Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information:

Surface-orientation- and ligand-dependent quenching of the spin magnetic moment of Co porphyrins adsorbed on Cu substrates

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I. TRACKING THE RING-CLOSURE REACTION FROM CoOEP TO CoTBP BY SCANNING TUNNELING MICROSCOPY

CoOEP molecules were deposited onto the clean Cu(100) surface held at a temperature of 300 K. The sample was subsequently cooled down and transferred into the scanning tunneling microscope (STM). STM measurements were carried out at 4.6 K in a home-built set-up. An STM image of the as-prepared sample is shown in Fig. S1a. The molecules are identified by their clover shape, with the ethyl groups exhibiting a larger apparent height than the Co center (see inset). Almost all molecules are found in the same orientation with respect to the substrate. This indicates that the adsorption configuration, and in particular the orientation of the molecules, is steered by molecule-substrate interactions.

Annealing this sample to 470 K results in a strong modification of the molecules (Fig. S1c). They appear flatter and without any structure within the organic ligand. The shape resembles that of FeTBP molecules on a Au(111) surface.[1] In that case, a temperature-induced electrocyclic ring-closure reaction of the ethyl moieties led to the formation of the benzoporphyrin macrocycle. The CoTBP molecules on Cu(100) seem randomly distributed on the surface without island or cluster formation. The separation of the CoTBP molecules hints at an electrostatic repulsion due to charge on the molecules.

Deposition of CoOEP on a Cu(111) surface at 320 K leads to a planar adsorption with similar molecular shapes as on Cu(100) (Fig. S1b). The molecules stay isolated on the clean copper terraces. Only the step egdes provide nucleation centers for the molecules. Annealing the molecules to 490 K on the Cu(111) surface (Fig. S1d) results in a similar molecular appearance as on Cu(100) or Au(111), suggesting the formation of CoTBP.

The STM images therefore clearly reveal the catalytically activated electrocyclic ring-closure reaction of CoOEP to CoTBP on both Cu surfaces. The separation of the molecules hints at charged species.

