SUPPLEMENTARY INFORMATION

Single Molecule Vibrational Spectroscopy: Cobalt-tetraphenylporphyrin Deposited on Cu_2N Ultrathin Insulating Layer

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CoTPP molecule on Cu(100): Calculated DOS

By comparing the calculated DOS for CoTPP deposited on Cu_2N (Figure 2b) with the results for CoTPP on Cu (Figure S1) one can notice that the peaks appear broader for the CoTPP on Cu substrate, once the interaction of the molecule is stronger with the metallic surface than with the insulating layer.

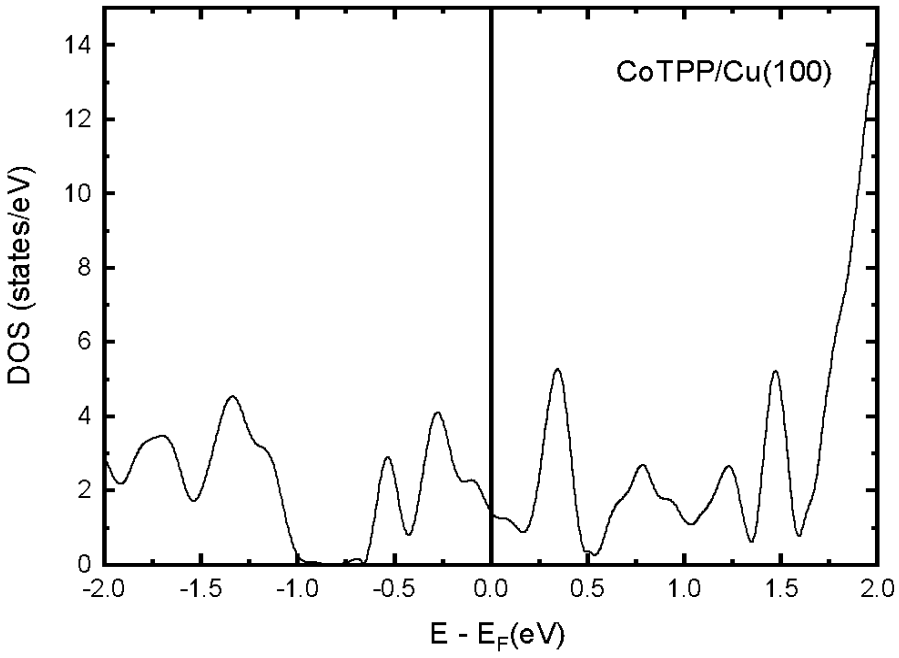

Figure S1. DOS results for CoTPP molecule deposited on bare Cu(100).

Cu_2N/Cu(100) substrate: Calculated DOS

Figure S2 presents the calculated DOS of the Cu_2N/Cu(100) substrate. Notice that the graph was not obtained for the isolated surface, but by calculating the projected partial DOS of substrate atoms on the CoTPP/Cu_2N/Cu(100) calculation. In the Figure are presented two curves, one for the overall DOS of the substrate and another one for the N atoms in the upper surface (Cu_2N). The density of states of the nitrogen atoms on Cu_2N surface is multiplied by 100 to fit the same scale. The supercell used for the calculations of conformation and electronic properties for both surface and molecule was composed of a thin slab with 3 copper layers and 1 layer of Cu_2N, as represented in Figure 2c (main text), which means only the upper surface is covered by Cu_2N. Hence, the peaks close to Fermi level are due to residual DOS from copper atoms of the substrate that could not be separated in the calculation.

