Supporting Information

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

Hannes Böckmann[1], Sylwester Gawinkowski [2], Jacek Waluk[2,3], Markus B. Raschke[4], Martin Wolf[1], and Takashi Kumagai[1,5] *

[1]Department of Physical Chemistry, Fritz-Haber Institute of the Max-Planck Society, Faradayweg 4-6, 14195 Berlin, Germany.

[2]Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, Warsaw 01-224, Poland.

[3]Faculty of Mathematics and Natural Sciences, College of Science, Cardinal Stefan Wyszyński University, Dewajtis 5, 01-815 Warsaw, Poland.

[4]Department of Physics, Department of Chemistry, and JILA, University of Colorado, Boulder, CO 80309, USA.

[5]JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.

* kuma@fhi-berlin.mpg.de

1. Radial Distribution of *trans → 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,

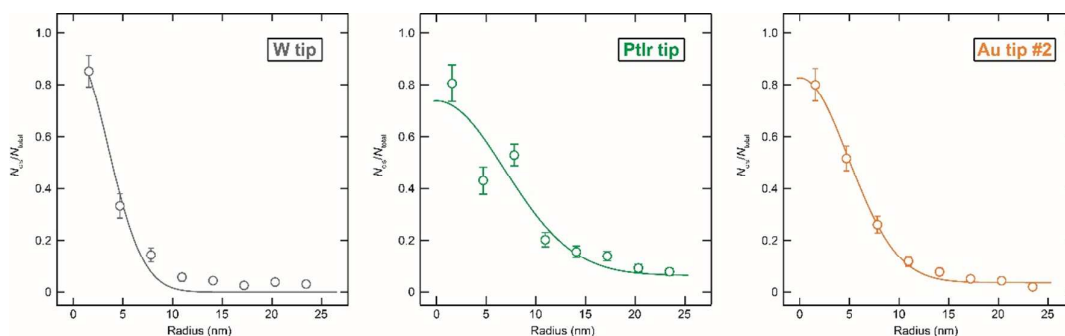$A\exp\left(-\frac{r^2}{2\sigma^2}\right)$, where we define the effective radius $r_{\text{eff}} = \sigma$.

Figure S1. Radial dependence of the *trans → 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_{ph} = 2.5(±0.2)×10^{18} cm^{-2}) for the W tip, at 860 nm (n_{ph} = 4.9(±0.3)×10^{17} cm$^-$) for the PtIr tip and at 860 nm (n_{ph} = 3.5(±0.2)×10^{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]
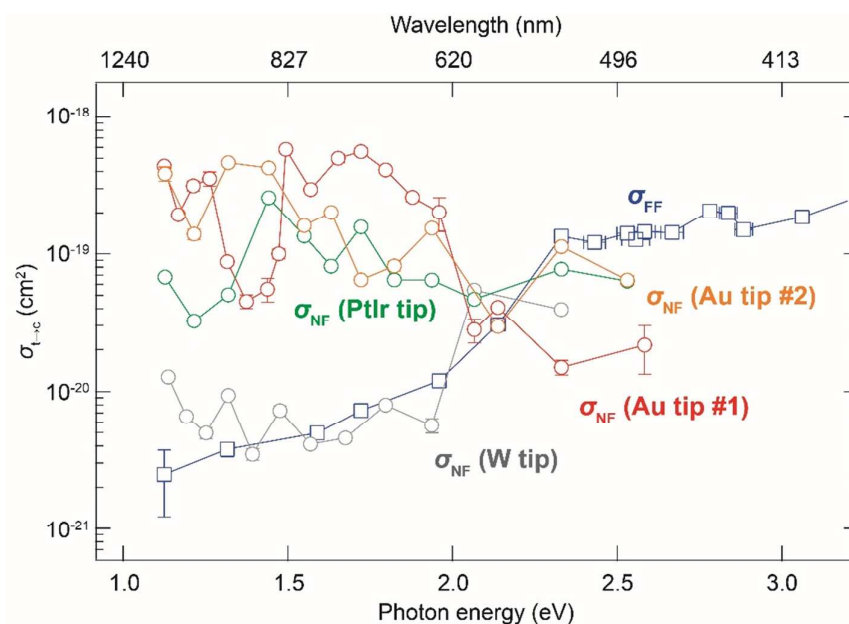

Figure S2. Wavelength dependent cross sections of the *trans → cis* tautomerization measured with different tips.

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 πr^2 and the scan area A_{scan} therefore underestimates the measured near-field cross section σ_{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.
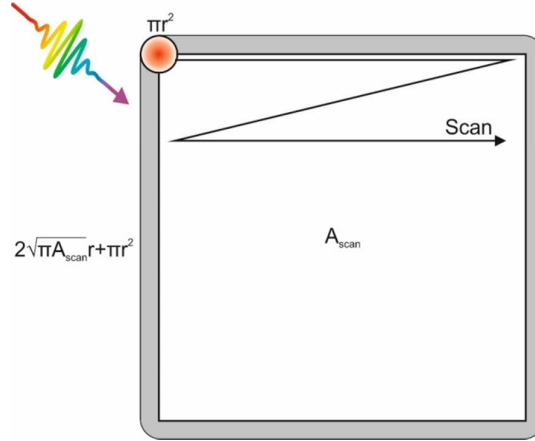

Figure S3. Experimental procedure to determine tip-enhanced cross section. The red circle represents the estimated tip-enhanced spot on the surface with area πr^2, while r is determined from **Fig. 1c**. During illumination, the spot is scanned across the scan frame area $A_{\text{scan}} = 60 \times 60$ 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

[1] Fojtík, P.; Perronet, K.; Pelant, I.; Chval, J.; Charra, F. *Surf. Sci.* **2003**, *531*(2), 113.