Probing the electronic and catalytic properties of a bimetallic surface with 3 nm resolution

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S1.1 Preparation of Pd/Au(111) bimetallic model catalyst

The Au(111) single crystal bead was fabricated by Clavilier’s method and was electrochemically-polished and flame-annealed before use. The underpotential deposition (UPD) of Pd on the Au(111) single crystal surface was performed by cyclic voltammogram (CV) at a scan rate of 1 mV/s, in a solution of 1 mM H₂PdCl₄ and 0.1 M H₂SO₄. The measurements were conducted in a three-electrode configuration on Autolab PGSTAT128N potentiostat (Metrohm, the Netherlands). The Au(111) single crystal was the working electrode. A Pd wire and a Au wire were used as the reference electrode and counter electrode, respectively. Since the area of the naturally-formed (111) facet is relatively small, a droplet method was used to perform the electrochemistry on the (111) facet. The coverage of the Pd layer was controlled by stopping the CV at different end points (potentials). Generally, more negative potential leads to higher coverage. A full monolayer Pd is formed when the potential is controlled at the lower end of the UPD peak.

S1.2 Adsorption of PIC on model catalyst surfaces

The bare Au(111) and Pd/Au(111) bimetallic substrates were immersed in a 20 μM ethanoic solution of PIC for 30 min to allow the formation of a self-assembled monolayers (SAMs) on the surfaces. The samples were rinsed by ethanol and dried under N₂ atmosphere. Then the samples were directly used for scanning tunneling microscope (STM) and TERS measurements.

S1.3 Interfacial capacitance measurements

For the interfacial capacitance measurements, a commercial Au(111) single crystal (MaTeck, Germany) was used as the working electrode. A Pt foil and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. The CV were performed in a deoxygenate solution of 0.1 M KNO₃ in a hanging meniscus configuration, at a scan rate of 5 mV/s.

S1.4 STM and TERS measurements

The STM and TERS experiments were performed on a home built TERS setup with a Nanoscope
The morphology of the samples was first obtained using a mechanically cut Pt–Ir tip. For the TERS imaging experiments, an electrochemically etched Au tip was used to obtain both the morphology and TERS spectra. The Au tips were cleaned with concentrated sulfuric acid before each measurement.

S1.5 Computational methods for electronic structure and vibrational frequency

S1.5.1 Electronic and geometric

Periodic density functional theory (DFT) calculations were performed with Perdew-Burke-Ernzerhof (PBE) functional of the generalized-gradient approximation (GGA) to the exchange-correlation potential, as implemented in Quantum ESPRESSO package. Projector augmented-wave (PAW) method was applied. Energy cutoff of 50 Ry for plane-wave basis was used for all Quantum ESPRESSO calculations. In geometric optimization, the residual total force for the unconstrained degrees of freedom was converged within 0.026 eV/Å. We used pseudopotentials from PSlibrary version 1.0.0 for all elements in this work. Γ-centered Monkhorst-Pack k-point sampling grid of 11×11×11 for primitive cell of Pd and Au lattice was applied and total energy was converged within 0.01 eV/cell.

S1.5.2 Terrace and step edge models

The terrace model of the PdML/Au(111) surface was mimicked by a slab with six layers of Au(111) substrate covered by a Pd monolayer (Figure 4e in the main text). A thickness of six layers of Au substrate is sufficient to eliminate the work function deviation when evaluating the density of states (DOS). The periodic repeated slabs were separated by vacuum layers of 15 Å in the direction perpendicular to the slabs. The Pd monolayer and the top two layers of Au were relaxed in geometric optimization, while the bottom layers of the slabs were fixed at their corresponding bulk positions. Adsorption coverage of 0.75 (surface supercell of p-(2×2) per molecule) was applied in the terrace model. The k-point sampling grid was 5×5×1 and 33×33×1 Γ-centered k-points for geometric optimization and DOS plot, respectively. As shown in Figure 4f in the main text, the model for
simulating the electronic structure of step edge sites were emerged from truncating one of the 2-dimensional periodicity of the terrace model. The supercell of the substrate slab with 2-dimensional periodicity was extended to p-(2×12). The p-(2×8) Au layer and the covered p-(2×7) Pd layer were truncated from terrace structure to model the edge sites. The $\Gamma$-centered k-point sampling grid for the supercell of edge sites was $5\times1\times1$ and $33\times1\times1$ for geometric optimization and DOS plot, respectively.

**S1.5.3 Free molecules**

Isolated molecule for evaluation of the adsorption energies and frequency was modeled by molecule in large cubic cell with edges of 25 Å. For the DOS plot of Figure 4h in the main text, the molecules are located in the vacuum layer between slabs of the terrace model, with a separation of $\sim$10 Å from metal slabs.

**S1.5.4 Bader charge analysis**

Bader charge analysis were performed using code from Henkelman group. Charge density grid in real-space for the Bader analysis was obtained by performing DFT calculation using the Vienna ab initio simulation package (VASP). We applied the geometric configuration from Quantum ESPRESSO results and performed the ionic relaxation. Within VASP calculations, PBE-GGA density functional and PAW method was applied. Energy cutoff of 400 eV for plane-wave basis was used. The residual total force for the unconstrained degrees of freedom was converged within 0.025 eV/Å.

**S1.5.5 Vibrational frequency and Raman intensity computation**

We first calculated vibrational frequencies for free PIC molecule with PBE density functional, Gaussian basis (6-311G**). Vibrational frequencies of the free and adsorbed PIC molecule were calculated with density-functional perturbation theory (DFPT) as implemented in Quantum ESPRESSO package. All the degrees of freedom from surface metal atoms were frozen in the frequency computation. The convergence threshold of $|\langle \Delta V_{SCF} \rangle|^2$ was set to $10^{-12}$, and frequencies of vibrational modes higher than 300 cm$^{-1}$ was converged within 3 cm$^{-1}$.
Non-resonance Raman differential cross-section of $\ell$-th vibrational mode under double-harmonic approximation is evaluated by:\textsuperscript{17}

$$
\left(\frac{d\sigma}{d\Omega}\right)_\ell = \frac{\pi^2}{\varepsilon_0^2} (\nu_{in} - \nu_\ell)^4 \frac{h S_\ell}{8\pi^2 c v_\ell} \frac{1}{45} \exp\left(-\frac{h c v_\ell}{k_B T}\right)
$$

(S1)

where $h$, $c$, $k_B$ and $\varepsilon_0$ are Planck constant, speed of light, Boltzmann constant and dielectric constant of vacuum, respectively. Incident laser frequency $\nu_{in}$ is set as experimental value $1/632.8$ nm$^{-1}$. Temperature $T$ in evaluating Boltzmann population of vibrational states is 298.15 K. A Lorentzian line-shape broadening was applied for plotting the Raman spectra with full-width at half-maximum (FWHM) of 10 cm$^{-1}$. Raman activity of $\ell$-th vibrational mode:

$$
S_\ell = 45A_\ell^2 + 7B_\ell^2
$$

(S2)

is calculated by the \textit{ab-initio} electronic structure method,\textsuperscript{15} with the term from isotropic polarizability derivatives:

$$
A_\ell = \frac{1}{3} \sum_i (\alpha_{ii})_\ell
$$

(S3)

and the term from polarizability anisotropy:

$$
B_\ell^2 = \frac{1}{2} \sum_{ij} \left[3(\alpha'_{ij})_\ell^2 - (\alpha'_{ii})_\ell(\alpha'_{jj})_\ell\right]
$$

(S4)

where $i$ and $j$ were summed over Cartesian coordinates indices $x$, $y$, $z$ of the polarizability tensor. In the double harmonic approximation,\textsuperscript{17} only the first order derivative of non-resonance electronic polarizability $\alpha_{ij}$ respect to the vibrational eigenvector $q_\ell$

$$
(\alpha'_{ij})_\ell = \left(\frac{\partial \alpha_{ij}}{\partial q_\ell}\right)_0
$$

(S5)

contributes to the transition matrix element.