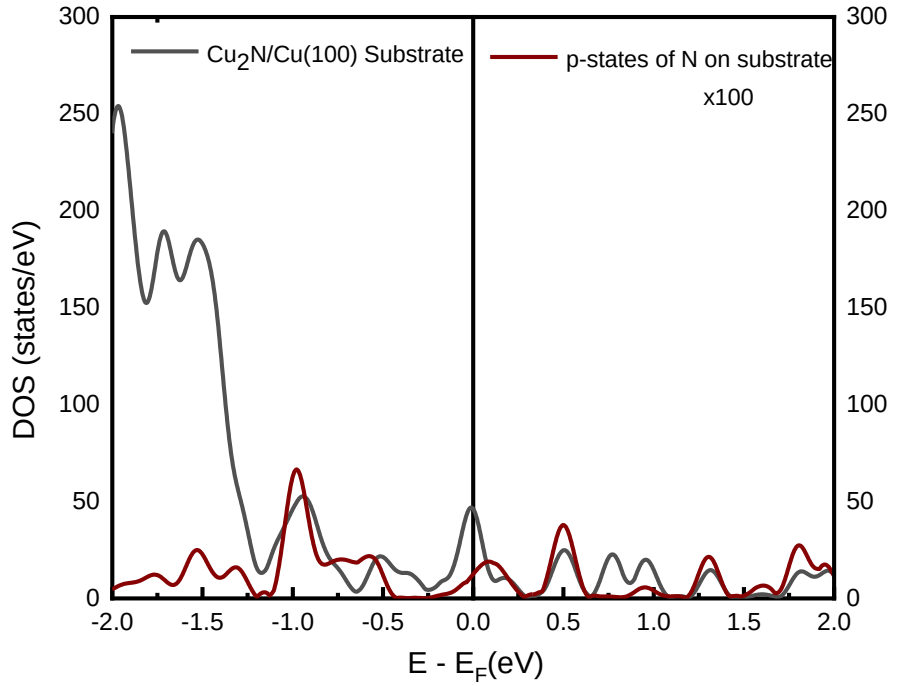

Figure S2. DOS results for Cu_2N-Cu(100) insulating layer.

CoTPP molecule on Cu_2N/Cu(100): DOS for CoTPP over Cu and N atoms

Two possible positions for adsorption of CoTPP molecules on Cu_2N layer were considered: central Co atom aligns over the Cu atoms or with N atoms of insulating layer. Figure S3 presents the calculated DOS for both cases, showing no significant changes between the two situations. Also the calculations have shown that adsorption on N atoms is slightly favorable from an energetic point of view, with total energy values for the CoTPP molecule and substrate of -1162.89 eV and -1162.77 eV for N top and Cu top, respectively.

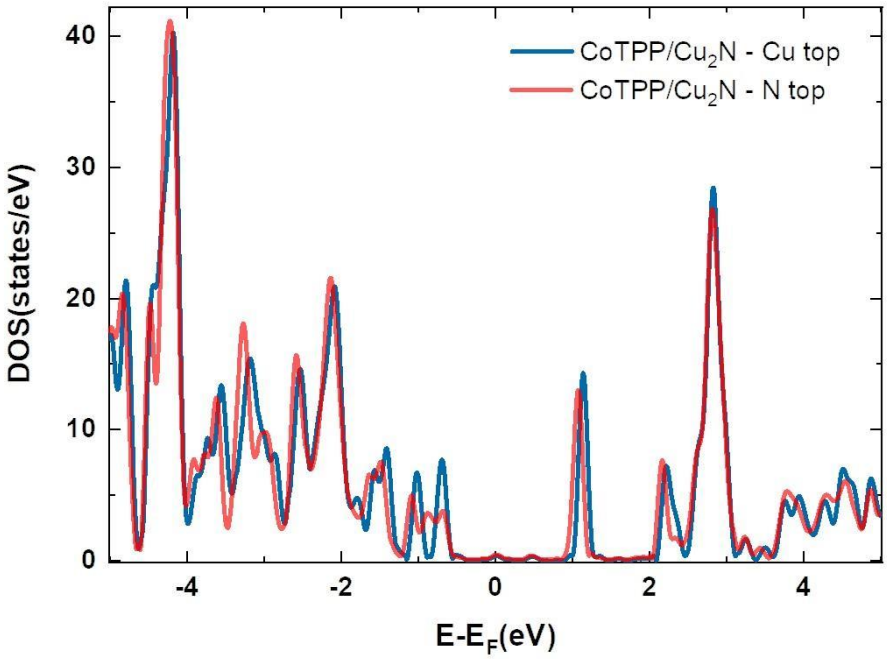

Figure S3: DOS results for CoTPP on Cu_2N-Cu(100) for the situation that the central Co atom is positioned on top of N (red curve) and top of Cu (blue curve) of the insulating layer**.**