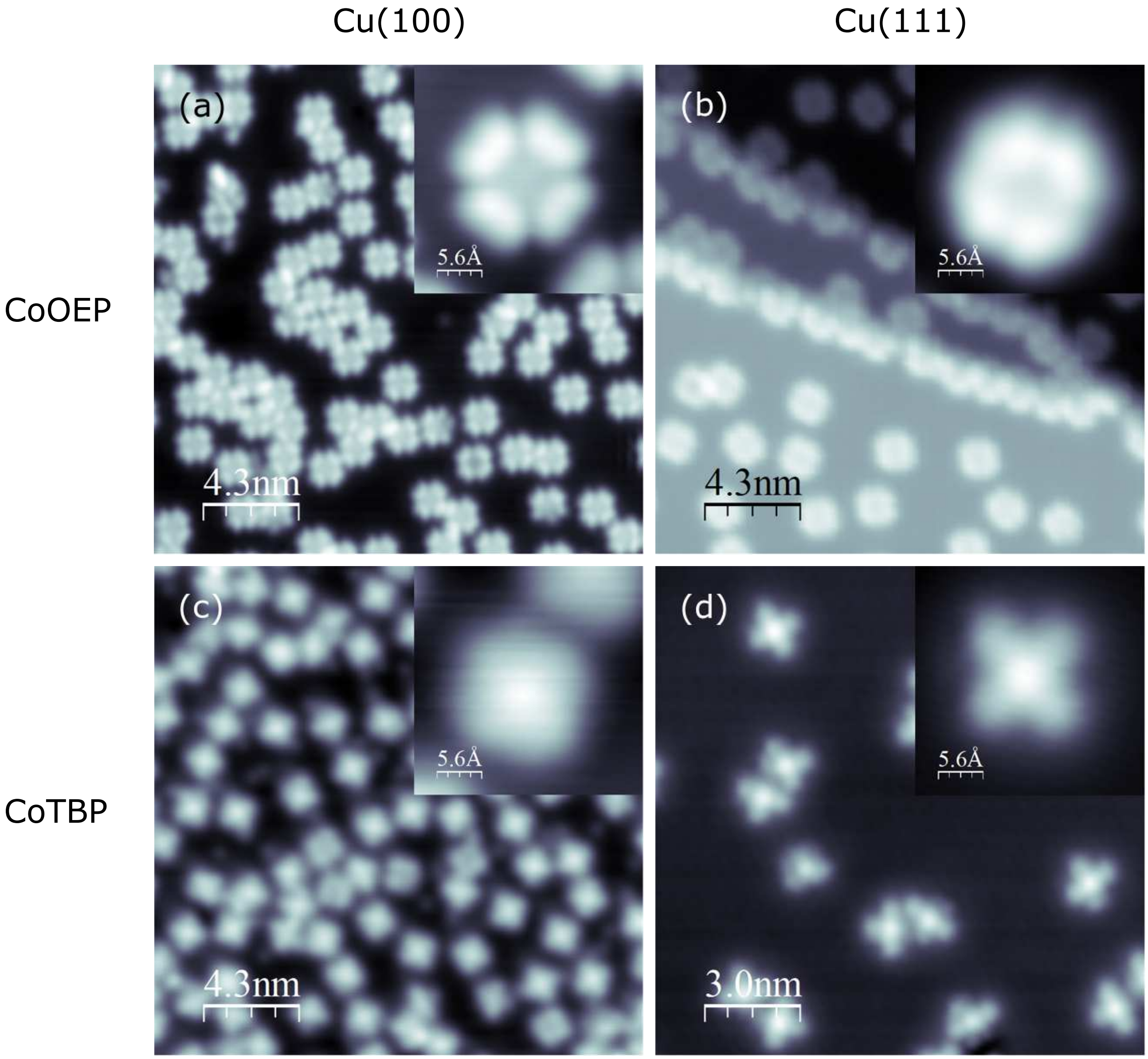


Fig. S1 STM images of the CoOEP molecules deposited on Cu(100) ((a); main image: $U = 500\,\mathrm{mV}$, $I = 100\,\mathrm{pA}$; inset: $U = 50\,\mathrm{mV}$, $I = 200\,\mathrm{pA}$; $T = 1.1\,\mathrm{K}$) and Cu(111) ((b), main image and inset: $U = 1\,\mathrm{V}$, $I = 100\,\mathrm{pA}$, $T = 4.5\,\mathrm{K}$), and CoTBP molecules on Cu(100) ((c); main image: $U = -50\,\mathrm{mV}$, $I = 100\,\mathrm{pA}$; inset: $U = 50\,\mathrm{mV}$, $I = 100\,\mathrm{pA}$; $T = 1.1\,\mathrm{K}$) and Cu(111) ((d); main image: $U = -1\,\mathrm{V}$, $I = 32\,\mathrm{pA}$; inset: $U = -700\,\mathrm{mV}$, $I = 26\,\mathrm{pA}$; $T = 4.5\,\mathrm{K}$).

II. ELECTRONIC STRUCTURE DETERMINATION FROM X-RAY ABSORPTION SPECTROSCOPY

The nitrogen K edge x-ray absorption (XA) spectra are shown in Fig. S2 for three x-ray incidence geometries on both substrates before and after the ring-closure reaction. The characteristic reduction in intensity of the second main peak of the π^* orbitals region, around 402 eV, is the confirmation that the ring closure has taken place. This was verified[2] in N K edge x-ray absorption spectroscopy (XAS) studies of an iron porphyrin that was confirmed to undergo the ring closure reaction with STM[1,3] as mentioned in the main text. It is clear, however, that the behavior of the first main peak of this region, at 399 eV, is very different on the two substrates. While the molecules deposited on Cu(100) show a significant increase in the intensity of this peak after ring closure, the molecules on Cu(111) display almost no change. This becomes clear when the total integrated intensity for the magic angle of incidence is taken: there is a 14% increase for the molecules deposited on Cu(100) after ring closure, and a 13% decrease for the ones deposited on Cu(111), when the loss of intensity of the second main peak is not counteracted by an intensity increase of the first one.

There are still some peaks visible in the π^* orbitals region of the vertical polarization spectra in Fig. S2. This usually indicates non-planarity of the molecule or a tilted adsorption to the substrate. While porphyrin molecules tend to adsorb flat on most substrates, buckled macrocycles have been observed, usually when the ligands undergo steric hindrance when adsorbed on the surface. In that case, these peaks would indicate that the molecule is adsorbing in a slight saddle-shape geometry or that the cobalt ion is being pushed out of the molecular plane, which indicates a strong interaction with the substrate. Such strong interaction is expected from the hybridization of the ion's orbitals observed upon adsorption. Alternatively, it has been pointed out for similar molecules that such remnant features in vertically polarized and normal incidence spectra might also be associated with a rehybridization of the LUMO states on nitrogen atoms,[4] indicating that the molecules might still lay in a very planar geometry despite the observed π^* orbitals peaks.

