Supporting Information

Adsorption Conformation and Lateral Registry of Cobalt Porphine on Cu(111)

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S0 – Geometric factor in XSW

The coherent fraction f_{co}^{111} can be expressed as a product of the ordered fraction (C), a geometric factor (a_{111}) and the Debye-Waller factor (D-WF) such that:

$$f_{co}^{111} = C \cdot a_{111} \cdot \text{D-WF}, \tag{1}$$

which model, respectively, the level of order, the static geometric distribution, and the dynamic geometric distribution of the atomic species under investigation.[1]

Taken that the molecular coverage was low (~20%) during our experiments and the STM images suggest a unique, well-defined adsorption configuration for the Co-P molecules, the ordered fraction C is assumed to be ~0.90, the coherent fraction of the Co $2p_{3/2}$ core level.

The Debye-Waller factor D-WF $\leq$ 1 takes into account thermal vibrations. In the harmonic approximation, it is defined as

$$\text{D-WF} = exp(-(q^2 \langle u^2 \rangle)/3), \tag{2}$$

where q is the scattering vector:

$$q = \frac{2\pi}{d_{111}} . \tag{3}$$

Here, $\langle u^2 \rangle$ is the mean-square vibrational amplitude of the considered atom and d_{111} denotes the spacing of the used diffraction planes.[2]

S1 – XSW triangulation measurement

XSW allows to determine the lateral atomic registry via real-space triangulation.[1] In the case of an fcc (111) surface, a set of two experiments at both the (111) and the $(1\bar{1}1)$ Bragg reflections are needed in order to distinguish the high-symmetry adsorption sites of the surface. The obtained layer spacings p^{111} and $p^{1\bar{1}1}$ can then be used to determine the lateral atomic position. In case the adsorbed atom occupies the bridge site, the relationship between the two layer spacings is given by[1]

$$p^{1\bar{1}1} = \frac{p^{111}}{3} + \frac{1}{2},$$

(4)

taking into account the three distinct bridge sites. The same layer spacing relationship is obtained for an adsorbed atom equally populating fcc and hcp hollow sites.[1]
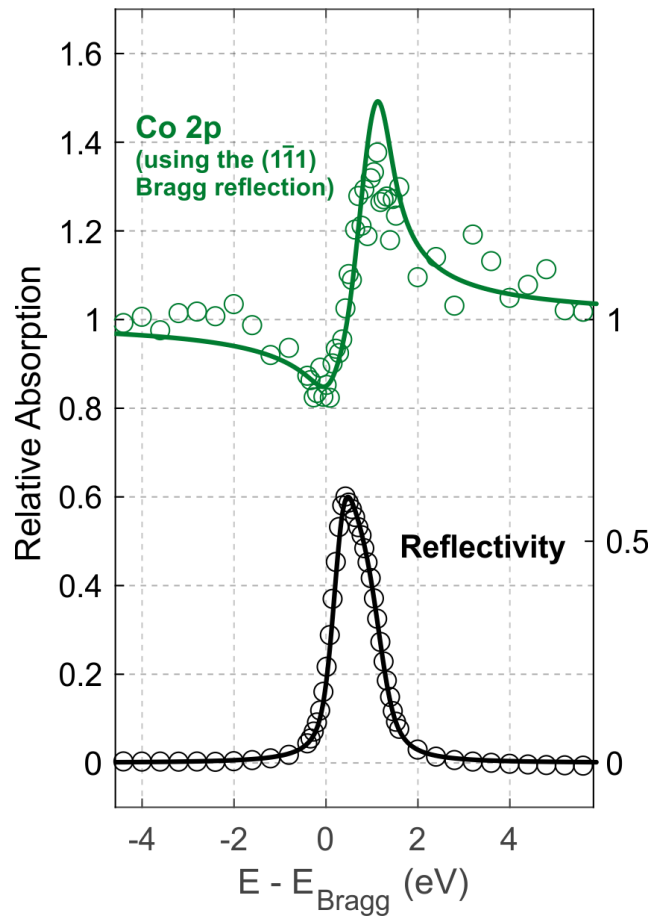

Figure S1 – Normal-incidence XSW absorption profile for Co $2p_{3/2}$ of a sub-monolayer of Co-P on Cu(111) using the $(1\bar{1}1)$ Bragg reflection. A Debye-Waller factor of 0.95 is included in the XSW fit to account for the thermal vibrations of the substrate at room temperature. The solid green line denotes the fit to the data. Black data points represent the reflectivity curve.