CoTPP molecule on Cu_2N/Cu(100): Calculated DOS

We present in Figure S4 the projected density of states (PDOS) for the molecule on top of the Cu_2N surface. In a detailed analysis of the theoretical results. One can see that the contribution to DOS is mainly due to the carbon π-states of the porphyrin macrocycle. Carbon states appear from -0.5 V, though Co-d states are observed around -1.3 eV (HOMO). The results for CoTPP/Cu_2N/Cu(100) also show small peaks close to the Fermi level, which are due to hybridizations between molecule-surface and have origin in the physisorption of the CoTPP on the substrate. Yet, most of the peaks close to the Fermi level in Figure 2(b) are due to residual DOS from the Cu_2N/Cu(100) substrate and it is not possible to observe those peaks in the experimental measurements.

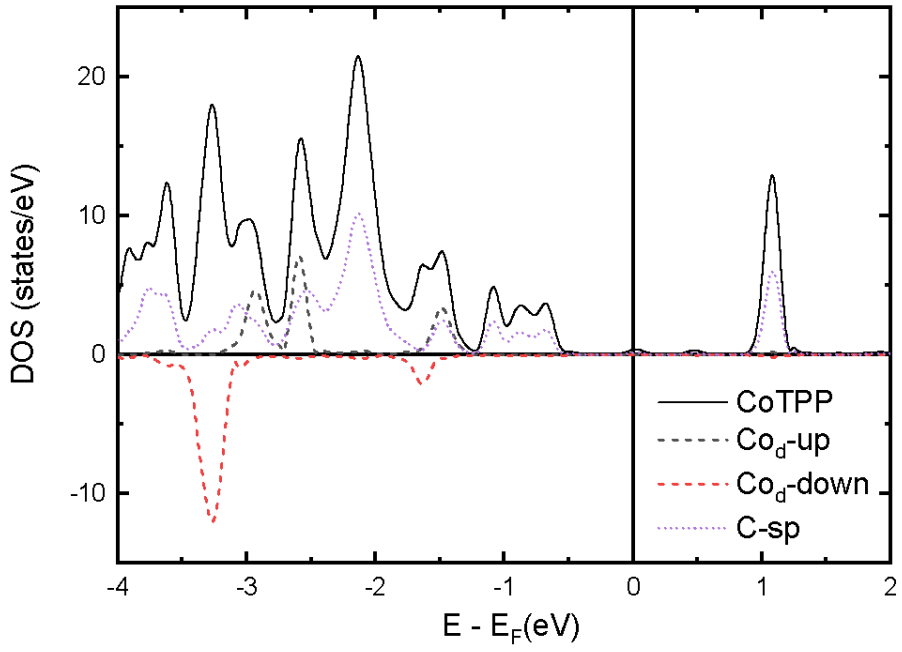

Figure S4. DOS results for CoTPP molecule deposited on Cu_2N-Cu(100).

CoTPP molecule on Cu_2N/Cu(100): STS at different points of the molecule docked on a step of Cu_2N

STS measurements were obtained at different points of the molecule, as shown in Figure S5. The dI/dV curves for the center of the molecule, phenyl ring, macrocycle and substrate are represented by the same color as the dots displayed on the STM image according to the position over CoTPP the measurement was taken. Regardless of whether the phenyl ring is positioned, on the step or on the bottom layer, no significant difference in the spectra was observed (not shown). Note that for the spectrum obtained at the center of the molecule, the positions of the peaks do not vary compared to the positions of those observed for the phenyl rings. The molecular orbitals for CoTPP positioned in this accommodation site are observed at 1.16 V (LUMO) and -1.12 V (HOMO). The energy gap of approximately 2.3 eV, in this case, is slightly smaller than that observed for a uniform Cu_2N region.