The similarities between the nitrogen K edge of both molecules on Cu(111) are repeated in the cobalt $L_{2,3}$ edges as seen in Fig. S3, where the linear polarization Co $L_{2,3}$ XAS of all the systems are displayed. As discussed in the main text for the circular polarization spectra, the similarities between the CoOEP and CoTBP molecules on Cu(111), and to a lesser degree CoTBP on Cu(100), suggest very similar electronic configurations among all those systems. The visible differences of the CoOEP sample on Cu(100) before and after ring closure is an indication of hybridization, charge transfer, or reorganization within the molecular orbitals. The small variation in the integrated intensity for magic angle of incidence across different molecules on the same substrate and the same molecule on different substrates indicates that there is no significant change to the oxidation state of the various systems. The integrated XA intensity of CoOEP on Cu(111) is $(9 \pm 3)\%$ higher than the one of CoOEP on Cu(100). For CoTBP on Cu(111) the integrated intensity is $(12 \pm 3)\%$ lower than on Cu(100), which indicates fractional charge transfer, but not enough for a full change

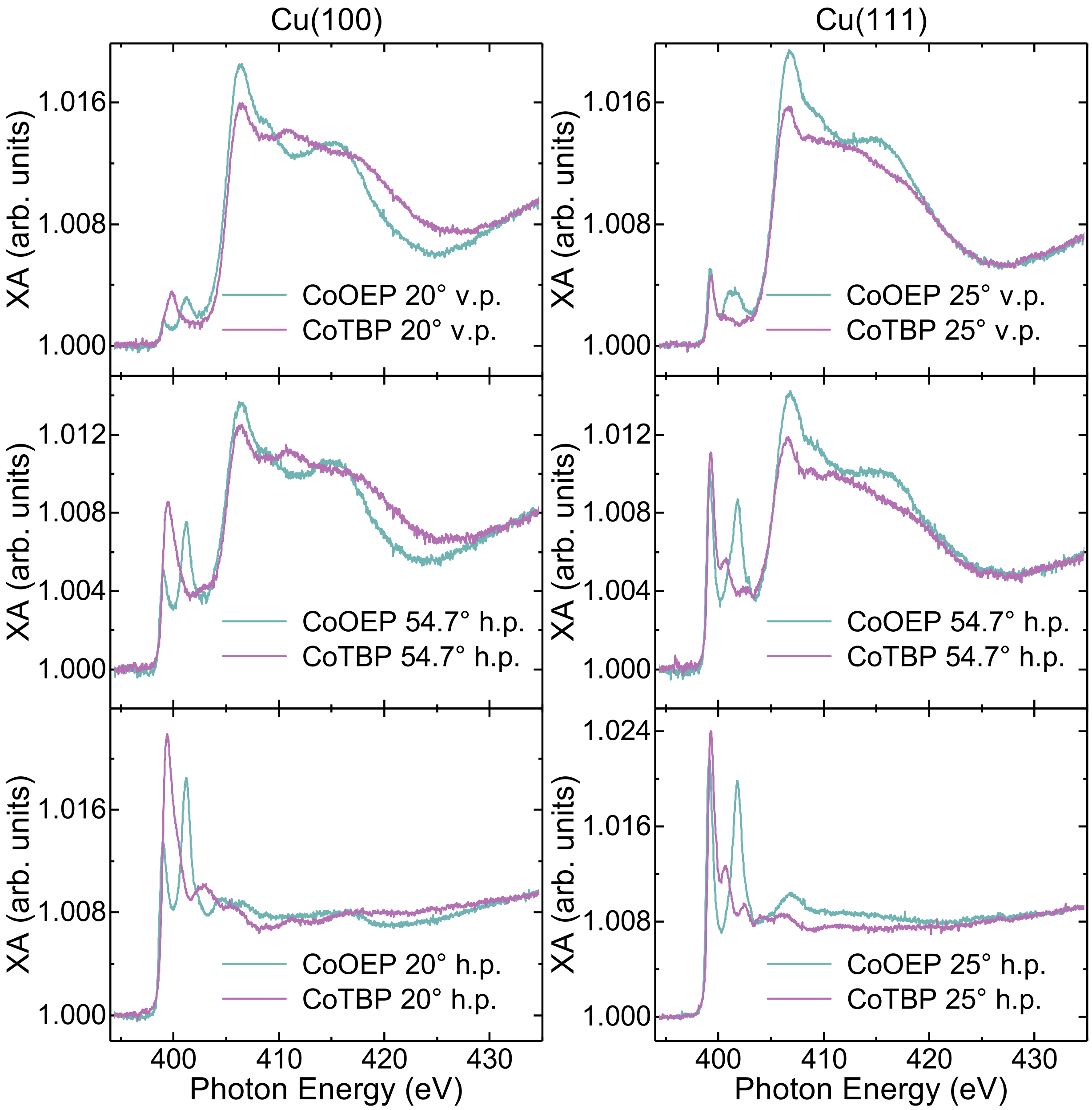


Fig. S2 Nitrogen K edge XAS for horizontal polarization at grazing incidence, magic-angle incidence, and vertical polarization at grazing incidence (from bottom to top), the latter being equivalent to horizontal polarization at normal incidence regarding the probed orbitals, on Cu(100) (left) and Cu(111) (right) before and after ring-closure reaction of the molecules. Measurements at $T = 300\,\mathrm{K}$.

in the oxidation state between the various samples.

