at the nanometer scale. In particular, we applied ambient STM-TERS (Scheme 1) to investigate the molecular degradation of a pyridine-4-thiol (4-PyS) self-assembled monolayer (SAM) on Au with a spatial resolution of 5 nm. 2D TERS imaging could successfully resolve the decomposition sites on an atomically flat Au(111) surface (Figure S1). Furthermore, by combining high-resolution TERS imaging with density functional theory (DFT) simulations, distinct reactive species were detected on a Au(111) surface and a key species could be assigned to the disulfide reaction intermediate. The present work opens up a new application area of TERS to study on-surface decomposition chemistry and related dynamics at the nanometer scale.
Scheme 1. Schematic diagram of the STM-TERS set-up used in this work to investigate on-surface decomposition chemistry of 4-PyS molecules on Au(111) surface.

Figures 1a and 1b show a schematic diagram of the experimental set-up and a TER spectrum of a 4-PyS adlayer on the Au(111) surface, respectively. In the TER spectrum, four characteristic bands can be observed at ca. 1005, 1100, 1200 and 1617 cm$^{-1}$, which are assigned to $v_{\text{ring-stretching}}$, $v_{\text{C-S}}$, $v_{\text{C-H}}$ and $v_{\text{ring-deformation}}$, respectively. The spectral fingerprint region is slightly different from the powder Raman spectrum of 4-PyS due to the dissociation of the thiol proton and/or the TERS surface selection rules. The degradation rate of 4-PyS SAMs on Au is known to depend on the immersion time in ethanolic solutions. However, the degradation mechanism and the nature of intermediate species involved in the degradation process remain unclear.

To investigate the on-surface decomposition process of 4-PyS SAMs on a Au(111) surface, both chemical information and surface coverage of the adsorbed species are required, which is impossible to obtain from STM images (Figure S2). Thus, large-scale 2D TERS imaging was applied to establish the degree of sample degradation over different immersion times. Molecules adsorbed in the highly localized TERS near-field were measured in 100 pixels over a 1 µm$^2$ area to sample 100 data points for analysis. The characteristic Raman peak of 4-PyS at 1617 cm$^{-1}$ was chosen as the marker to visualize the abundance and spatial distribution of molecules on Au(111).

Figure 1. (a) Schematic diagram of the STM-TERS set-up probing a 4-PyS adlayer on a Au(111) surface using an etched Ag tip. (b) TER spectrum of a 4-PyS functionalized Au(111) sample (blue trace). For comparison, a confocal Raman spectrum of 4-PyS powder (red trace) is also displayed. TERS images of the 1617 cm$^{-1}$ peak intensity measured on a 4-PyS functionalized Au(111) surface prepared via (c) 1 min and (f) 25 h immersion. (d, g) TER spectra measured at the positions marked in (c) and (f). Note that the intensity scales in panels (d) and (g) are not identical. Waterfall plots of the spectra measured in the TERS images of 4-PyS SAM on Au(111) surface prepared via (e) 1 min and (h) 25 h immersion methods.
The TERS image in Figure 1c shows the variation of the 1617 cm\(^{-1}\) peak intensity of a sample prepared via 1-min immersion in 10 mM 4-PyS ethanolic solution. A high signal intensity is observed throughout the sample surface indicating that the Au surface is well covered by 4-PyS SAM. Figure 1d displays the TER spectra from four different positions labeled in Figure 1c, where a nearly constant Raman fingerprint signal with similar intensity is observed at different surface locations. To examine this further, all spectra measured in the TERS images are displayed as a waterfall plot in Figure 1e. In the plot, a uniform 4-PyS intensity is observed over the TERS image, confirming the existence of 4-PyS molecules on the entire surface. In contrast, when the Au(111) substrate was immersed for 25 h, only a negligible 4-PyS signal is detected on the surface as shown in Figure 1f and averaged spectrum in Figure S3. This indicates that only a miniscule number of molecules remain intact on the surface after 25 h immersion time. Furthermore, TERS spectra (from positions marked in Figure 1f) plotted in Figure 1g and the waterfall plot of all spectra in Figure 1h further validate the extremely low abundance of 4-PyS molecules on Au(111) surface after 25 h immersion.