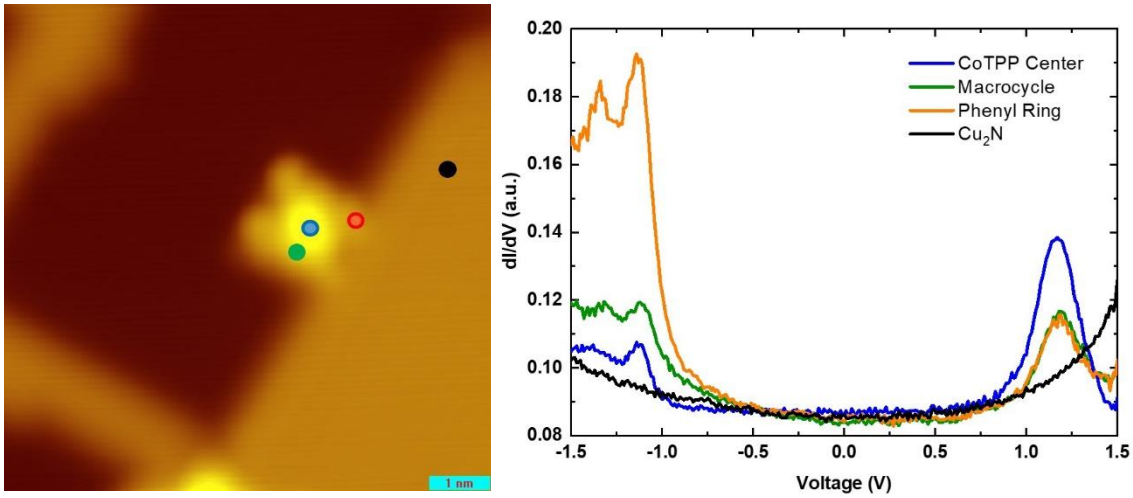

Figure S5. STM image and STS curve for CoTPP deposited on a step of Cu_2N-Cu(100) substrate. a) STM image at V = 1.0 V and I = 190 pA. b) The measurement in the center of the molecule is represented by the blue curve, the phenyl ring and macrocycle the orange and green curves, respectively, the black curve is the substrate for comparison.

CoTPP molecule on Cu_2N/Cu(100): Differences between the measured STS and calculated DOS

The simulated and the measured STM images at the cobalt site showed some differences which could be related to several trends. In the main text we speculate about some gas adsorption to the cobalt center. One possibility of gas adsorption is Nitrogen gas which could occur through nitrogen desorption from Cu_2N layer. Results for the calculations assuming the bonding of N_2 to the Co atom, with van der Waals interaction between the molecule and the substrate are presented in Figure S6. Notice that the adsorption of N_2 over Co does not change the LUMO, but introduces a new molecular orbital above 2 eV, as can be seen in Figure S6(a). In Figure S6(b) the atomic structure of N_2-CoTPP, showing that the N_2 lies about 2.44 A above the cobalt atom. Figures S6 (c-e) show STM simulated images of the N_2-CoTPP/Cu_2N system for different biases. For potential values higher than 2 eV the simulated image are very similar to the one measured at 1 V. We have not considered the adsorption of other types of molecules. In the case of the calculated vibrational modes, we observed that the adsorption of N_2 over Co site of CoTPP/Cu_2N promotes changes in the vibrational modes less than 0.5 %, i.e., almost indistinguishable from the results without N_2 adsorption.