\textbf{S1.6 Electromagnetic field simulation}
The simulation model consists of an Au tip above a Pd covered Au film with step edges (Figure 3e). The deposited Pd is one-atomic thick and the thickness is set to be 3 Å for simplicity. According to the STM observations, one layer of gold is leached to form two-atomic height steps (~6 Å), which is also considered in the model. The three-dimensional finite-difference time-domain (3D-FDTD) method was introduced to calculate the TERS enhancement factor for the tip located above the Pd surface, step edge and Au surface. All calculations were performed using commercial software (FDTD Solutions 8.7). The curvature radius and cone angle of the tip were chosen to be 20 nm and 30°, respectively. The tip-film distance was fixed at 1 nm. Considering the actual experimental conditions, the p-polarized plane wave with electric field amplitude of 1.0 V/m was incident into the tip-film gap at an angle of 60°, where the excitation wavelength was 633 nm. Uneven meshes were used for the calculation to save the calculation resource while ensuring the calculation accuracy. The size of mesh on the tip apex and the step edge were set as 0.5 nm and 0.1 nm, respectively. To accurately model the 1 nm tip-film gap, we set the size of mesh as 0.2 nm.

S2. Gold leaching during molecule adsorption

Supplementary Figure 1 | STM images of PIC/Au(111) surface. a,b, STM images of Au(111) surfaces after immersion in (a) 20 μM and (b) 2 mM PIC ethanoic solution for 30 min under Ar atmosphere. c,d, Height profile taken along the dashed yellow (c) and solid blue (d) lines marked in (b). e,f, STM images of PIC/Au(111) (e) and PIC/PdML/Au(111) (f) surfaces at a higher resolution.

Supplementary Figure 1a is an STM image of a Au(111) surface after immersion in 20 μM PIC
ethanoic solution, which was obtained from the same sample as that shown in Figure 1f in main text. Single atomic layer gold holes distribute homogeneously on a large surface area. When PIC is assembled from a more concentrated solution of 2 mM (Supplementary Figure 1b), similar single atomic layer gold holes can be observed, but with a much larger lateral size than that of Supplementary Figure 1a. In addition, some deeper gold holes can be observed (marked by the white arrows in Supplementary Figure 1b), some of them can be as deep as six atomic height (Supplementary Figure 1d). This observation may be attributed to the leaching of gold due to the strong complexation of cyanide with gold. It is well known that cyanide is commonly used as lixiviant in mining industry for the extraction of gold from mineral and ores. Similar surface features with gold holes on the STM image of a Au(111) surface covered by a self-assembled monolayer of 4-chlorophenyl isocyanide (which has a similar molecular structure to phenyl isocyanide used in this work) was observed previously.

The leaching of gold was confirmed by inductively coupled plasma mass spectrometry (ICP-MS). The ethanoic solution of 2 mM PIC was characterized by ICP-MS before and after the immersion of gold substrate. The concentration of gold in the original solution is ~20 ppb, which is from the residual gold in the substrate (2% HNO₃) used for ICP-MS detection, as confirmed by a control experiment. The concentration of gold increases to ~660 ppb after immersion of gold substrate for about 3 h. Control experiments suggest that pure ethanol do not leach gold. The results confirm that PIC leaches gold to the solution, probably with the participation of adventitious oxygen in the solution.

It should be noted that we did not observe any ordered molecular arrangement features on PIC/Au(111) and PIC/Pdₓ ML/Au(111) surfaces (Supplementary Figure 1e,f), in agreement with previous reports, indicating PIC may not form an ordered monolayer on the surfaces.

S3. Computational results of the electronic structure and vibrational frequency

S3.1 Pd overlayer relaxation

The equilibrium lattice constants of Au and Pd was calculated to be 4.16 and 3.96 Å, respectively. For monolayer of Pd deposited on Au single crystal surface, Pd atoms was strained to commensurate
with Au substrate. Thus, in this work, we performed structure optimization in a fixed cell with the lattice constant of Au. After the geometrical relaxation, the average distance between Pd and the top Au layer is ~ 0.14 Å smaller than the interlayer distance of bulk Au(111) lattice plane.

**S3.2 Adsorption geometries and energies**

![Chemical structure and optimized molecular geometries of PIC (a) and phenyl isocyanate (b), and optimized adsorption structure of PIC on Au(111) (c) and PdML/Au(111) (d) surfaces (intracell bonding are shown explicitly). The numbers in a,b are indicated for geometric description and vibrational mode analysis. The optimized geometries are obtained based on PBE/PAW. All optimized molecular and supercell structures, and atomic models in the main text are rendered by VMD package.](image)

The structure of free PIC molecule is shown in Supplementary Figure 2a. The N≡C group is connected to phenyl ring in a linear C_2-N_12-C_13 configuration. The adsorption of aryl isocyanide on Au and Pd surfaces has been extensively studied by SERS (on rough Au, Ag, Pd, and Pt surfaces)\(^{23}\), and gap-mode SERS (on single crystal Au(111), Pd(111), and Pt(111) surfaces)\(^{20, 25-28}\). Our experimental frequencies of TERS spectra on Au(111) and Pd\(_{ML}/\)Au(111) surfaces agree well with these reports. According to these reports, the preferable adsorption sites were determined to be atop site on Au and bridge site on Pd surfaces,\(^{20, 25-28}\) with vertical orientation of the benzene and NC group
on both surfaces. Therefore, we first considered these adsorption configurations in theoretical calculation. The optimized adsorption structure of PIC on Au(111) and PdML/Au(111) surfaces are shown in Supplementary Figure 2c and d, respectively, showing a vertical orientation of PIC on both surfaces. After geometrical optimization, the corresponding local energy minimum could be achieved in our theoretical calculations. PIC molecules adsorbed at step edge Pd sites were found to tilt with an angle of 30° between surface normal and the direction of NC group, as shown in Figure 4f in the main text. The tilted orientation of molecules adsorbed at step edge was also suggested in previous reports.\textsuperscript{29,30} Furthermore, due to the strong adsorption interaction at step edge sites, the linear C\textsubscript{2}-N\textsubscript{12}-C\textsubscript{13} configuration was slightly bended to \( \sim 175° \).