Having established that the on-surface decomposition process was nearly complete after 25 h of immersion, 2D TERS mapping was then performed to investigate a “partially-degraded” sample to spatially distinguish the decomposed and non-decomposed sites at the same time. As can be seen in the TERS image presented in Figure 2a, the 1617 cm\(^{-1}\) signal intensity differs significantly over the sample surface after 18 h of immersion, suggesting a clear spatial variation in the distribution and abundance of 4-PyS molecules.

![TERS image](image.png)

**Figure 2.** (a) TERS image (1 µm\(^2\)) of the 4-PyS signal (1617 cm\(^{-1}\)) intensity on Au(111) surface after 18 h immersion. (b) Waterfall plot of the spectra measured in the TERS image in (a). (c) TER spectra measured at the positions labeled in (a). Step size: 100 nm. Spectrum integration time: 2 s.

Figure 2b shows waterfall plot of all spectra in the TERS image, which confirms an inhomogeneous distribution of 4-PyS molecules over the Au(111) surface as highlighted by the arrows. Figure 2c shows the TERS spectra at the surface sites marked in Figure 2a with the characteristic spectral features of 4-PyS highlighted with blue stripes. It can be observed that the 4-PyS signal at surface sites like P1, P3 and P5 is higher than at locations P2, P4 and P6. Considering that the TERS imaging was conducted using the same tip and that Au(111) substrate was atomically flat, such spectral and intensity differences are attributed to the abundance variation of 4-PyS molecules on Au(111) surface after 18 h of immersion. Representative tip-retracted spectra before and after TERS imaging are provided in Figure S4 to demonstrate that the Ag tip does not get contaminated with the thiol molecules during TERS measurements. In addition, control experiments on a rough Au surface further support that the surface roughness won’t cause the signal disappearance in the current system (Figure S5).

To further explore the on-surface species involved in the degradation process, a higher resolution TERS image with a step size of 5 nm was recorded on a 4-PyS functionalized Au(111) surface. Interestingly, in addition to the typical fingerprint Raman bands from 4-PyS molecules, new Raman bands were detected in some regions on the surface. Figure 3a shows four representative TER spectra containing new Raman bands extracted from this higher resolution TERS image, together with a reference TER spectrum of pristine 4-PyS on Au(111). Besides the expected 4-PyS bands, additional bands at 500–550 cm\(^{-1}\) and 880–905 cm\(^{-1}\) are observed in the TERS spectra, which are highlighted with yellow and red stripes. Furthermore, some vibrational modes also appear from time to time at 1350–1450 cm\(^{-1}\) in the Raman spectra, which were assigned to the C-H/N-H in-plane wagging modes from the pyridine backbone. The appearance of these bands is justified by TERS
surface selection rules. According to the on-surface decomposition mechanism proposed previously, disulfide species and related decomposition products like 4-PyS-Py and 4-Py-Py species are the main intermediates formed during the degradation process. Given that the $v_{3,5}$ region is located at 450–550 cm$^{-1}$, we propose that the new vibrational bands observed at 500–550 cm$^{-1}$ in Figure 3a represent $v_{3,5}$ modes of the disulfide species.