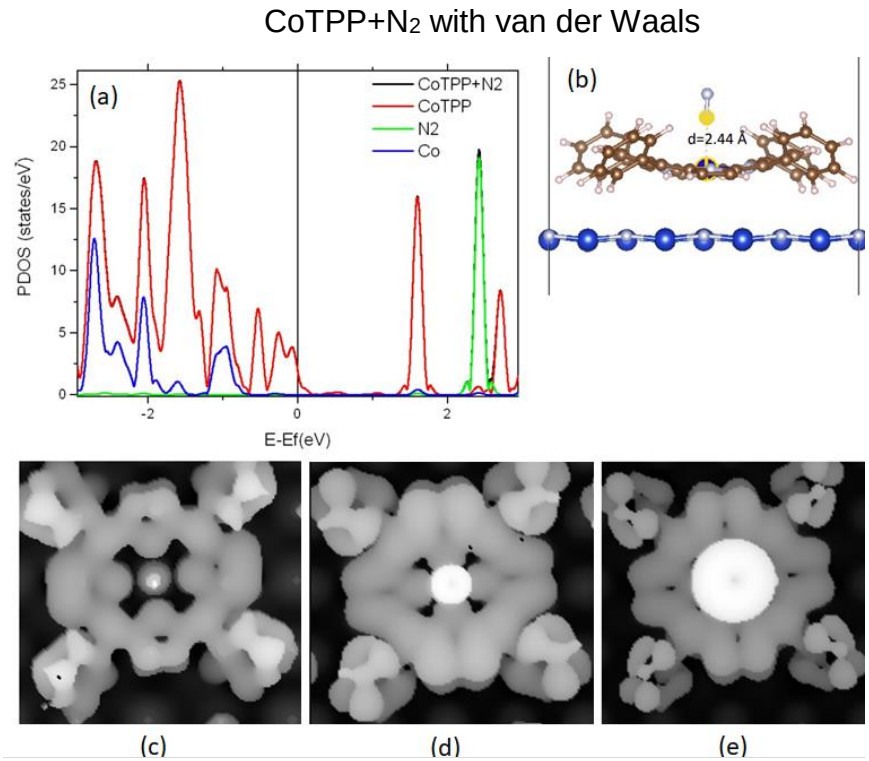

Figure S6: Calculation for the system N_2-CoTPP/Cu_2N. a) DOS, b) atomic structure and c) simulated images at bias 1.5 eV, d) 2.0 eV and e) 2.5 eV.

In addition to the gas adsorption, other mechanisms could be speculated as well, for instance, the possibility of the CoTPP molecule being docked over a Cu_2N defective site, such as an N vacancy, however, few of these defective sites were observed in the experiments. Cobalt hybridization to metallic tip could also be discussed, but is rather unlikely. The bias dependence should be also discussed, once slight energy shifts are expected between calculated DOS and measured STS. Figure S7 presents STM images obtained at different biases. Notice that the image obtained at 2.0 V agrees better to the simulated one with a bias of 1.2 eV, in comparison to the image measured at 1.0 V.

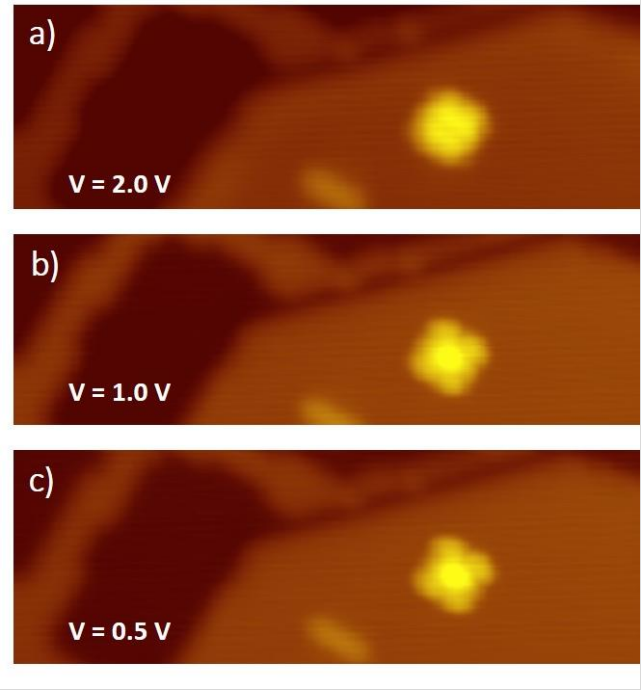

Figure S7: STM images obtained for CoTPP on Cu_2N at different potential values V= 2.0 V, 1.0V, 0.5 and current i = 80 pA.