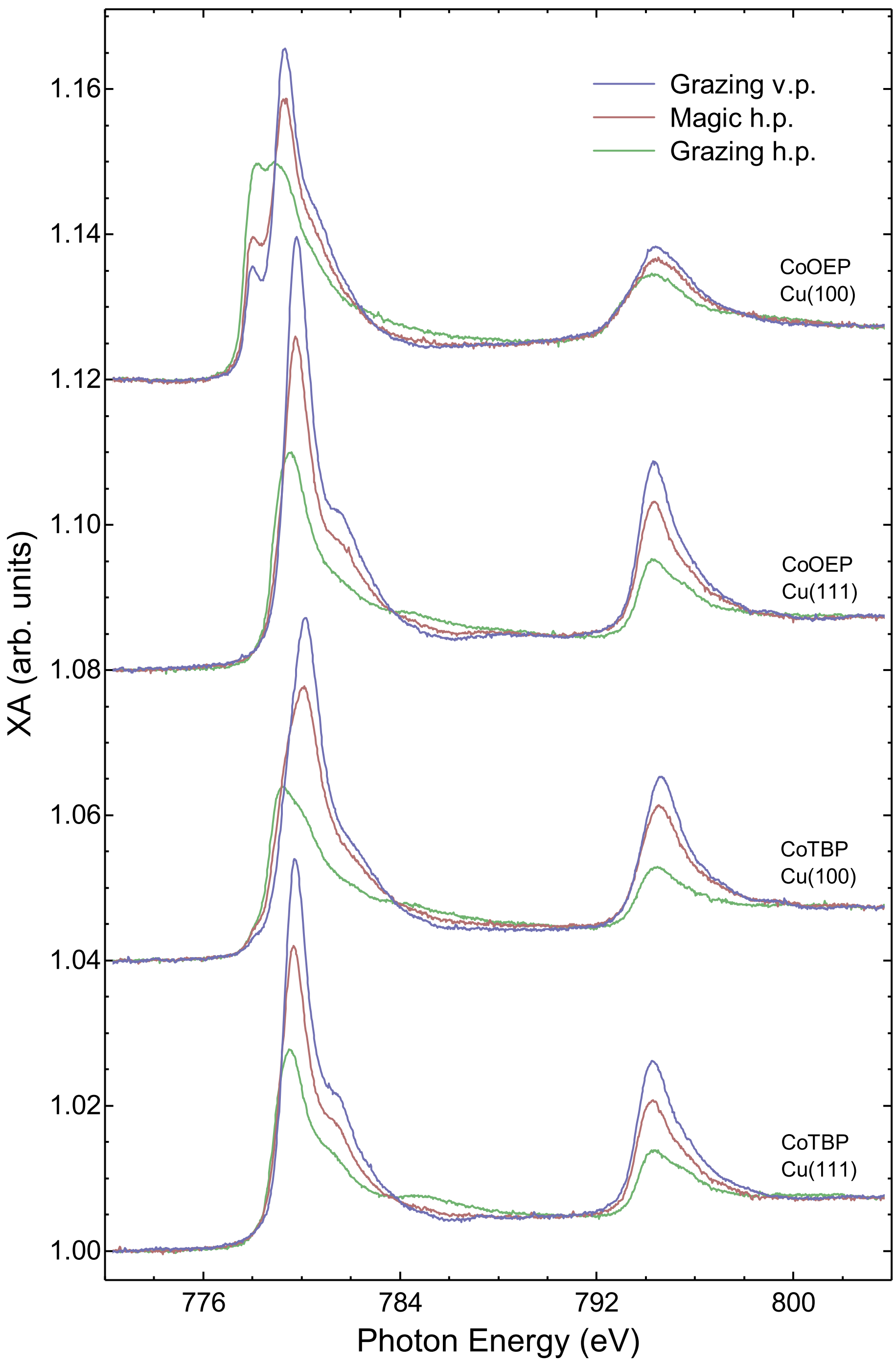


Fig. S3 Co $L_{2,3}$ edge XAS of the CoOEP and CoTBP molecules for vertically polarized grazing and horizontally polarized magic and grazing incidence angles of the x-rays on Cu(100) and Cu(111). For samples on the Cu(100) substrate the grazing angle was 20° from the surface, while on Cu(111) it was 25°. Measurements taken at $T = 300\,\mathrm{K}$.