To verify our hypothesis, DFT calculations were performed to simulate Raman spectra of isolated potential intermediates. Besides the disulfide species, two more possible intermediates based on the proposed mechanism were also investigated. Figure 3b shows the DFT simulated Raman spectra of 4-PyS-SPy, 4-PyS-SH, 4-PyS-Py, 4-Py-Py and 4-PyS molecules. Notably, the 4-PyS-SPy, 4-PyS-SH and 4-PyS-Py species shows all main vibrational modes of 4-PyS (marked with blue stripes), whilst 4-Py-Py is different both in terms of the positions and intensities of the characteristic bands. For the disulfide species, simulated spectra reveal a strong S-S stretching mode and relatively weak out-of-plane S-S vibrational mode at ca. 436 and 552 cm$^{-1}$ for 4-PyS-SPy, and ca. at 456 and 526 cm$^{-1}$ for 4-PyS-SH. For 4-PyS-SH, an additional band is observed at ca. 885 cm$^{-1}$ representing a twisting C-H vibrational mode. Comparing the experimental and simulation results suggests that the observed spectra in Figure 3a likely originate from 4-PyS-SH species, based on the appearance of vibrational modes at both 500–550 cm$^{-1}$ and 885 cm$^{-1}$. Notably, only the out-of-plane S-S vibrational mode is observed in the 500–550 cm$^{-1}$ region. However, the S-S stretching mode at ca. 456 cm$^{-1}$ remains silent in the TER spectra. Considering that the disulfide species would adopt an orientation with the S-S bonds directly adsorbed on the Au(111) surface, such in-plane orientation could cause the silence of the S-S stretching mode.

Figure 3. (a) Four representative TER spectra showing new Raman bands (in addition to 4-PyS) highlighted using red and yellow stripes. (b) Calculated Raman spectra of di-pyridine (green trace), 4-PyS-Py (pink trace), 4-PyS-SPy (blue trace), 4-PyS-SH (red trace) and 4-PyS (black trace). (c) High-resolution TERS image of 890 cm$^{-1}$ intensity measure from 4-PyS functionalized Au(111) surface. (d) Zoomed-in TERS image of the region marked in (c). (e) TER spectra measured at the pixels labeled in (d). Step size: 5 nm. Spectrum integration time: 1 s.
According to the proposed on-surface degradation mechanism of 4-PyS SAM at an ethanolic solution/Au interface, 4-PyS molecules tend to dimerize at the sulfur position to form a disulfide. After the formation of disulfide, the cleavage of C-S bond was proposed to generate adsorbed atomic S and Py species.\(^8\)\(^9\) This mechanism is different from the mechanism of S-S cleavage\(^5\), which can be caused by the electronic properties of the heterocyclic pyridine entity as reported previously\(^9\). Whilst the degraded S-S species have been observed using high-resolution STM before, the identity of the intermediate species has never been confirmed. Our correlative high-resolution TERS and DFT calculation results provide the first clear spectroscopic evidence for the generation of 4-PyS-SH intermediate species during on-surface degradation of 4-PyS. Further systematic investigation and analysis of the intermediate chemistry are underway.

Furthermore, taking advantage of the spectral differences between 4-PyS-SH and 4-PyS, the spatial resolution of the TERS system can be estimated from the high-resolution TERS image of the characteristic Raman bands of the reactive intermediate. Since the thermal drift of our system is 0.02–0.03 nm/s under laser illumination at ambient conditions, a relatively short spectrum acquisition time of 1 s was chosen to minimize the effect of drift.\(^9\) Figure 3c and Figure S6 display the TERS images of the 890 cm\(^{-1}\) signal of 4-PyS-SH on 4-PyS functionalized Au(111) samples prepared via different immersion time. Notably, 4-PyS-SH intermediates are detected at only at a few locations in the image, i.e., it would be completely invisible in a confocal Raman spectrum due to averaging. Thus, high-resolution TERS imaging is key for identifying these species on the surface. A zoomed-in image of the region marked in Figure 3c is shown in Figure 3d, in which the 4-PyS-SH signal is detected only in a single pixel. This is further confirmed by the TERS spectra from 5 pixels (marked in Figure 3d) shown in Figure 3e, where the 4-PyS-SH signal at 890 cm\(^{-1}\) is detected only at pixel 3. Two additional areas of the sample showing similar behavior are presented in Figures S7 and S8. From these results, the spatial resolution of TERS imaging is established to be ca. 5 nm, which provides two key information: (1) whether the intermediate species are present on the sample or not. With a large step size or with low-resolution TERS imaging we might otherwise miss these species. (2) The relative abundance of the intermediate species detected on the surface can be determined qualitatively after different immersion times. Note that spatial resolution (smallest features that can be distinguished) of a TERS image is limited by the step size of the measurement and a smaller step size is likely to yield a higher resolution. However, this also increases the measurement time causing significant drift issues.