The adsorption energies \( E_{\text{ads}} \) were evaluated by:

\[
E_{\text{ads}} = E_{\text{PIC/metal}} - E_{\text{metal}} - E_{\text{PIC}} \quad (S6)
\]

where \( E_{\text{PIC/metal}} \), \( E_{\text{metal}} \) and \( E_{\text{PIC}} \) are DFT-calculated total energies of PIC-adsorbed slabs, clean metal slabs and free PIC molecule, respectively. As shown in Supplementary Table 1, the adsorption interaction on Pd\textsubscript{ML}/Au(111) terrace (\( E_{\text{ads}} = -2.13 \text{ eV} \)) is stronger than that on Au(111) terrace (\( E_{\text{ads}} = -0.56 \text{ eV} \)). Furthermore, the adsorption of PIC at Pd step edge (\( E_{\text{ads}} = -2.29 \text{ eV} \)) was found to be more stable than that on terrace with a stabilization energy difference of 0.16 eV per molecule.

The adsorption interaction of PIC molecule with transition metal surfaces agrees with the widely accepted Blyholder model.\textsuperscript{31,32} Two kinds of electronic interaction contribute to the isocyanide-metal bonding: the \( \sigma \) donation of the lone electron pair of C\textsubscript{13} (Fig. S2a) to metal, and the \( \pi \) back-donation from the metal d band to the NC \( \pi* \) orbital. The bridge adsorption on Pd\textsubscript{ML}/Au(111) surface enhanced the back-donation interaction because of the favorable d-\( \pi* \) orbital overlap, while the atop adsorption on Au(111) was dominated by 5d\textsubscript{z2}-\( \sigma \) coordination.\textsuperscript{33,34} This results in an increase of the bond length of NC (\( r_{\text{NC}} \)) from 1.18 Å (atop adsorption) to 1.21 Å (bridge adsorption). The stronger adsorption of PIC on Pd surface than on Au surface was proved to be dominated by the enhancement of back-
donation interaction because the σ donation was generally accepted as a Pauli repulsion interaction,\textsuperscript{33, 34} which is consistent with the order of adsorption energies in our computational results.

The adsorption sites can be further determined by correlating the experimental and theoretical frequencies, especially the direction of frequency shift relative to the free PIC. From the calculated $v_{NC}$ frequencies in Supplementary Table 1 we can see that, $v_{NC}$ is blue shifted for atop site adsorption and red shifted for bridge site adsorption compared with the free PIC. Therefore, we can assign the detected $v_{NC}$ frequency of 2,190 cm$^{-1}$ on Au to be atop site adsorption, and the frequency of 1,995 cm$^{-1}$ on Pd to be bridge site adsorption, in agreement with previous reports.\textsuperscript{25, 26} For the bridge site adsorption, the back-donation of the d-band electrons of Pd to $2\pi^*$ anti-bonding orbitals of PIC leads to the weakening of the NC bond, and thus the red-shift of $v_{NC}$ relative to the free PIC. It should be pointed out that $v_{NC}$ red shifts dramatically by more than 250 cm$^{-1}$ for hollow site adsorption. Therefore, the adsorption of PIC on Pd cannot be assigned to be hollow site. Note that it is difficult to theoretically predict preferable adsorption sites of PIC on transition metals simply by adsorption energy, similar to the case of CO adsorption.\textsuperscript{33, 35-37} Because GGA density functional methods underestimate the LUMO level, which overestimates the back-donation interaction. This overestimation also leads to the systematical underestimation of $v_{NC}$ frequencies compared with experimental values, as seen in Supplementary Table 1. This problem has been the topic of enormous amounts of theoretical works.\textsuperscript{33, 36-39} Nevertheless, the assignment based on the trend and direction of frequency shift is convincing and in agreement with the result of a similar system of CO adsorption on metal surfaces.\textsuperscript{34}
Supplementary Table 1 | Experimental and theoretical vibrational frequencies of $v_{NC}$ and the adsorption energies of PIC on various surface sites.

<table>
<thead>
<tr>
<th></th>
<th>$v_{NC}$ / cm$^{-1}$</th>
<th>$r_{NC}$ / Å</th>
<th>$E_{ads}$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIC (free)</td>
<td>2,120</td>
<td>1.183</td>
<td></td>
</tr>
<tr>
<td>Au(111) terrace-atop</td>
<td>2,190</td>
<td>2,138</td>
<td>1.182</td>
</tr>
<tr>
<td>Au(111) terrace-bridge</td>
<td>1,998</td>
<td>1,200</td>
<td></td>
</tr>
<tr>
<td>Pd$_{ML}$/Au(111) terrace-atop</td>
<td>2,133</td>
<td>1.187</td>
<td>$-1.68$</td>
</tr>
<tr>
<td>Pd$_{ML}$/Au(111) terrace-bridge</td>
<td>1,995</td>
<td>1,965</td>
<td>1.210</td>
</tr>
<tr>
<td>Pd$_{ML}$/Au(111) terrace-hollow</td>
<td>1,866</td>
<td>1,224</td>
<td>$-2.35$</td>
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<tr>
<td>Pd$_{ML}$/Au(111) step edge-bridge</td>
<td>1,933</td>
<td>1,909</td>
<td>1.208</td>
</tr>
</tbody>
</table>

S3.3 Peak assignments and adsorption configuration analysis

Supplementary Table 2 summarizes the vibrational modes of free and adsorbed PIC molecule, and the corresponding atomic displacement vectors are shown in Supplementary Table 3. For the free molecule, the vibrational frequencies calculated with PAW method agree well with that calculated with Gaussian basis, indicating that an energy cutoff of 50 Ry for the plane-wave basis is reasonable for the frequency computation.

In both experimental and theoretical results, we do not observe much difference for the calculated frequencies of the benzene ring vibration modes ($\alpha_{ring}$, $\beta_{CH}$, $v_{C-NC}$ and $v_{CC}$) when PIC is adsorbed at Au(111) and Pd$_{ML}$/Au(111) terraces. The preferable linear configuration of C$_2$-N$_{12}$-C$_{13}$ on terraces preserved the intramolecular symmetry. Therefore, the displacement vectors of vibrational modes were similar between free and adsorbed molecules. The invariance of these modes indicates
that the benzene ring does not directly interact with the metal substrates. The frequency of $v_{NC}$ has been discussed above and can be explained by different adsorption sites on Au and Pd surfaces.

After geometrical optimization for PIC adsorption at Pd step edge sites, the linear C$_2$-N$_{12}$-C$_{13}$ configuration was bent to $\sim$175°, resulting in the reorganization of the coupled modes between phenyl ring and $v_{C2-N12}$. Therefore, the frequencies of 1,159 and 1,220 cm$^{-1}$ in terrace Pd adsorption shifted to 1,092 and 1,278 cm$^{-1}$ in step edge Pd adsorption, respectively. The ring deformation mode of 983 cm$^{-1}$ was red-shifted to 918 cm$^{-1}$ due to the coupling with out-of-plane modes.

