Supporting Information

Cis-dicarbonyl binding at cobalt and iron porphyrins with saddle-shape conformation

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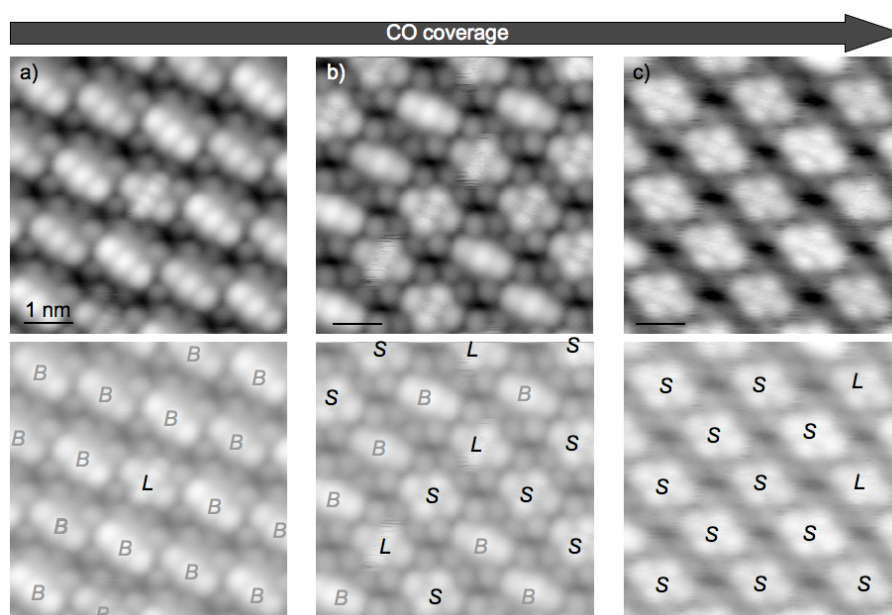
1. Coverage dependence

Fig. S1: CO coverage on CoTPP arrays with increasing CO dose: The sequence of topographic STM images from a) to c) illustrates the transition from a nearly bare CoTPP array to essentially full CO saturation. The averaged coverage increases from 0.06 CO per CoTPP in a) to 1.06 in b) and 1.85 in c). To facilitate the identification of the three species, i.e. CoTPP, CO/CoTPP and $(CO)_2$/CoTPP, the bottom panels include labels for every molecule. *B* stands for bare CoTPP, *L* for a labile cross (CO/CoTPP) and *S* for the static cross $((CO)_2$/CoTPP) (a: V=-666mV, I=0.11nA; b: V=-590mV, I=30pA; c: V=-609mV, I=0.43pA).

2. Charge analysis of CoTPP on Cu(111) exposed to CO

The charge state of the Co cation is of interest to understand the chemistry of CoTPP on Cu(111). Here we further explore the results of Fig.4 by considering the electronic configuration of the Co cation of the different species studied in the present work.

Before studying the case of CoTPP on Cu(111) let us briefly review the existing data on gas-phase CoTPP and CoTPP(CO)$_2$ where two apical CO's are added, from Ref. 1. Figure S2 gives a schematic account of selected energy levels of these gas-phase molecules[1]. Free CoTPP presents a Co (II) cation due to the effect of the TPP ligands. The ligand field splits the d-electron manifold leading to a singly occupied a_{1g} molecular orbital originating in the d_z^2 Co orbital[1]. The LUMO is a ligand π-orbital, the doubly degenerated $2e_g$, and just above in energy, there is the planar b_{1g} orbital that is basically the $d_{x^2-y^2}$ atomic orbital.

When two CO are apically adsorbed[1] the d_{xz} and d_{yz} orbitals are stabilized and decrease their energy. At the same time, the a_{1g} increases in energy which facilitates oxidation to Co(III). However, the b_{1g} states reduces its energy and in presence of an electron donor can be populated. Nevertheless, reduction of CoTPP would actually take place through the population of the LUMO's $2e_g$, which also diminish their energy. The large perturbation of CO adsorption on the molecule complicates the extrapolation of these gas-phase results into the chemisorbed configuration. One further complication comes from the geometry itself, that is not apical contrary to what the theoretical modeling of Ref. 1 assumed.