Another point to discuss is the slight differences in relative DOS amplitude when comparing theoretical predictions and STS experimental measurements. These differences could be related to the decay of the orbital wave function to the vacuum, which might be different for the carbon macrocycle and the cobalt center. The decay length of the wave function changes the tip-molecule hybridization and could reduce the conductance of some orbitals. Additionally, the presence of small peaks close to Fermi energy and between -0.5 eV and 0.5 eV seen in Figure 2(a) can be related to orbitals weakly binding the molecule to the substrate surface.

CoTPP molecule on Cu_2N/Cu(100): Calculated Vibrational States

The calculations have shown 375 normal modes for the system, which involve atomic displacements of both CoTPP and Cu_2N monolayer. Among those 375, 147 are exclusive of the molecule. Figure S6 shows a representation of a few of the vibrational modes found in our theoretical results.

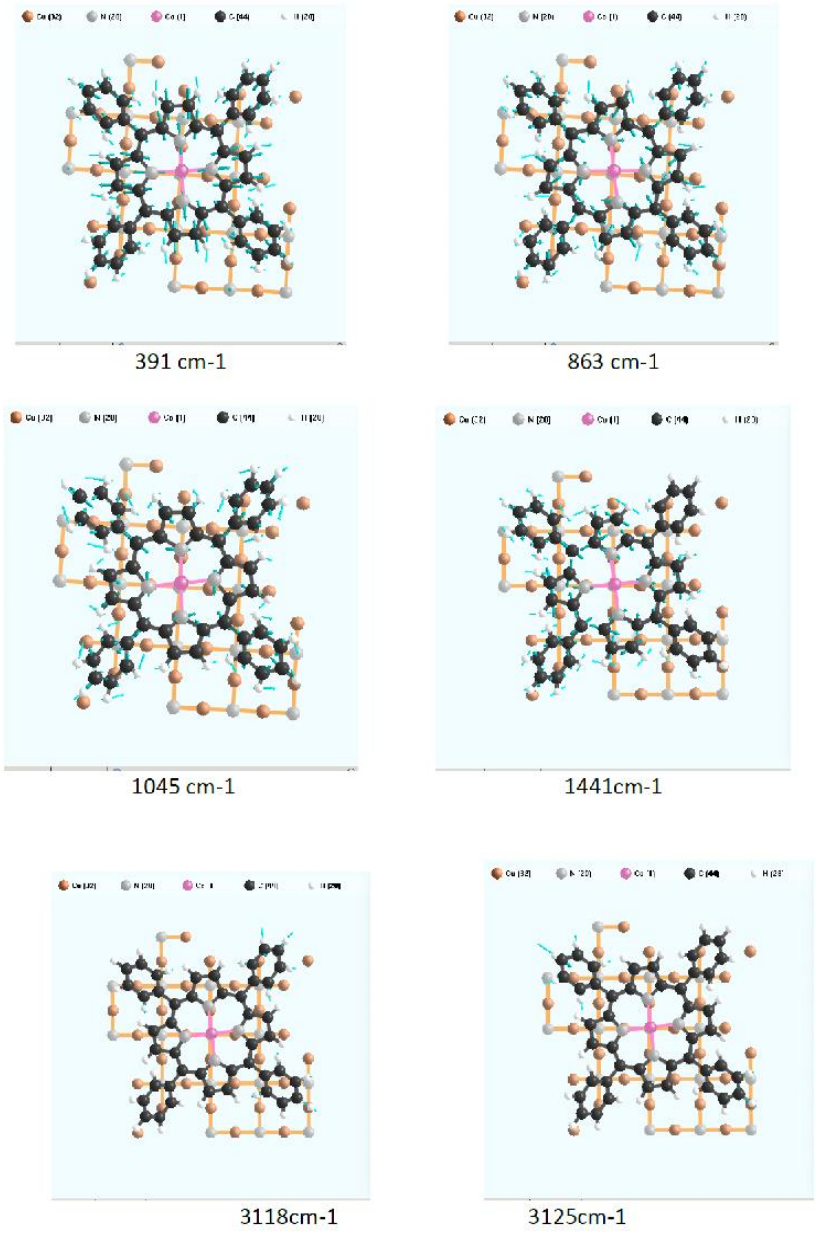

Figure S8. Eigenvectors for selected phonons for CoTPP molecules deposited on Cu_2N-Cu(100).