S2 – XSW triangulation calculations
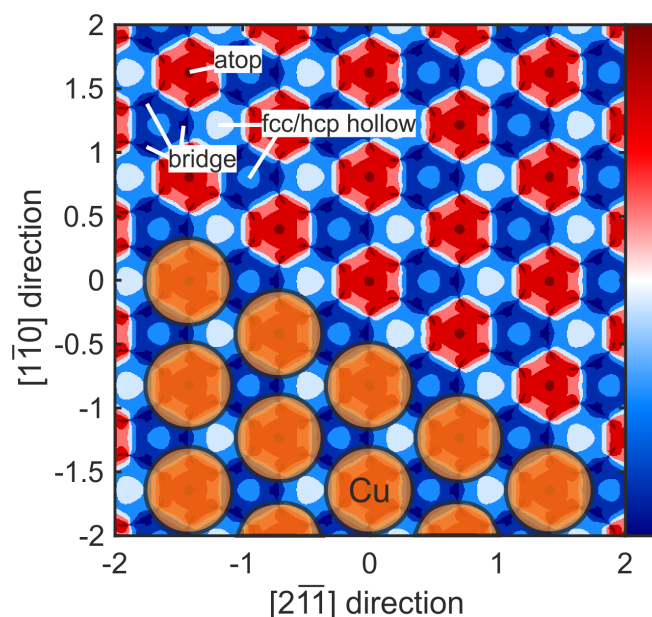
Figure S2 – XSW triangulation calculation by refinement assuming a single site adsorption model. The map shows a cut above the surface that corresponds to the adsorption height of the cobalt atom in the (111) direction. The color indicates the minimum difference between the theoretically expected coherent position in the $(1\bar{1}1)$ direction and the experimentally determined coherent position $p^{1\bar{1}1}$. The (0,0) position (and thus, all dark red spots) corresponds to a direct atop site, indicated by the superimposed model of the Cu substrate lattice (orange). The best fit, *i.e.* a minimum (colored dark blue) is obtained for a (slightly) off-bridge site.

S3 – Tip-induced rotation of a Co-P molecule
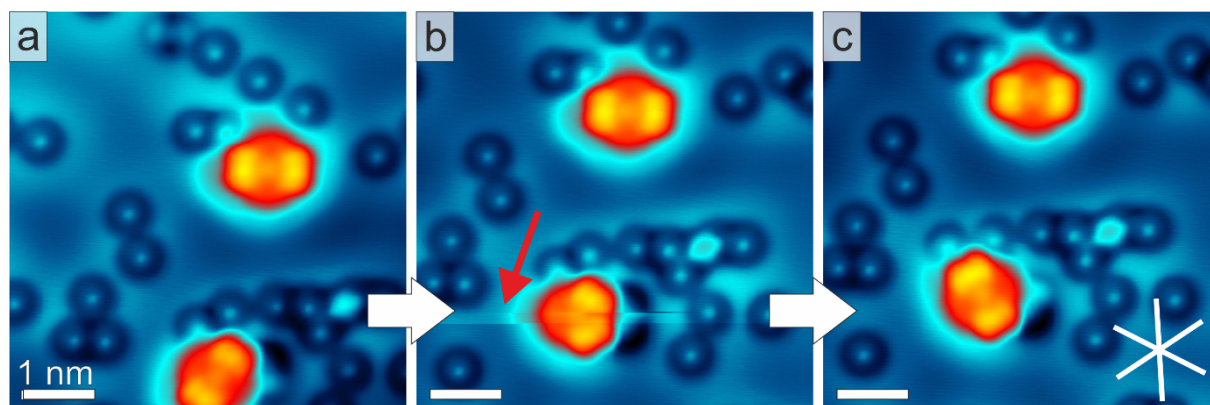
Figure S3 – (a)-(c) Series of STM images that display the rotation of an individual Co-P molecule and its alignment with respect to the high-symmetry directions of the Cu(111) crystal. During the scan of the image shown in (b), the bottom molecule rotates by 60°

(indicated by the red arrow). The short axis of all the molecules is aligned with one principal $\langle 1\bar{1}0 \rangle$ direction of the crystal. Scan parameters of all images: U_b = 0.5 V, I_t = 900 pA.