When chemisorbed, the molecule undergoes sizable charge transfer from the metal substrate. Experimentally, there is important evidence of the reduction of the cation after CoTPP chemisorption. When adsorbed on Ag(111)[2], Co reduces but a definite assignment to a Co(0) state is not possible because the XPS spectrum has final state effects that contribute and are difficult to account for[2].

Adsorption on Cu (111) is likely different from the Ag (111) case, but charge transfer from the surface should be large and a reduced Co state is to be expected. In order to elucidate the cation state, we have completed the previous LDA calculations with LDA+U calculations in the scheme by Dudarev and co-workers[3]. These calculations[4] show that LDA suffices to account for the cation charge state and the adsorption properties of CoTPP on Cu (111). The effect of introducing an extra charging energy U in the LDA+U method leads in the present case to a level shift of less than 0.5 eV for the occupied orbitals towards negative energies, permitting us to have a clearer picture on the actual atomic occupancies. Indeed, the extra U term in the Hamiltonian favors the formation of magnetic solutions, which is fundamental to test the absence of magnetic moment in some LDA solutions.
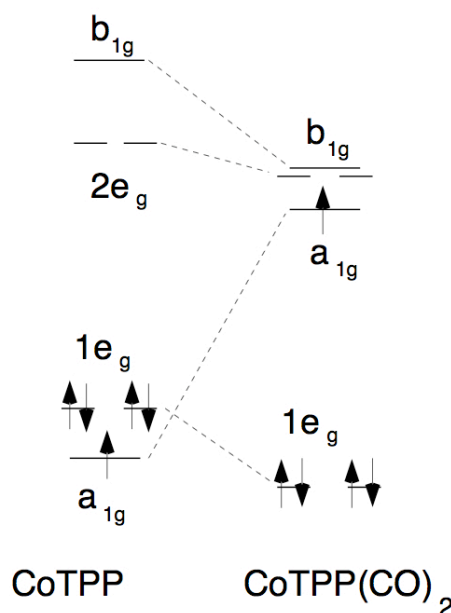

Fig. S2: Selected orbital energy levels for gas-phase CoTPP (left) and CoTPP(CO)$_2$ (right) taken from Ref. 1. The a_{1g} level has a large contribution from the Co d_z^2 atomic level and is singly occupied. The $1e_g$ orbitals correspond to d_{xz} and d_{yz} Co orbitals. The $2e_g$ orbitals are the LUMO of CoTPP and are π-orbitals of the ligands. The b_{1g} orbital has a large contribution from the Co $d_{x^2-y^2}$ orbital. When two apical CO's are adsorbed the a_{1g} level is promoted and the b_{1g} reduces its energy[1].

Figure S3 shows the projected density of states (PDOS) onto the cation d-manifold. Since the molecule is rotated with respect to the unit cell of the calculation, the *x* and *y* axis do not exactly correspond to the molecular ones and certain extra mixing among *d*-orbitals is caused. This is clearly seen in the projection onto the $d_{x^2-y^2}$ that is very mixed with the d_{xy} orbital and give peaks at the same energies. The b_{1g} orbital should then give a peak coincidental with the maxima of the $d_{x^2-y^2}$ and d_{xy} PDOS at high energy. From the upper panel of Fig. S3 we can conclude that the b_{1g} orbital of the chemisorbed molecule stays empty as in the free molecule.

Our LDA+U calculations permit us to be confident about the calculation of the magnetic moment of the cation. We find than when chemisorbed the molecule loses its magnetic moment, revealing the reduction process we mentioned above. However, the reduction process is not enough to populate the b_{1g} state. From these facts, we conclude that the molecule is in a Co(I) oxidation state.