**Figure 4.** Waterfall plots of the spectra extracted from TERS images measured on a 4-PyS functionalized Au(111) sample prepared via (a) 1 min, (b) 13 h and (c) 5 h immersion times from an aged solution. Step size: 100 nm. Spectrum integration time: 2 s. (d) TERS image of the 1617 cm\(^{-1}\) signal measured on the sample with 5 h immersion time. (e) TERS spectra measured at the positions labeled in (d). (f) Plots of the surface coverage of 4-PyS SAM on Au(111) as a function of immersion time in fresh and aged solutions.

To further confirm that the observed spectral variation in the TERS imaging is derived from on-surface decomposition, additional measurements were conducted on 4-PyS functionalized Au(111) samples prepared from a solution aged for 3 months. It has been shown that fresh 4-PyS solution begins to decompose within days forming disulfide species.\(^40\) Thus, it is expected that the on-surface decomposition process in an aged solution will be faster compared to the fresh one. To confirm this, waterfall plots of TERS images measured on 4-PyS functionalized Au(111) samples prepared from the aged solution with an immersion time of 1 min, 5 h and 13 h are presented in Figures 4a-4c. Whilst a stable 4-PyS signal is observed over the surface of the sample with 1 min immersion time (Figure 4a), the decomposition is
mostly complete on the sample with 13 h immersion time (Figure 4b). Spatial variation of the 1617 cm\(^{-1}\) peak intensity and corresponding TERS spectra measured at different positions of the samples with 1 min and 13 h are presented in Figure S9, which reveal the spectral evolution of the decomposition process. Control mapping measurement on a 1 min immersion sample was performed to check the enhancing capability of the Ag tip, which indicates the tip was active during all the mapping measurements (Figure S10). Furthermore, for the sample with 5 h immersion time, a significant variation in the intensity of 4-PyS signal (1617 cm\(^{-1}\)) is observed over the surface, as shown in Figures 4c and 4d. Typical point spectra at six positions labeled in Figure 4d are shown in Figure 4e. The lack of 4-PyS signal at positions P1 and P3 indicates that the decomposition process has already occurred at several places on the sample. In contrast, in the case of a fresh solution, the Au(111) surface remains covered with 4-PyS molecules after 5 h of immersion time, as shown in Figure S11. Figure 4f shows plots of a 4-PyS SAM on Au(111) as a function of immersion time prepared from fresh and aged solutions, calculated from the TERS images. For each immersion time point, three TERS images at different areas were used to calculate the surface coverage. TERS spectra with a signal-to-noise ratio smaller than 2 were distinguished by manual inspection and assumed to represent decomposed sites. Surface coverage was determined by dividing the number of pixels with undecomposed molecules by the total number of pixels (100) measured in the TERS image. The non-linearity of the plots suggests the prevalence of combination effects during the decomposition process caused by solvent, interface, reaction pathways, adsorption capacity, etc. The decomposition rate of 4-PyS in the SAM prepared from the aged solution is found to be almost two times higher than that prepared from the fresh solution. This clearly demonstrates the unique capability of TERS to quantitatively monitor on-surface decomposition chemistry at solid-liquid interfaces.

In summary, we have performed a comprehensive and quantitative investigation of the on-surface decomposition process of a 4-PyS SAM on Au(111), using high-resolution STM-TERS imaging. Intermediate reactive species involved in the decomposition process were captured in 2D TERS images with a spatial resolution of 5 nm and clearly identified with the support of DFT calculations for the first time. The ability to probe and visualize intermediate reactive species at the nanoscale using spectroscopic fingerprints has promising applications in the characterization of material, chemical, and dynamic processes/conversions on metallic surfaces. This work clearly demonstrates that high-resolution TERS imaging can become a powerful nano-analytical tool to visualize on-surface decomposition processes for elucidation of material degradation mechanisms at molecular scale.