III. MODELING OF MAGNETIZATION WITH BRILLOUIN FUNCTION

The results of the sum rule analysis shown in Table 1 of the main text enables an estimation of the spin state of the system. Neglecting anisotropy, the expected values for the measured magnetic moment of a paramagnetic system not in magnetic saturation at a given temperature can be obtained from modeling the magnetization with the Brillouin function. In this model we have the unsaturated measured magnetic moment in the direction of the external field given by:[5]

$$\langle m \rangle = gJ\mu_\mathrm{B} B_J(\alpha). \tag{S1}$$

From eq. S1 and the ratio between the spin and the orbital angular momenta obtained from the sum rules, one can obtain the values of $\langle m \rangle$ for an external field of 6 T and temperature of 4.4 K, the conditions in which the measurements were made. Taking $\langle m \rangle = 1.5\,\mu_\mathrm{B}$, from the results displayed in Table 1 for the magic angle and $n_\mathrm{h} = 3$, one obtains $S = 0.85$. This points to a non-integer valence state, as discussed in the main text, evidencing hybridization between the Co ion and the substrate. It is not surprising, considering how reactive the copper substrate is, that it would result in a strong interaction with the molecule, causing hybridization. From the results discussed earlier for the integrated intensity of the cobalt edges, it is inferred that this is also the oxidation state of the cobalt ion of the molecule deposited on Cu(111) and of the CoTBP molecules. An oxidation state of $+2$ would not allow for the spin moment of the ion to be readily quenched by simple charge reorganization due to an increase of the ligand field energy, since this oxidation state results in an odd number of electrons in the valence orbitals of the metal. This attests this value for the oxidation of this sample is not ideal, supporting the non-integer oxidation state discussed in the main text.

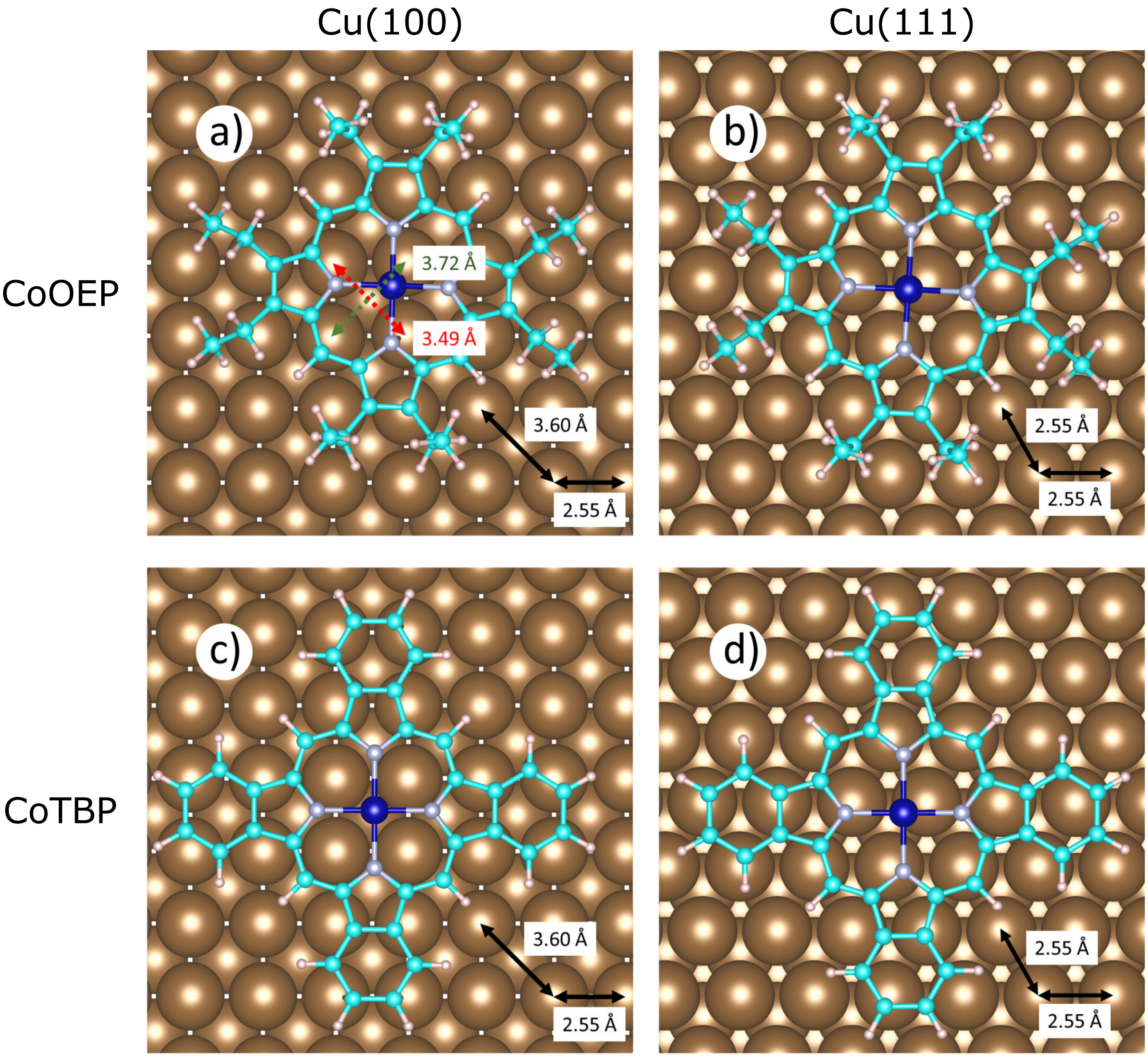


Fig. S4 Adsorption geometry of the CoOEP molecules deposited on Cu(100) (a) and Cu(111) (b), and CoTBP molecules on Cu(100) (c) and Cu(111) (d).