In summary of the computational results of PIC adsorbed at step edge, the vibrational modes below 1,300 cm$^{-1}$ are more sensitive to the structural distortion of phenyl group in PIC molecules as a result of the stronger adsorption at step edge, especially because the C$_{2v}$ intramolecular symmetry was broken. The various possible geometric structure of PIC adsorbed at step edge may further complicate the analysis of phenyl group. In our theoretical computation, the structure with local energy minimum achieved in this geometric optimization shall be considered as one of the representative phenyl configuration. We did not see obvious changes for these low vibration modes of PIC adsorbed at step edges in experiments. This is because the simulated structure may still differ from the real configuration in experiments, which is still very challenging to determine at present by STM images. In contrast, the NC group were directly bonded to the metal atoms with a relatively defined adsorption geometry (vertical to the surface). The $v_{NC}$ frequency was more sensitive to the variation of electronic structure on different surface sites than phenyl group. Therefore, our calculation can successfully explain the NC bonding interaction and $v_{NC}$ frequency shift (as discussed in the main text), because of the relatively defined adsorption geometry of NC bond and the high Raman activity of $v_{NC}$ mode.

The optimized geometry of free phenyl isocyanate molecule is shown in Supplementary Figure 2b. All atoms of the molecule are in the same plane, with the angle of N$_{12}$-C$_{13}$-O$_{14}$ to be 172.7°. Calculated vibrational frequencies of free phenyl isocyanate molecule are shown in Supplementary
Table 4, the corresponding atomic displacement vectors are shown in Supplementary Table 5. A comparison of the theoretical Raman spectra of PIC and phenyl isocyanate is shown in Supplementary Figure 3. As can be seen, most of the vibration modes of phenyl isocyanate appear at similar frequencies to that of PIC (see also Supplementary Table 2 and 4). The exceptions are those in-plane coupled modes of phenyl ring and the NCO group, i.e., mode 26 (1,436 cm$^{-1}$) and 28 (1,515 cm$^{-1}$), and the stretching vibration of N=C=O ($\nu_{\text{NCO}}$, mode 31, 2,324 cm$^{-1}$). Therefore, these three peaks are the most characteristic vibrational modes of phenyl isocyanate compared with PIC. It should be pointed out that the 1,436 and 1,515 cm$^{-1}$ peaks have much stronger Raman activity than the 2,324 cm$^{-1}$ peak. We will discuss the experimental results related to the spectra of phenyl isocyanate in Section 4.
## Supplementary Table 2 | Comparison of the theoretical and experimental frequencies (cm⁻¹) of selected fundamental vibrations of PIC.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Free (Gaussian basis)</th>
<th>Raman Activity /Å⁴ (amu)⁻¹</th>
<th>Free (PAW)</th>
<th>Au(111) terrace (atop)</th>
<th>PdML/Au(111) terrace (bridge)</th>
<th>PdML/Au(111) step edge (bridge)</th>
<th>Mode Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>988</td>
<td>28.8</td>
<td>998</td>
<td>995</td>
<td>1,000</td>
<td>983</td>
<td>1,000</td>
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<tr>
<td>17</td>
<td>1,022</td>
<td>12.7</td>
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<td>1,022</td>
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</tr>
<tr>
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<td>16.3</td>
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</tr>
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<td>1,195</td>
<td>47.0</td>
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<td>1,192</td>
<td>1,220</td>
<td>1,192</td>
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<td>27</td>
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<td>101.3</td>
<td>1,600</td>
<td>1,590</td>
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<td>1,585</td>
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<tr>
<td>28</td>
<td>2,110</td>
<td>526.7</td>
<td>2,120</td>
<td>2,138</td>
<td>2,190</td>
<td>1,965</td>
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<td>29</td>
<td>3,110</td>
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<td>3,113</td>
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<td>31</td>
<td>3,130</td>
<td>98.8</td>
<td>3,128</td>
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<td>33</td>
<td>3,142</td>
<td>298.3</td>
<td>3,145</td>
<td>3,135</td>
<td>3,134</td>
<td></td>
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</tr>
</tbody>
</table>

Abbreviation: \(v\), stretching; \(\alpha\), in-plane ring deformation; \(\beta\), in-plane bending.
Supplementary Table 3 | Atomic displacement vectors of vibrational modes of PIC illustrated in Supplementary Table 2.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Atomic Displacement Vectors</th>
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<tbody>
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<td>16 (A₁)</td>
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</tr>
<tr>
<td>17 (A₁)</td>
<td><img src="image2.jpg" alt="Image" /></td>
</tr>
<tr>
<td>20 (A₁)</td>
<td><img src="image3.jpg" alt="Image" /></td>
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</tr>
<tr>
<td>27 (A₁)</td>
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<td>28 (A₁)</td>
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<tr>
<td>29 (A₁)</td>
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<td>31 (A₁)</td>
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<td>33 (A₁)</td>
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### Supplementary Table 4 | Theoretical frequencies (cm⁻¹) of selected fundamental vibrations of phenyl isocyanate.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Free (Gaussian basis) Theo.</th>
<th>Raman Activity /Å⁻¹ Theo.</th>
<th>Free (PAW) Theo.</th>
<th>Mode Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>987</td>
<td>31.4</td>
<td>996</td>
<td>α_{ring}</td>
</tr>
<tr>
<td>19</td>
<td>1,022</td>
<td>16.3</td>
<td>1,028</td>
<td>VC7-C5+VC5-C3+α_{ring}</td>
</tr>
<tr>
<td>21</td>
<td>1,119</td>
<td>19.0</td>
<td>1,112</td>
<td>VC11-N12+α_{ring}+VC13-N12+VC11-C9+VC2-C11</td>
</tr>
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<td>51.4</td>
<td>1,430</td>
<td>βC2-H1+βC3-H4+βC5-H6+βC7-H8+βC9-H10+VC13-O14+VC13-N12</td>
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<td>28</td>
<td>1,515</td>
<td>133.7</td>
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<td>1,588</td>
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<td>28.1</td>
<td>2,296</td>
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<td>32</td>
<td>3,103</td>
<td>25.7</td>
<td>3,099</td>
<td>VC2-H1+VC3-H4+VC5-H6</td>
</tr>
<tr>
<td>33</td>
<td>3,111</td>
<td>125.4</td>
<td>3,105</td>
<td>VC2-H1+VC7-H8+VC5-H6</td>
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<tr>
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<td>3,119</td>
<td>70.8</td>
<td>3,120</td>
<td>VC2-H1+VC3-H4+VC5-H6+VC7-H8</td>
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<tr>
<td>35</td>
<td>3,129</td>
<td>97.6</td>
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<td>VC3-H4+VC5-H6+VC9-H10</td>
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<tr>
<td>36</td>
<td>3,136</td>
<td>274.0</td>
<td>3,136</td>
<td>VC9-H10+VC7-H8+VC5-H6</td>
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**Abbreviation:** ν, stretching; α, in-plane ring deformation; β, in-plane bending.
Supplementary Table 5 | Atomic displacement vectors of vibrational modes of phenyl isocyanate illustrated in Supplementary Table 4.