**ASSOCIATED CONTENT**

**Supporting Information.** The Supporting Information is available free of charge at …

Contents: Experimental section; STM images of Au(111); High-resolution TERS map and spectra of 4-PyS/Au(111) prepared from aged solution; TERS intensity map, waterfall plot and TER spectra of 4-PyS/Au(111) prepared from fresh solution.

**AUTHOR INFORMATION**

**Corresponding Author**

*zenobi@org.chem.ethz.ch*

**Notes**

The authors declare no competing financial interest.

The original data used in this publication are made available in a curated data archive at ETH Zurich (https://www.researchcollection.ethz.ch) under the DOI: 10.3929/ethz-b-000530774.

**ACKNOWLEDGMENTS**

We thank the High Performance Computing Team at ETH Zurich for help with DFT calculations and acknowledge financial support via an ERC Advanced grant (Grant # 741431–2DNaNoSpec).
(31) Zhang, L.; Bai, Y.; Shang, Z.; Zhang, Y.; Mo, Y. Experimental and theoretical studies of Raman spectroscopy on 4-mercaptopyridine aqueous solution and 4-mercaptopyridine/Ag complex system. *J. Raman Spectrosc.* 2007, 38, 1106-1111.
Supporting information

Visualizing On-Surface Decomposition Chemistry at the Nanoscale Using Tip-Enhanced Raman Spectroscopy

Zhen-Feng Cai, Timon Käser, Naresh Kumar, and Renato Zenobi*

Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 3, Zurich CH-8093, Switzerland.
Experimental Section

Sample preparation: 4-mercaptopyridine (4-PyS) was purchased from Sigma-Aldrich and used without further purification. 4-PyS solutions were prepared by dissolving the solid sample in ethanol and further dilution to generate concentration series. Au(111) single-crystal substrates were prepared by the Clavilier method. To prepare “immersion samples”, a freshly prepared Au(111) substrate was immersed in a 10 mM solution of 4-PyS in ethanol for different durations. The immersion process was carried out in the dark environment of the fridge. After the immersion, the sample was rinsed thoroughly using ethanol and then dried using N₂ gas in order to prevent the formation of a physically attached adlayer on top of the SAM.

TERS setup: All TERS measurements were performed with a top-illumination TERS setup combining an STM with a Raman spectrometer (NT-MDT, Russia). A 100×, 0.7 NA air objective (Mitutoyo, Japan) was used for both excitation and collection of the TERS signals. STM and TERS measurements were performed using electrochemically etched Ag tips. A 632.8 nm He-Ne laser (Newport, Germany) was used as the excitation source. As reported in our previous work, a high laser power (>0.17 mW) was found to induce chemical reactions in a SAM of organic molecules. Therefore, a significantly lower laser power (0.07 mW) was used for all TERS measurements. For all TERS measurements, the tunneling current was set to 200 pA, tunneling bias was set to 0.5 V. TERS imaging was performed with a step size of 5-100 nm and spectrum integration time of 1-2 s.

