Supporting Information:
A Single-Molecule Chemical Reaction Studied by High-Resolution Atomic Force Microscopy and Scanning Tunneling Microscopy-Induced Light Emission

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Force-distance spectroscopy on vanadyl phthalocyanine and vanadium phthalocyanine

To corroborate the findings for the different molecular species obtained by AFM imaging, we performed force-distance spectroscopy, $\Delta f(z)$. This allows to determine differences in the adsorption height within a molecule, allowing inferences on the adsorption geometry. To this end, $\Delta f$ was recorded as a function of tip height $z$ at different positions atop the molecules, i.e., above the center of the macrocycle and one of the phenylene groups at the periphery of the molecule, respectively, as indicated in the inset in Figure S1. In the resulting $\Delta f(z)$-curve, the tip height for which the frequency shift is minimal, $z^*$, is identified using a parabolic fit to the data around the minimum. Figure S1 shows the recorded $\Delta f(z)$-spectra and the corresponding $z^*$ for the different species, i.e., VOPc O-up, VOPc O-down and VPc.

![Figure S1: Force-distance spectroscopy data obtained on VOPc O-up (left), VOPc O-down (center) and VPc (right) with a CO-functionalized tip. The tip height $z$ is given with respect to the STM set point of $I = 0.5$ pA and $V = 0.2$ V on bilayer NaCl (next to the molecule). The spectra were recorded above one of the phenylene groups (blue) as well as the center (orange), as indicated in the inset. Around the minimum of $\Delta f(z)$, the curve is fitted using a parabolic fit-function (red) to obtain the relative tip height corresponding to the minimum in $\Delta f(z)$, i.e., $z^*$, indicated by the black cross. The corresponding $z^*$ for the different tip positions are given in the insets in the plots.](image)
To draw conclusions on the adsorption geometry, the \( z^* \) obtained at different positions within the molecule, \( i.e., \) the center of the macrocycle \( z^*_c \) and one of the phenylene groups at the periphery \( z^*_p \), were compared. Note that, since the distance dependence of the frequency shift gives a chemical contrast/is sensitive on chemical properties and the atomic species of the different positions are dissimilar (C in the phenylene group, V/O in the center of the macrocycle), an exact one-to-one comparison of the adsorption height is not possible. However, in combination with high-resolution AFM images, a qualitative conclusion on the geometry/shape of the molecule is possible.

Table S1 summarizes \( z^* \) determined with a CO-functionalized tip above a phenylene group (\( z^*_p \)) and the center (\( z^*_c \)) of the molecules as well as the relative difference in height of both positions (\( \Delta z^* = |z^*_c| - |z^*_p| \)) for all three species. For the error of \( z^* \), we follow the error estimation of Ref. S1 of around 0.05 Å.

|         | \( z^*_p \) (Å) | \( z^*_c \) (Å) | \( \Delta z^* \) Å |
|---------|-----------------|-----------------|------------------|
| VOPc O-up | 4.28            | 6.41            | 2.13             |
| VOPc O-down | 4.35           | 4.63            | 0.28             |
| VPc      | 4.51            | 4.01            | -0.5             |

**Plasmonic emission in STM-LE**

In advance to STM-LE measurements on the different molecular species, the purely plasmonic emission on the bare NaCl bilayer was recorded. This, on the one hand, allows an assessment of the quality of the tip in terms of its capability to excite gap plasmon modes. On the other hand, since the coupling between molecular exciton and gap plasmon plays a crucial role in the efficiency of the radiative decay of the exciton, and possibly already in the exciton formation,\(^{82-84}\) knowledge of the plasmon spectrum is essential for the interpretation of
the occurrence and/or relative intensities of radiative transitions within the molecules. An exemplary STM-LE spectrum recorded on the bare bilayer NaCl is shown in Figure S2 for a set point of $I = 150\, \text{pA}$ and $V = -2.5\, \text{V}$. It shows the purely plasmonic emission for the same tip as in Figure 4b in the main manuscript, with maximum intensity around 630 nm.

![STM-LE spectrum recorded on bare bilayer NaCl, showing the purely plasmonic emission for this particular tip. The spectrum was recorded at a set point of $I = 150\, \text{pA}$ and $V = -2.5\, \text{V}$ and an integration time per frame of 4 min summed over 2 frames. The data is Savitzky-Golay- and Hampel-filtered. The supposed increase in intensity for larger wavelengths is an artifact stemming from the background correction.](image)

**References**

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