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**Supplementary Figure 3** | Simulated normal Raman spectra of PIC (top) and phenyl isocyanate (bottom). All spectra are broadened with a Lorentzian of 10 cm\(^{-1}\) width. The shadow highlights the three characteristic peaks of phenyl isocyanate in different from PIC.

**S3.4 DOS evaluation**

We examined the effect of supercell size for modeling the edge sites, the DOS profile of edge sites was well-retained when reducing the thickness of Au substrate from six layers to three layers, as shown in Supplementary Figure 4. Therefore, we adopted a three-layer Au substrate to reduce the computational cost in the adsorption model at step edge sites.

To clearly show the global d-band shift from terrace sites to edge sites on clean surfaces, a Gaussian broadening in DOS plot was set to 0.136 eV. While in the DOS projection on molecular orbitals and adsorbed metal atoms, we set the broadening to 0.034 eV to show the orbital hybridization and level splitting clearly. In Figure 4 of main text, \(\sigma\)-d hybridization peaks clearly match for molecular orbital projection (Figure 4i) and atomic projected DOS of adsorbed Pd atoms (Figure 4j) at \(\sim -8\) eV, and the small d-\(\pi^*\) resonating peaks at \(\sim 1.8\) eV indicate a strong back-donation interaction at step edge sites.
Supplementary Figure 4 | Projected DOS of different Pd atoms (as indicated in Figure 4f in the main text) when using a gold thickness of three layer (dash lines) and five layer (solid lines).

S3.5 Projected DOS on molecular orbitals

The peaks at \(-2.7\) eV in molecular projected DOS (marked by * Figure 4i in the main text) is originated from the level crossing of molecular states in small supercell, and k-point sampling was very dense in the Brillouin zone for the DOS plot. DOS projection from adsorbed states to molecular states were evaluated by the following formula, \(^7\) (note the projection to molecular orbitals also covered in full k-points).

\[
\rho(E_n, \psi) = \sum_{\mathbf{k}} w_{\mathbf{k}} \left[ \sum_i |\langle \psi_{n,\mathbf{k}} | \psi_{i,\mathbf{k}} \rangle|^2 \delta(E - \epsilon_{i,\mathbf{k}}) \right]
\]

(S7)

S4. Bulk gold catalyzed reaction of isocyanide

Despite its reputation as a poor catalyst, bulk gold (including gold single crystals) can still
catalyze various reactions of adsorbed isocyanide. For instance, the adsorbed isocyanide on bulk gold surface was found to react quickly with amine under ambient condition and at room temperature. When exposed to air, the adsorbed isocyanide on bulk gold surface can be oxidized to isocyanate (from R-N=C to R-N=C=O). Similar oxidative degradation was observed in metal-isocyanide complexes.

The high reactivity of isocyanide can be understood by the electrophilic character of the isocyanide carbon. Supplementary Table 6 lists the charges on nitrogen and carbon atoms of NC group of PIC adsorbed on Au and Pd surfaces. When isocyanide is adsorbed on gold surface, the interaction involves the σ donation of the lone electron pair of isocyanide carbon to gold. Since bulk gold is a poor π donator, there is little π back-donation from gold to isocyanide. The σ donation leads to the electrophilic character of the isocyanide carbon (Supplementary Table 6), which accounts for its high reactivity towards nucleophilic attack by oxygen (oxygen and amine species with lone electron pair are normal nucleophile). Indeed, the nucleophilic attack on coordination-activated isocyanide ligands has been an important subject of the synthetic chemistry of isocyanide (especially for the synthesis of aminocarbene complexes). In contrast to gold, palladium is a good π donator. Therefore, the π back-donation dominates the isocyanide-palladium bonding, as reflected by the bridge site adsorption and the redshift of v_{NC}. The π back donation from Pd makes the isocyanide carbon electron-rich (Supplementary Table 6), thus unfavorable for nucleophilic attack by oxygen.

In addition, from Supplementary Table 1 we can see that the calculated adsorption energy of PIC on Au terrace (−0.56 eV) is much weaker than that on Pd terrace (−2.13 eV) and Pd step edge (−2.29 eV). This relatively weak binding affinity makes it favorable for C–Au bond activation and product desorption on Au surface, and can explain the higher activity of Au than Pd according to the Sabatier principle.
Supplementary Table 6 | Charges on nitrogen and carbon atoms of NC group of PIC from Bader analysis (Bader method). The values are relative to that of free PIC molecule.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Au(111)-atop</th>
<th>PdML/Au(111)-bridge</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>+0.09 e</td>
<td>+0.19 e</td>
</tr>
<tr>
<td>C</td>
<td>−0.08 e\textsuperscript{a}</td>
<td>+0.03 e</td>
</tr>
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\textsuperscript{a}Minus value means less electron density and thus more favorable for nucleophilic attack by oxygen.

Furthermore, in our TERS experiments, the surface plasmon resonance may assist the activation of O\textsubscript{2}\textsuperscript{52} thus promoting the oxidation of PIC in the gap of Au tip-Au(111) substrate. Therefore, it is reasonable to expect a much higher oxidation activity than under the normal ambient conditions (without laser and plasmon effect).

S4.1 TERS evidence of PIC oxidation on Au(111)

Supplementary Figure 5 | Reaction of PIC on Au(111) surface as probed by TERS. \textbf{a,b}, Time-dependent TERS spectra of PIC adsorbed on Au(111) surface obtained at different conditions: (a) 50 \(\mu\)W, 10 s and (b) 3.4 mW, 1 s. The inset shows an enlarged view of the \(\nu_{NC}\) peak region. \textbf{c}, Representative TERS spectra of PIC on the Au hole region obtained in a line trace imaging experiment on a Pd\textsubscript{ML}/Au(111) surface (extracted from the data shown in Figure 3c).

The reaction of PIC on Au(111) surface is evidenced in the TERS spectra in Figure 2a in the main
text. Supplementary Figure 5 shows more TERS data of PIC adsorbed on Au(111) surface, obtained under relatively low (Supplementary Figure 5a, 50 µW) and high (Supplementary Figure 5b, 3.4 mW) laser power conditions. The spectra in Supplementary Figure 5b are essentially the same as that shown in Figure 2a in the main text, in which the $\nu_{NC}$ peak disappears in a short time. The decrease of the intensity of $\nu_{NC}$ peak is not so obvious in Supplementary Figure 5a, because in this case the laser-induced reaction can be negligible. Supplementary Figure 5c shows representative TERS spectra obtained in a line trace imaging experiments from PIC/Pd$_{0.8ML}$/Au(111) sample (data extracted from Figure 3c in the main text). Here, the absence of $\nu_{NC}$ peak indicates that NC bond has been reacted.