CoTPP molecule on Cu_2N/Cu(100): Comparison of Vibrational States

Table S1 shows a comparison of the vibration modes presented in this work (experimental and theoretical results) with data from literature for the Tip-Enhanced Raman Spectroscopy.

Experimental (cm^{-1})	Calculated (cm^{-1})	TERS (cm^{-1}) [ref. 35]	TERS (cm^{-1}) [ref. 55]
742	391	388	621
903	863	982	880
1508	1045	1568	1001
1613	1441		1466
			1550
			1592

Table S1: Comparison of vibrational modes found in this work (experimental and theoretical data) with results from literature.

[35] Crampton, K. T.; Lee, J.; Apkarian, V. A., Ion-Selective, Atom-Resolved Imaging of a 2D Cu_2N Insulator: Field and Current Driven Tip-Enhanced Raman Spectromicroscopy Using a Molecule-Terminated Tip. *ACS nano* **2019,** *13* (6), 6363-6371.
[55] Lee, J.; Tallarida, N.; Chen, X.; Liu, P.; Jensen, L.; Apkarian, V. A., Tip-enhanced Raman spectromicroscopy of Co (II)-tetraphenylporphyrin on Au (111): Toward the chemists' microscope. *ACS nano* **2017,** *11* (11), 11466-11474.

CoTPP molecule on the Edge of Cu_2N/Cu(100): Kondo Temperature Estimation

The Kondo Temperature (T_K) value was estimated using the Fano equation shown below [46].

$$\frac{dI}{dV} \propto \rho_0 \frac{\left(q + \frac{E - E_K}{\Gamma}\right)^2}{1 + \left(\frac{E - E_K}{\Gamma}\right)^2} \qquad \text{(Equation 1)}$$

As the width has a dependence on temperature, it is possible to estimate T_K with

$$2\Gamma = \sqrt{(\alpha k_B T)^2 + 2(k_B T_K)^2} \qquad \text{(Equation 2)}$$

where q is the Fano parameter; E_K is the energy of resonance; Γ is half-width at the half maximum of the resonance of the Kondo peak; ρ_0 and α are constant.

Figure S7 presents the experimental dI/dV measurement (black curve) with the Fano fitting (red curve). The fitting parameters are presented in Table 2.

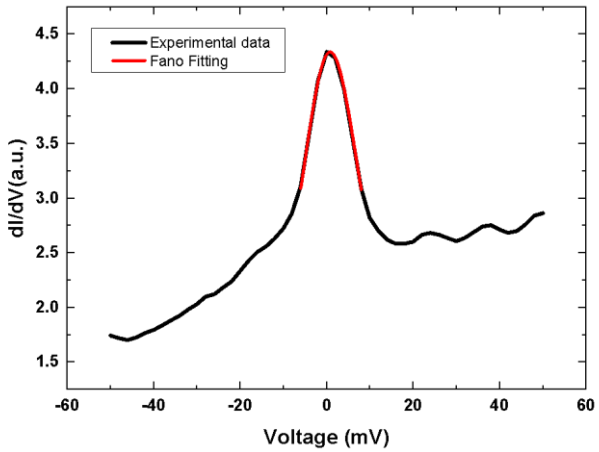

Figure S9: Fit of a Fano line shape (eq. 1) to the experimental data.

Fano Fitting		
Reduced Chi-Sqr 7.58263E-4		
Adj. R-Square 0.99691		
Parameters	**Value**	**Standard Error**
q	24.93895	19.68847
E_K	3.6703E-4	4.36646E-4
Γ	0.01092	1.45095E-4
ρ_0	0.00696	0.011

Table S2: Fitting Parameters