IV. DENSITY FUNCTIONAL THEORY CALCULATIONS

Fig. S4 shows birds-eye's views of the adsorption geometries obtained by the DFT+U calculations for the four systems. The position of the central Co atom with respect to the surface-layer atoms of the substrates slightly differs from each other. On Cu(111), both the CoOEP and CoTBP occupy a very similar adsorption site, between an on-top and a threefold hollow site. On Cu(100), on the other hand, the Co atom of CoTBP sits very close to a perfect fourfold hollow site, while in CoOEP it is found in between the on-top, the fourfold hollow, and the bridge site. It has also been realized that first-layer Cu atoms of the Cu(001) substrate under the CoOEP are displaced from their bulk positions by up to about 3%, see Fig. S4 (a), much more compared to the Cu(111) atoms underneath the CoOEP. This is due to the different arrangement of the surface-layer Cu atoms in the two substrates. On the (111) surface, atoms are laterally confined in a close-packed configuration with trigonal symmetry. On Cu(001), in contrast, surface atoms are arranged in a square lattice, in which Cu atoms can more easily undergo further lateral displacement due to the interaction with CoOEP.

We find a charge transfer from the Cu substrates to the molecules in all four systems, as listed in Table S1. It is smallest in the case of CoOEP/Cu(111), the only molecule–substrate system for which the calculations yield an unquenched magnetic moment. Table S2 presents the 3d orbital population of CoOEP and CoTBP as free molecules, as well as adsorbed on the Cu(100) and Cu(111) substrates, calculated by integrating the m_l-resolved density of states (DOS) up to the Fermi level. The population analysis indeed reflects that the lone 3d unpaired electron of Co in the free CoOEP and CoTBP molecules resides in the d_{z^2} orbital. This results in the total magnetic moments being 0.86 and 0.93 μ_B for CoOEP and CoTBP, respectively (see Table S3 below).

Table S1 Calculated charge transfer from the Cu substrates to the CoOEP and CoTBP molecules in electrons, obtained from a Bader charge analysis.

System	Charge transfer
CoOEP/Cu(100)	0.31
CoOEP/Cu(111)	0.16
CoTBP/Cu(100)	0.43
CoTBP/Cu(111)	0.34

The 3d spin moments of the Co atoms as well as total spin moments are tabulated for all systems in Table S3. The total moments are always found to be smaller than the 3d-moments because of the strong opposite spin polarizations on the N atoms bonded to the central Co atom. The orbital populations tabulated in Table S2 were extracted by integrating the d_{ml}-projected DOS up to the Fermi level, however, the atomic and total spin moments in Table S3 were obtained from the Kohn-Sham density/wavefunction projected onto the atomic orbitals. Thus the former one is an indirect approach, while the latter systematically evaluates the total 3d-orbital occupations and spin moments. The numbers obtained from these two approaches differ slightly from each other, but keeping the features of the electronic structure intact.

The computed DOS obtained from DFT+U calculations for the free CoOEP molecule as well as

Table S2 Calculated $3d$ orbital populations of CoOEP and CoTBP single molecules as well as adsorbed on Cu(100) and Cu(111) substrates. The first number in each cell gives the total orbital electron occupation, whereas the number in brackets gives the spin-majority electron occupation. The latter is given only when minority and majority spin populations are unequal for the considered orbital.

System	d_{xy}	d_{xz}	d_{yz}	d_{z^2}	$d_{x^2-y^2}$	Total
CoOEP	1.84	1.84	1.84	0.92 (0.92)	0.72	7.18
CoOEP/Cu(100)	1.88	1.76	1.76	1.44	0.64	7.46
CoOEP/Cu(111)	1.86	1.82	1.88	1.13 (0.92)	0.63 (0.35)	7.32
CoTBP	1.84	1.84	1.84	0.97 (0.93)	0.78	7.27
CoTBP/Cu(100)	1.84	1.66	1.66	1.44	0.58	7.18
CoTBP/Cu(111)	1.92	1.72	1.76	1.56	0.60	7.56

Table S3 The DFT+U computed $3d$ magnetic moments on the central Co atoms as well as the total moment of the free Co-porphyrin molecules or molecule-substrate systems.