A new peak at $\sim$2,245 cm$^{-1}$ was observed, which can be assigned to $\nu_{NCO}$ according to the theoretical calculation (Supplementary Table 4), and consistent with reported IR frequency at $\sim$2,270 cm$^{-1}$. The results confirm the oxidation of NC bond to NCO bond on Au(111) surface. The theoretical Raman results suggest that the Raman activity of $\nu_{NCO}$ band (28.1 Å$^4$ (amu)$^{-1}$) is much lower than that of $\nu_{NC}$ band (526.7 Å$^4$ (amu)$^{-1}$) (see comparison of Supplementary Table 2 and 4), which makes it difficult to detect $\nu_{NCO}$. Indeed, the $\nu_{NCO}$ peak is observed in Supplementary Figure 5c but not in Supplementary Figure 5a and 5b, and Figure 2a in the main text, possibly because Supplementary Figure 5c is from a sample after a few hours of laser illumination in TERS imaging experiments, in which most of the PIC has been oxidized.

As suggested by the theoretical results (Supplementary Figure 3), two in-plane coupled modes of phenyl ring and NCO group should appear in the spectral region of 1,300–1,600 cm$^{-1}$ in the Raman spectrum if PIC is oxidized to phenyl isocyanate. We do observe a peak at $\sim$1,540 cm$^{-1}$ in Figure 2a in the main text and Supplementary Figure 5a, and a peak at $\sim$1,520 cm$^{-1}$ in Supplementary Figure 5c (all indicated by dashed red lines). Supplementary Figure 6 presents TERS spectra of the three consecutive line trace imaging experiments (the same data as the color-code map in Figure 3c in the main text), from which we can generally observe a peak at $\sim$1,520–1,550 cm$^{-1}$ showing up near step edge sites (indicated by dash lines). We assign these peaks to mode 28 of phenyl isocyanate
(theoretical frequency of 1,515 cm\(^{-1}\)). This mode is often observed because it is one of the strongest modes of phenyl isocyanate, comparable to the \(\nu_{CC}\) band (see Supplementary Table 4 and Supplementary Figure 3). Occasionally, a peak at \(\sim 1,450\) cm\(^{-1}\) can also be observed for the near step edge sites in Supplementary Figure 6, which may be assigned to mode 26 of phenyl isocyanate (theoretical frequency of 1,436 cm\(^{-1}\)). This result also suggests a higher reactivity of PIC adsorbed at step edge, in consistent with the appearance of \(\nu_{NCO}\) at step edge sites (see Figure 4 in the main text and Supplementary Figure 14). We note the frequency of these two in-plane coupled modes differs a little bit in different sets of measurements, which might be attributed to the broken planar symmetry when phenyl isocyanate adsorbed on surfaces with different configurations. Because this in-plane coupled modes are sensitive to the disturbed conjugation of phenyl ring and NCO group.

Besides the features of these peaks, the spectra on Au surface are often just broad peaks that are difficult to assign. Similar broad spectral features at 1,000–1,600 cm\(^{-1}\) were also observed at positive potentials for 1,4-phenylene diisocyanide adsorbed on rough gold electrode surface, which was ascribed to the electro-oxidation of 1,4-phenylene diisocyanide.\(^{24}\) Also, some other peaks at 1,000–1,600 cm\(^{-1}\) range are not stable and fluctuate with time. Therefore, we speculate that there may be photochemical reaction during TERS experiments, which accounts for the broadening of the 1,590 cm\(^{-1}\) peak and the fluctuated peaks at 1,000–1,600 cm\(^{-1}\) spectral region.

Overall, a comparison of the results on Au(111) and Pd\(_{\text{ML}}$/Au(111) surfaces suggest a higher activity of Au(111). Furthermore, we can expect a similar thermal effect on the Au(111) and Pd\(_{\text{ML}}$/Au(111) surfaces under the same laser illumination conditions, especially for the nearby Au and Pd surface sites in a line imaging experiment. Therefore, it is mainly the electronic and catalytic effect of the substrate rather than the thermal effect that leads to the reaction of PIC on surfaces.
Supplementary Figure 6 | TERS spectra of the three consecutive line trace imaging experiments (the same data as the color-code map in Figure 3c in the main text). The dashed lines indicate the peak at ~1,520–1,550 cm⁻¹ attributed to in-plane coupled mode 28 of phenyl isocyanate, suggesting the higher reactivity of PIC adsorbed at Pd step edges.

S4.2 XPS evidence of PIC oxidation on Au(111)

The oxidation of PIC was further evidenced by XPS results. Supplementary Figure 7a presents the XPS N1s spectra of PIC/Au(111) sample. For the fresh sample of PIC/Au(111) (Supplementary Figure 7a, bottom panel), the N1s peak is mainly centered at 400 eV, assigned to aromatic isocyanide adsorbed on gold surface. After exposed to the ambient air for ~3 h, the main peak shifts
negatively to 398.8 eV (Supplementary Figure 7a, middle panel), which can be assigned to the nitrogen of N=C=O.\textsuperscript{41} The results indicate that NC has been oxidized to NCO. Laser irradiation would further promote the oxidation of PIC (Supplementary Figure 7a, top panel), which is consistent with our time-dependent TERS results and literature results.\textsuperscript{42} We note that, for the fresh sample, a small shoulder peak at 398.8 eV of the oxidized products can already be observed, which can be attributed to either (1) oxidation of NC by adventitious oxygen in the argon-purged solution, or (2) oxidation of NC when exposed to the ambient during transfer to the XPS chamber. The result further suggests that the oxidation of isocyanide is a fast process.\textsuperscript{41} The degree of PIC oxidation can be reflected by the percentage of the integrated intensity of the NC peak (400 eV) and NCO peak (398.3 eV), as plotted in Supplementary Figure 7c. The percentage of the NC peak decreases from 0.72 (fresh sample) to 0.35 (sample exposed to ambient) and 0.22 (sample exposed to ambient and laser irradiation), suggesting the increase of the degree of PIC oxidation.

Supplementary Figure 7b presents XPS spectra of N1s peak for the sample of PIC/Pd\textsubscript{ML}/Au(111) surface, with no difference for the fresh and the laser irradiated samples. The N1s peaks are centered at 398.3 eV, indicative of isocyanide adsorbed on Pd surface.\textsuperscript{41} The XPS result is in good agreement with TERS result, suggesting no obvious catalytic reaction of PIC on Pd\textsubscript{ML}/Au(111) surface. Note that the binding energy of N1s of PIC on Pd\textsubscript{ML}/Au(111) surface is 1.7 eV negative of that on Au(111) surface, which arises from the enhanced electron density of nitrogen by an increased $\pi$ back-donation of Pd.
Supplementary Figure 7 | XPS evidence for the oxidation of PIC on Au(111) surface. a, XPS N1s spectra of the fresh (bottom panel), after exposed to ambient air (middle panel) and additional laser irradiated (top panel) samples of PIC/Au(111). b, XPS N1s spectra of the fresh (bottom panel) and laser irradiated (top panel) samples of PIC/Pd_{ML}/Au(111). c, The percentage of the integrated intensity of the NC peak (400 eV) and NCO peak (398.3 eV) of PIC/Au(111) samples for different treatment. Ambient: the sample is exposed to laboratory ambient air for 3 h to allow the oxidation of PIC. Laser: the sample is exposed to laboratory ambient air for 2 h and 45 mins, and further exposed to a 633 nm laser for additional 15 mins. The diameter of the laser beam is ~ 3 mm on the sample surface, with a power of 3.1 mW (power density of ~44 mW/cm^2). This power density is much lower than that used in TERS measurements (~1×10^7 mW/cm^2). Even so, most of the PIC has been oxidized. Therefore, we can expect the degree of PIC oxidation would be very high in TERS measurements.