## S4 – STM voltage series of an individual Co-P molecule
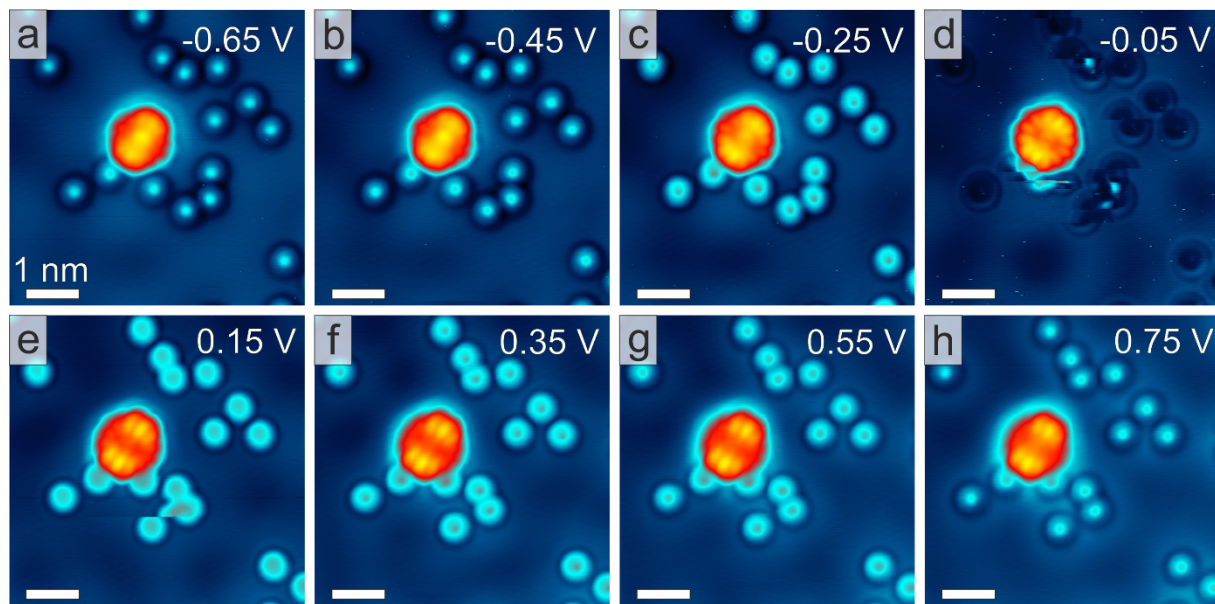
Figure S4 – (a)-(h) STM voltage series of a single Co-P molecule on Cu(111) (imaged orange) coadsorbed with several CO molecules (light blue). Current set point of all images: I_t = 800 pA.

S5 – Co-P molecules imaged with different tips
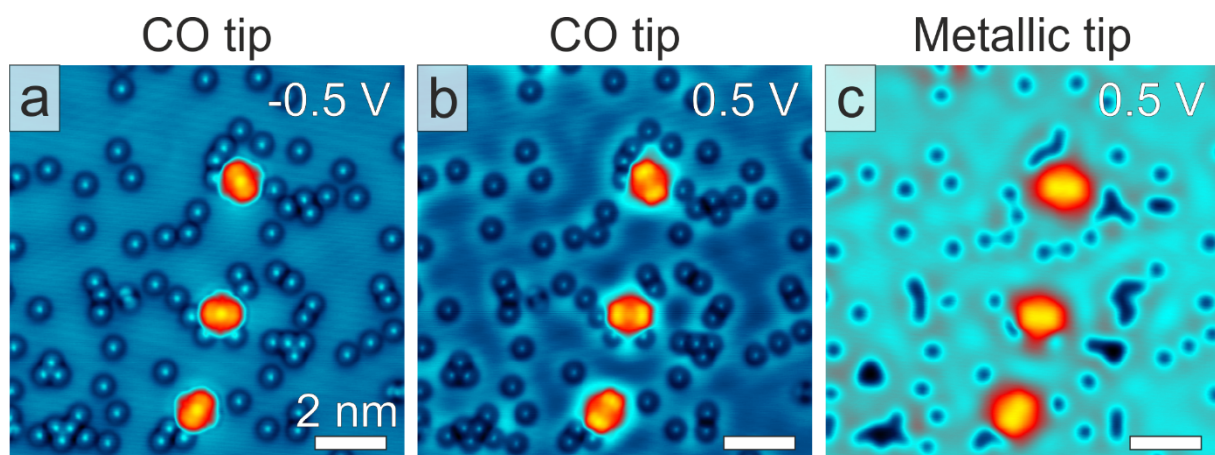
Figure S5 – STM images of Co-P molecules with three distinct orientations on Cu(111) imaged with (a) a CO-terminated tip at negative bias, (b) a CO-terminated tip at positive bias, and (c) a metallic tip at positive bias. Current set point of all images: I_t = 800 pA.