System	$3d$ [μ_B]	Total [μ_B]
CoOEP	0.98	0.86
CoOEP/Cu(100)	0.00	0.00
CoOEP/Cu(111)	0.68	0.35
CoTBP	1.00	0.93
CoTBP/Cu(100)	0.00	0.00
CoTBP/Cu(111)	0.00	0.00

deposited on Cu(100) and Cu(111) are presented in Fig. S5. The electronic configuration of free CoOEP is well in line with the understanding that the unpaired electron responsible for the ground spin state resides in the d_{z^2} orbital; this could be confirmed from the empty spin-minority orbital's peak for d_{z^2} and two empty orbital's peaks for $d_{x^2-y^2}$ as shown in Fig. S5 (a). The m_l-resolved DOS peaks are quite sharp for the free molecule, which indicates the pure $3d$ orbital characteristic without strong atomic orbitals' hybridizations.

Once the CoOEP is deposited on the different Cu substrates, the above-mentioned free molecular DOS features change drastically, see Figs. S5 (b) and (c). Here we observe an almost non-magnetic DOS, i.e. with vanishing exchange splittings for CoOEP/Cu(100). Like CoTBP/Cu(100) and CoTBP/Cu(111) (see main text), the spin moments on the Co atom vanish due to charge transfer to the d_{z^2} orbital. This charge transfer is not the mere compensation of the spin moment in the d_{z^2} orbital, but it causes a fundamental change in the Co atomic centers that turns off the exchange