It should be noted that the Raman signal of 4-chlorophenyl isocyanide (which has a similar molecular structure to phenyl isocyanide used in this work) adsorbed on Au(111) surface has been obtained by the gap-mode SERS. No oxidation reaction products were observed in the gap-mode SERS studies, possibly because very low laser power was used because tens to a few hundreds
of nanoparticles (hot spots) were detected in a single laser spot. In TERS measurements, a relatively high laser power is needed to achieve a good noise-to-ratio, due to the only one ‘hot spot’ in TERS. Much less molecules were detected in TERS, making it more sensitive to any reactions occurred underneath the tip. However, we did not try to avoid the reaction of PIC, because it offers clear chemical contrast between Au and Pd surfaces, and serves as a good model for mapping the catalytic activity.

**S4.3 PIC oxidation on Pd\textsubscript{ML}/Au(111) surface**

It is also observed that, after a few hours of measurements, PIC adsorbed at the terrace Pd site on Pd\textsubscript{ML}/Au(111) surface could also be oxidized. As shown in Supplementary Figure 8, the new small peaks at $2,240 \text{ cm}^{-1}$ ($v_{\text{NCO}}$) and $1,520 \text{ cm}^{-1}$ (mode 28 of phenyl isocyanate) ascribed to the oxidation product can be observed (top two spectra). Furthermore, it can also be observed that the $1,590 \text{ cm}^{-1}$ peak becomes slightly broadened compared with the fresh sample (bottom two spectra), and some other new peaks at $1,200$–$1,500 \text{ cm}^{-1}$ show up (with very low intensity), probably due to the photochemical reaction of the benzene ring, in analogue with the observations on Au surface. However, the $v_{\text{NCO}}$ peak is very weak, and the spectra are generally the same as the fresh spectra, even after a few hours of measurements. The results further suggest that Pd\textsubscript{ML}/Au(111) surface is much less active than Au(111) surface for the oxidation of PIC.
Supplementary Figure 8 | Reaction of PIC on Pd_{ML}/Au(111) surface. Typical TERS spectra of PIC on Pd_{ML}/Au(111) surface (terrace site), acquired at the beginning (black and red line) and after a few hours measurement (blue and pink line).

S5. Reliability and reproducibility of the TERS imaging measurements

Supplementary Figure 9 | A trace and retrace TERS line imaging measurement. a, An STM image of the PIC/Pd_{0.8ML}/Au(111) surface obtained using a gold tip. The image is the same as that shown in Figure 4a in the main text. b,c, Trace (b) and retrace (c) TERS line imaging results obtained
along the dashed line in \textbf{a, d}, Height profile corresponding to the dashed line in \textbf{a}.

\textbf{S6. Procedure for TERS intensity analysis.}

To analyze TERS intensity, the original TERS spectra (black line in Supplementary Figure 10a) were subtracted by far-field background (spectrum obtained when tip-retracted, red line in Supplementary Figure 10a) to obtain the near-field signal (blue line in Supplementary Figure 10b), which was used for intensity analysis (using peak height). To plot the imaging results in a color-code map, a further background fitting (purple line in Supplementary Figure 10b) and subtraction were performed to obtain the spectrum in Supplementary Figure 10c for color-code mapping, which allows a better view of the variation of Raman intensities.

\textbf{Supplementary Figure 10} | Procedure for intensity analysis of a typical TERS spectrum.

\textbf{S7. Coverage of PIC on Au and Pd surfaces}

The coverage of PIC on Au(111) and Pd$_{M}$/Au(111) surfaces was characterized by the difference of the interfacial capacitance of the bare and PIC covered metal surfaces. The interfacial capacitance can be modeled by a classical plate capacitor. After the adsorption of PIC, the effective surface dielectric constant ($\varepsilon$) is decreased, and the distance of the capacitance ($l$) is increased, which result in the decrease of capacitance in considering $C = \varepsilon\varepsilon_0/l$ ($\varepsilon_0$ is the vacuum permittivity).

The interfacial capacitance can be obtained from the cyclic voltammogram measurements. At a low scan rate, the interfacial capacitance ($C$) can be deduced by $C = j/v$, where $j$ is the current density and $v$ is the scan rate. The measurements were carried out in 0.1 M KNO$_3$ aqueous solution within the potential window of the double layer region (no faradic reaction), which is reflected by the near
rectangular shape of the cyclic voltammograms (Supplementary Figure 1a,b). Here, we use a scan rate of 5 mV/s, and the current density at 0.1 V is used to calculate \( C \).

For the bare Au(111) surface, \( C \) is determined to be 25.1 ± 2.0 \( \mu \)F/cm\(^2\). For the Pd\(_{ML}\)/Au(111) surface, \( C \) is determined to be 23.0 ± 1.5 \( \mu \)F/cm\(^2\). These values are within the typical values of interfacial capacitance for metal surfaces.\(^{55}\) After the adsorption of PIC, a clear decrease of the current density for the PIC/Au(111) and PIC/Pd\(_{ML}\)/Au(111) surfaces can be observed compared with the bare Au(111) and Pd\(_{ML}\)/Au(111) surfaces (Supplementary Figure 1a and b), which indicates a lower interfacial capacitance after molecular adsorption. More specifically, the current density of PIC/Pd\(_{ML}\)/Au(111) surface is smaller than that of PIC/Au(111) surface. Quantitatively, for the PIC/Au(111) surface, \( C \) is 11.3 ± 2.0 \( \mu \)F/cm\(^2\), which is about twice of the value for the PIC/Pd\(_{ML}\)/Au(111) surface, 6.0 ± 0.2 \( \mu \)F/cm\(^2\).

The molecular coverage (\( \theta \)) can be estimated by a well-accepted electrochemical method considering the overall capacitance is contributed from two parallel capacitances of the PIC-adsorbed area and the bare electrode area:\(^{55}\)

\[
C_d = (1 - \theta)C_d^0 + \theta C_d^1 \tag{S8}
\]

where \( C_d \) is the measured capacitance for a given electrode with molecular adsorption, \( C_d^0 \) is the capacitance of a bare electrode (\( \theta=0 \)), and \( C_d^1 \) is the capacitance of an electrode with full monolayer adsorption (\( \theta=1 \)).