DFT calculations: Density functional theory (DFT) calculations were carried out with hybrid exchange-correlation functionals, such as B3LYP. For free molecules 4-PyS, 4-PyS-SPy, 4-PyS-SH, 4-PyS-Py, and 4-Py-Py, the basis set used was 6-31G(d, p). Full geometry optimization and frequency analyses were carried out using Gaussian 09 package and GaussView 5.0 software (Gaussian Inc.) In the current study, the surface was not taken into account in DFT calculations. However, the calculated Raman spectrum of
PyS-Au has been reported in the literature in which characteristic bands were located at ca. 990 cm\(^{-1}\) [\(\delta(CH)\)], 1112 cm\(^{-1}\) [\(\nu(C=\text{C})\)], and 1571 cm\(^{-1}\) (\(\nu_{\text{ring}}\)). The position of these bands is slightly shifted compared to our experimental TERS spectrum shown in Figure 1b.
Figure S1. (a) Large-scale STM image of the atomically flat Au(111) surface. (b) The cross-section profile shows the topography variation along the black dashed line marked in (a) confirming the atomic scale flatness of the Au(111) substrate.
Figure S2. Large scale STM images of (a) bare Au(111) and (b) 4PyS adlayer modified Au(111) surface. According to the previous report, high coverage adsorption of S atoms can induce the corrosion of the Au surface, which can lead to the appearance of etch pits and irregularly shaped AuS islands. Such surface roughness could potentially modify the TERS signal, however, we do not expect it to disappear completely.
Figure S3. Averaged TER spectra of 4-PyS functionalized Au(111) samples prepared via 1 min (blue trace) and 25 h immersion (red trace) protocol.
Figure S4. (a, c) Typical TERS spectra in a TERS image of 4-PyS adlayer modified Au(111) surface prepared via 1 min and 18 h immersion protocol. For comparison, tip retracted Raman spectra before (black trace) and after (blue trace) the TERS imaging are also shown. (b, d) Waterfall plots of the spectra measured in the TERS images of 4PyS SAM on Au(111) surface prepared via 1 min and 18 h immersion methods. Step size: 100 nm. Spectrum integration time: 2 s.
Figure S5. (a) Waterfall plot of the spectra measured in the TERS images of 4-PyS SAM on TS-Au surface prepared via 1 min immersion methods. Step size: 50 nm. Spectrum integration time: 1 s. (b) Large-scale STM image of the TS-Au surface. (c) The cross-section profile shows the topography variation along the black dashed line marked in (b) showing the roughness of the TS-Au substrate.

In order to further support that the surface roughness won’t cause the signal disappearance in the current system, control measurements were also performed on a rough template-stripped Au (TS-Au) surface. As shown in the figure above, the consistent signal of 4-PyS can be observed on the TS-Au substrate, suggesting that the surface roughness is cannot the reason for the signal disappearance in the long-time immersion samples.
Figure S6. High-resolution TERS images of 890 cm$^{-1}$ intensity measured from 4-PyS functionalized Au(111) samples prepared via 5 h (a), 18 h (b) and 25 h (c) immersion time. Step size: 5 nm. Spectrum integration time: 1 s. The low surface density of the intermediate species at different immersion times is likely caused by their low stability and high reactivity. In fact the exact number of potential intermediates is expected to be affected by several factors including reaction rate, reaction pathways, adsorption capacity, surface topography, solvent etc.
Figure S7. (a) Additional high-resolution TERS image of the 890 cm\(^{-1}\) signal measured on a 4-PyS functionalized Au(111) surface. Step size: 5 nm. Spectrum integration time: 1 s. (b) Zoomed-in TERS image of the region marked in (a). (c) TER spectra measured at the pixels labelled in (b). 4-PyS-SH signal is detected only at pixel 3.
Figure S8. (a) Additional high-resolution TERS image of the 890 cm\(^{-1}\) signal measured on a 4-PyS functionalized Au(111) surface. Step size: 5 nm. Spectrum integration time: 1 s. (b) Zoomed-in TERS image of the region marked in (a). (c) TER spectra measured at the pixels labelled in (b). 4-PyS-SH signal is detected only at pixel 2.
Figure S9. TERS images of the 1617 cm$^{-1}$ peak intensity measured on a 4-PyS functionalized Au(111) surface prepared via (a) 1 min and (b) 13 h immersion from an aged solution. Step size: 100 nm. Spectrum integration time: 2 s. (c, d) TER spectra measured at the positions marked in (a) and (b).
**Figure S10.** Comparison of the waterfall plots of spectra extracted from TERS images measured on a 4-PyS functionalized Au(111) sample prepared via (a) 13 h, (b) 1 min immersion from an aged solution measured with the same tip. The tip fully retains its plasmonic activity after TERS imaging of the 13 h immersion sample. Step size: 100 nm. Spectrum integration time: 2 s.
Figure S11. (a) TERS image of the 1617 cm\(^{-1}\) peak intensity measured on a 4-PyS functionalized Au(111) sample prepared via 5 h immersion in a fresh solution. Step size: 100 nm. Spectrum integration time: 2 s. (b) Waterfall plot of spectra measured in the TERS image in (a). (c) TER spectra measured at the positions labelled in (a).
Supplementary references