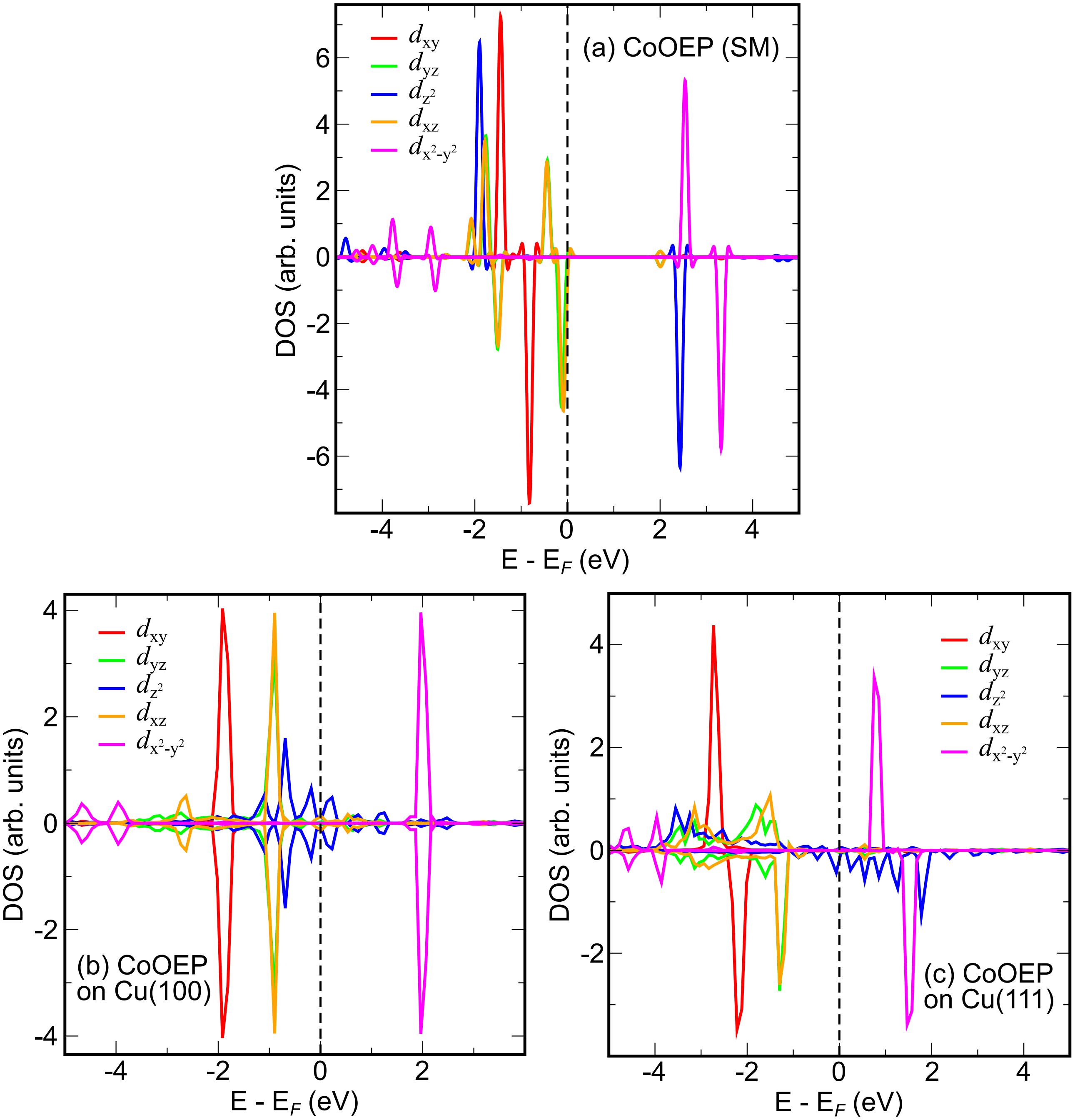


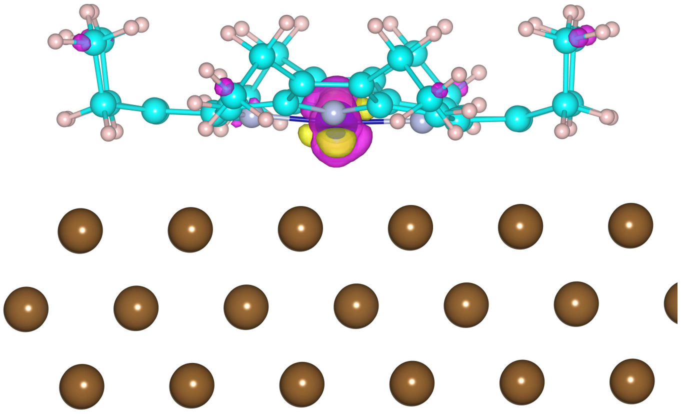
Fig. S5 Calculated orbital-resolved *d* DOS of the free CoOEP molecule (a); CoOEP deposited on Cu(100) (b), and CoOEP deposited on Cu(111) (c).

splittings and modifies the m_l-resolved DOS for the Co atom that is hence featured as non-magnetic center. In the case of CoOEP deposited on Cu(111), a different scenario prevails, i.e., a completely filled majority d_{z^2} orbital and a partially filled minority spin d_{z^2} orbital coexist. This imbalance of minority and majority spin populations in the d_{z^2} orbital does not turn off the exchange splittings of the 3*d* orbitals and results in the reduced magnetic moment.

As discussed in the main text, the observations for CoOEP/Cu(100) and CoOEP/Cu(111) do not match the experimental observations: In experiment, the Co magnetic moment is unquenched in CoOEP/Cu(100) and quenched in CoOEP/Cu(111), while our calculations yield the reverse. However, understanding gained for the quenching and reduced magnetizations is consistent with electron transfer to the Co d_{z^2} orbital, triggered by the presence of the substrate. If the electron transfer to the Co d_{z^2} orbital is below a critical level, it will reduce the magnetic moment without causing harm to the exchange splitting of the m_l-resolved d orbitals, otherwise it will turn off the exchange splitting completely, resulting in a non-magnetic atom. The substrate-molecule interactions thus play a crucial role in the transfer of the right amount of spin to the d_{z^2} orbital of Co and modifying its electronic structure and the interaction of the molecule with the substrate.

The spin-density plots for the CoOEP molecule deposited on the Cu(100) and Cu(111) substrates are shown in Fig. S6. The charge transfer from the Cu(100) substrate to the molecule leads to non-magnetic CoOEP, the spin density on the molecules are found to be extremely small. For better visualization, the isosurface value for the spin density is chosen as low as 1×10^{-7} μ_B/Å^3 in this case. For a better visual representation of CoOEP/Cu(111), an isosurface value of 1×10^{-3} μ_B/Å^3 is chosen, as it has a comparatively large spin polarization.

(a) CoOEP/Cu(100)



(b) CoOEP/Cu(111)

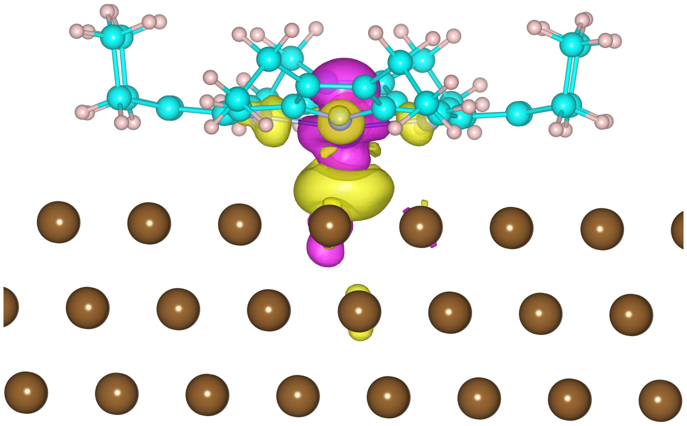


Fig. S6 Calculated spin density plot of the CoOEP molecule deposited on Cu(100) (a), and deposited on the Cu(111) substrate (b). The isosurface values are given in the text.

NOTES AND REFERENCES

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