Note that for a full monolayer adsorption case, the interfacial capacitance will reach a minimum. The interfacial capacitance for PIC/Pd\(_{ML}\)/Au(111) surface (6.0 ± 0.2 \( \mu \)F/cm\(^2\)) is close to our previous reported minimum value for a metal electrode with full monolayer adsorption of thiol.\(^{56}\) Therefore, the coverage of PIC on Pd\(_{ML}\)/Au(111) surface can be considered as 1. For PIC/Au(111) surface, \( C_d \) is 11.3 ± 2.0 \( \mu \)F/cm\(^2\), \( C_d^0 \) is 25.1 ± 2.0 \( \mu \)F/cm\(^2\) (\( \theta=0 \)). On the basis of these values, the coverage of PIC on Au(111) surface can be estimated to be 0.7. The results suggest a higher PIC coverage on Pd\(_{ML}\)/Au(111) (\( \theta=1 \)) than on Au(111) surface (\( \theta=0.7 \)), which explains the stronger TERS signal on
the former surface (see Figure 3 in the main text and Supplementary Figure 9).

Supplementary Figure 11 | Interfacial capacitance of PIC adsorbed Au and Pd surfaces. a, b, Cyclic voltammograms of the Au(111) (a) and PdML/Au(111) (b) electrodes before and after the adsorption of PIC, measured in 0.1 M KNO₃ aqueous solution at a scan rate of 5 mV/s. c, The interface capacitance of Au(111), PIC/Au(111), PdML/Au(111), and PIC/PdML/Au(111) electrodes. The error bar indicates the standard deviation from several measurements.

S8. Electron surface scattering effect in electromagnetic field simulation

In electromagnetic field simulation, optical constants for bulk Pd and Au were taken from refs. 57 and 58, respectively. However, the optical response of the Pd atomic layer should be different from that of the bulk. Therefore, the optical constant of the Pd atomic layer was modified in the classic framework. For the free electrons in bulk metal, the damping $\gamma_0$ is determined by interactions with electrons, phonons, lattice defects, and impurities. Since these collisions are slightly inelastic, only electrons near the Fermi level contribute. Thus,

$$\gamma_0 = \frac{\nu_F}{l_\infty} \quad (S9)$$

where $\nu_F$ is the Fermi velocity and $l_\infty$ is the mean free path of the conduction electrons in the bulk.

When the size is comparable or even smaller than $l_\infty$, the effect of surface scattering becomes important, which will lead to a reduced effective mean free path $L_{eff}$. According to ref. 60, $L_{eff} = 2d$ for thin films, where $d$ is the thickness of the film, in this work, $L_{eff} = 2 \times 0.3 \text{ nm} = 0.6 \text{ nm}$. In the frame of Matthiessen’s rule, the contribution of the surface scattering can be added to the former collisions. Therefore, the Drude free electron model can be modified as
\[
\varepsilon(\omega, L_{\text{eff}}) = \varepsilon_{\text{bulk}}(\omega) + \frac{\omega_p^2}{\omega^2 + i\omega\gamma_0} - \frac{\omega_p^2}{\omega^2 + i\omega\left(\gamma_0 + A_{\text{eff}}\right)} \tag{S10}
\]

where \(\varepsilon_{\text{bulk}}(\omega), \omega_p\) are the dielectric function and plasmon frequency of the bulk Pd, and \(A\) is a dimensionless parameter, usually assumed to be close to unity. According to ref.61, \(\omega_p = 7.34\) eV, \(v_p = 3.47 \times 10^6\) m/s, \(l_\infty = 25.5\) nm.

We have calculated TERS enhancement factor by using both the bulk and modified Pd optical constants, the results were shown in Supplementary Figure 12. These two cases show similar variation trends, with a clear enhancement at step edges, in agreement with experimental results. It can be seen that the enhancement factor is lower when modified Pd optical constant was used, which is reasonable because the surface scattering leads to the damping of oscillated free electrons and thus the weaker electric field. The results in Figure 3e in the main text are obtained using modified Pd constant.

Supplementary Figure 12 | Electromagnetic field simulation. a, Model for electromagnetic field simulation. b, Calculated TERS enhancement factor when a gold tip is located at different surface sites of a Pd-Au-Pd region. The bulk and modified optical constant of Pd were used for comparison.

We are aware that the classic framework is no longer adequate to describe the exact optical response of the monoatomic Pd layer on the Au surface and the atomic features, which are different from the bulk Pd, because of complex nonlocal screening,62 the smooth electronic density profile at the metal interface,63 and quantum size effects.64 A recent ab initio calculation based on time-
dependent density functional theory (TDDFT) suggests that the atomic-scale structure is able to significantly affect the localization and enhancement inside the plasmonic gap.\textsuperscript{65} It was further found that the enhanced field at the atomic features can be further intensified by the overall plasmonic background enhancement, which is in accordance with our simulation. Therefore, our simulation can qualitatively reflect the enhancement at terrace and step edges. More theoretical and experimental work should be done to gain an insight into the optical response of the atomic features. To avoid unphysical reflections at the boundary of the simulation domain, perfectly matched layer boundary conditions was used in our simulations.

S9. Spatial resolution analysis

![Spatial resolution analysis](image)

**Supplementary Figure 13 | Spatial resolution analysis.** Intensity profile of the 1,165 cm\textsuperscript{-1} peak as a function of surface distance.

As shown in Supplementary Figure 13, the intensity profile at step edges can also be fitted with a Gaussian function, considering the step edge as a plasmonic ‘hot edge’. The full-width at half-maximum (FWHM) analysis gives a spatial resolution of 3 nm, close to the value (2.6 nm) from a 10\%-90\% contrast analysis in Figure 3d in the main text. In our TERS line imaging experiments, one spectrum was acquired every 2 nm of surface distance. It can be seen from Figure 4c,d in the main text and Supplementary Figure 14 that the successive two spectra can be well distinguished. Such findings are consistent with a spatial resolution of about 3 nm.

Supplementary Figure 14 | Five more sets of experimental results on the distinct electronic properties of Pd step edges. Spatially resolved TERS line scan spectra obtained by moving the tip across a Pd terrace-Pd step edge-Au terrace region (from bottom to top). The spectra are obtained from the regions shown in Figure 3a and Figure 4a in the main text. The spectra are smoothed and background subtracted. The scale bars are 10 cps in all spectra. The fitted area of the 1,933 cm\(^{-1}\) peak is indicated aside the peak in light red.
S11. Electronic structure of Au atoms close to the step edge

Supplementary Figure 15 | Calculated projected DOS of bare Au atoms at different sites as indicated in the inserted atomic model.

Supplementary Figure 15 shows projected DOS of d-bands for the Au atoms close to the step edge. The Au step edge atoms have a higher d-band electronic profile, because of the decrease of nearest Au neighbors. The No. 1-2 Au atoms have a similar profile and thus similar electronic properties to the Au terrace. The adsorption of PIC is calculated to be stronger at the Au step edge (−0.86 eV) than that at the Au terrace (−0.56 eV). Since the activity of Au is much higher than Pd, the molecules adsorbed at the adjacent Au sites have already been reacted during our TERS imaging measurements. We therefore did not observe as distinct spectral features between the Au step edge and Au terrace as that observed on Pd surfaces. In addition, PIC is adsorbed much more strongly at the Pd step edge (−2.29 eV) than that at the Au step edge. Therefore, the molecules prefer to occupy the Pd step edge.

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