S6 – Structural Conformation of 90° rotated adsorption geometry
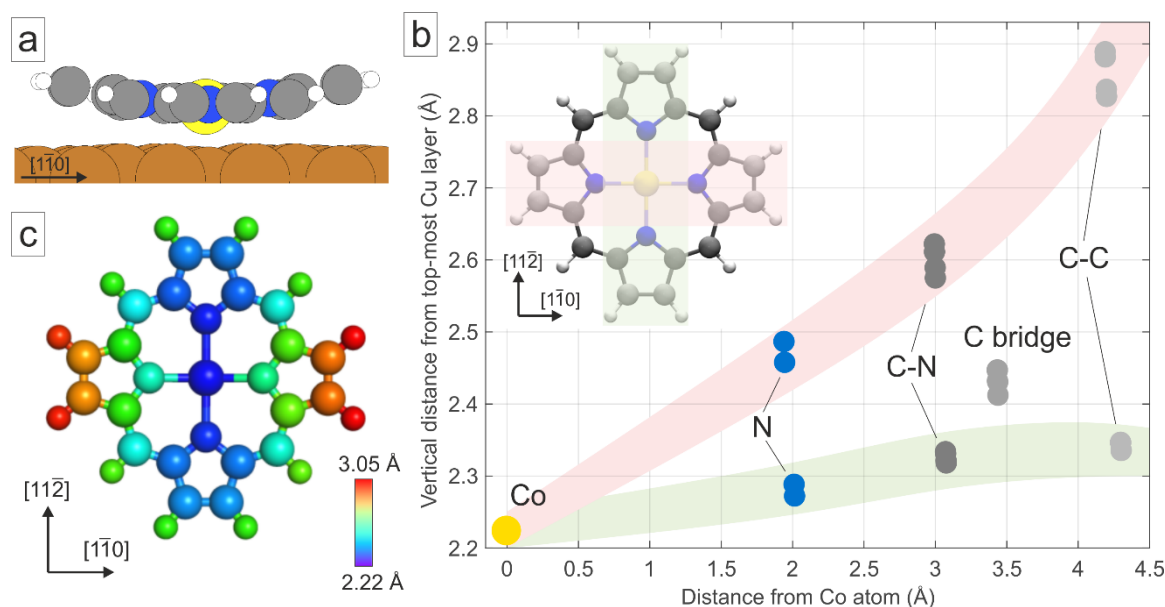
Figure S6 – Structural conformation of the 90° rotated adsorption geometry predicted by the DFT calculations to be stable but energetically less favorable (adsorption energy: -4.725 eV, 0.072 eV higher in energy) than the structure shown in Fig. 4 in the manuscript. (a) Side-view showing the porphine macrocycle being bent upwards along the $[1\bar{1}0]$ direction. (b) Plot of the vertical heights of the atoms in the Co-P molecule with respect to the mean top layer of Cu(111). Clearly, two axis (shaded red and green) can be identified. (c) Color-coded plot showing the vertical height of each atom in the 90° rotated Co-P with respect to the mean top layer of Cu(111).

References

(1) Woodruff, D. P. Surface Structure Determination Using X-ray Standing Waves. *Rep. Prog. Phys.* **2005**, *68*, 743–798.

(2) *The X-Ray Standing Wave Technique: Principles and Applications;* Zegenhagen, J.; Kazimirov, A., Eds.; Series on Synchrotron Radiation Techniques and Applications 7; World Scientific: Singapore, 2013.