Supporting Information

Near-Field Enhanced Photochemistry of Single Molecules in a Scanning Tunneling Microscope Junction

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1. Radial Distribution of \textit{trans} $\rightarrow$ \textit{cis} conversion probability with PtIr, W, and Au tips

We measured the effective radius of the tip-enhanced area for the W and PtIr (80:20) and Au (#2) tips in the same way as Fig. 1c in the main text for the Au tip #1. The effective radius was determined to be 4.6(±0.3), 9.7(±1.8) and 7.0(±0.3) nm for the W, PtIr and Au #2 tips, respectively, by fitting the experimental data to a Gaussian function, $A\exp\left(-\frac{r^2}{2\sigma^2}\right)$, where we define the effective radius $r_{\text{eff}} = \sigma$.

![Graphs showing radial distribution of conversion probability for PtIr, W, and Au tips](image)

**Figure S1.** Radial dependence of the \textit{trans} $\rightarrow$ \textit{cis} tautomerization probability as a function of radius from the tip position for the PtIr, W and Au #2 tip. The tip was positioned in the center of an STM image ($V_t = 50$ mV and $I_t = 30$ pA, size: 50×50 nm$^2$) and illuminated at 690 nm ($n_{\text{ph}} = 2.5(±0.2)\times10^{18}$ cm$^{-2}$) for the W tip, at 860 nm ($n_{\text{ph}} = 4.9(±0.3)\times10^{17}$ cm$^{-2}$) for the PtIr tip and at 860 nm ($n_{\text{ph}} = 3.5(±0.2)\times10^{17}$ cm$^{-2}$) for the Au tip #2.
2. Wavelength dependence of the near-field induced tautomerization for the PtIr tip

We measured the near-field induced tautomerization for the PtIr tip. Figure S2 shows the wavelength dependence of the cross section obtained from different tips. The PtIr tip shows a relatively large enhancement in the red and near-infrared range. This is somewhat surprising since PtIr at best supports a weak localized surface plasmon resonance in the near-IR to visible. Although the enhancement mechanism is not fully understood, the result is in line with the observation of relatively strong STM-induced luminescence from a PtIr tip.¹

![Figure S2. Wavelength dependent cross sections of the trans → cis tautomerization measured with different tips.](image-url)
3. Derivation of corrected near-field cross section

The wavelength-dependent near-field cross section (Fig. 2b in the main text) was obtained by exposing a statistically relevant number of molecules (~600) to the tip-enhanced near-field. At the given coverage on the surface, this number corresponds to an area of ~60×60 nm$^2$. However, the effective radius $r$ of the tip-enhanced spot was estimated from the radial distribution of the tautomerization probability (Fig. 1c in the main text). The discrepancy between the tip-enhanced spot size $\pi r^2$ and the scan area $A_{\text{scan}}$ therefore underestimates the measured near-field cross section $\sigma_{\text{NF}}$ and needs to be corrected to obtain the actual tip-enhanced cross section $\sigma_{\text{NF,corr}}$ when the near-field process is dominant ($\sigma_{\text{NF}} \gg \sigma_{\text{FF}}$). We estimated the corrected near-field cross section as:

$$\sigma_{\text{NF,corr}} \approx \left( \frac{A_{\text{scan}} + 2\sqrt{\pi A_{\text{scan}}r} + \pi r^2}{\pi r^2} \right)^{1-\frac{\sigma_{\text{FF}}}{\sigma_{\text{NF}}}} \cdot \sigma_{\text{NF}}.$$  

The bracketed part corresponds to the ratio of the tip-enhanced scan area on the surface and the spot size. The spill-over of the tip-enhanced spot across the STM scan frame was taken into account (see Fig. S3). Simultaneous contributions from far-field and near-field excitation during the measurement are accounted for by the exponent. The exponent is significant only when $\sigma_{\text{NF}} \approx \sigma_{\text{FF}}$, i.e., the tip-enhancement effect is weak.

![Figure S3](image_url)

Figure S3. Experimental procedure to determine tip-enhanced cross section. The red circle represents the estimated tip-enhanced spot on the surface with area $\pi r^2$, while $r$ is determined from Fig. 1c. During illumination, the spot is scanned across the scan frame area $A_{\text{scan}} = 60\times60$ nm$^2$. The scan duration was identical to the illumination time. The gray area depicts the spill-over of the tip-enhanced spot across the scan frame, corresponding to $2\sqrt{\pi A_{\text{scan}}r} + \pi r^2$. 


REFERENCES