When a CO molecule is added onto the adsorbed CoTPP, the mid panel of Fig. S3 shows the evolution of the cation electronic structure. The first noticeable effect is that the main *d*-electron structure shifts to lower energies. Indeed, Fig. S3 shows the electronic structure associated with
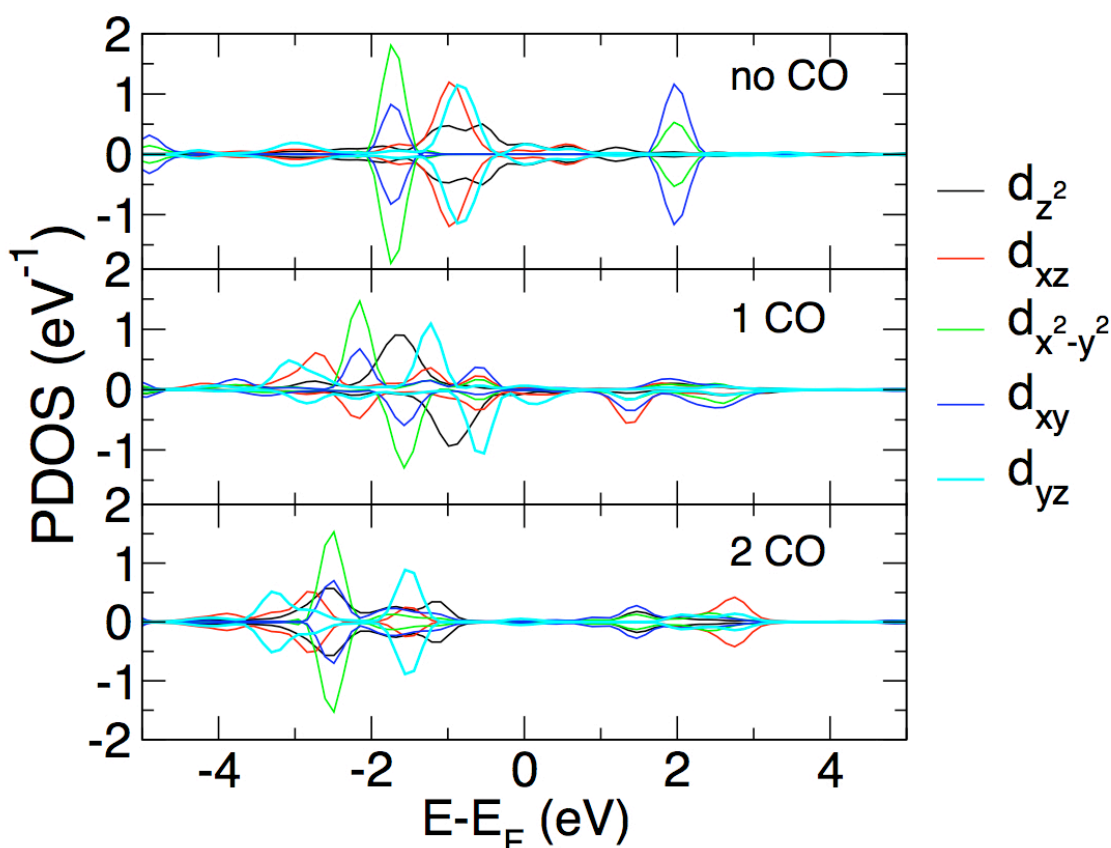
Fig. S3: Projected density of states (PDOS) onto the *d*-manifold of the Co cation for CoTPP chemisorbed on Cu(111) (upper panel), CO adsorbed on CoTPP / Cu (111) (mid panel) and 2 CO's adsorbed on CoTPP / Cu (111) (lower panel). Positive values of the PDOS correspond to majority spin contributions and negative values to minority spin. Only the CO-CoTPP / Cu (111) case shows magnetisation.

the b_{1g} state corresponds to occupied states. There is a substantial donation from the CO molecule.

However, the minority-spin PDOS shifts up in energy, and indeed, one d_{xz} orbital that has one of the largest overlaps with the CO molecule is partially emptied. The molecule is then magnetized by adsorption of one CO molecule. We obtain a magnetic moment of one Bohr magneton which corresponds with the picture of taking one electron away from the *d*-orbitals. This is the back-donation to the CO molecule.

Hence, our study reproduces the donation-back-donation scheme of CO adsorption. Furthermore, a Mulliken charge analysis gives the same charge for the cation in the cases with and without CO. The oxidation state is Co(I) again but with an electronic structure very different from the CoTPP/Cu (111) case.

When a second CO is adsorbed, there is a net donation of charge. The electronic structure shifts to lower energies, see Fig. S3 lower panel.

The Mulliken charges show an increase of half an electron with respect to the previous cases, and there is no trace of magnetisation of the molecule. We conclude that 2CO-CoTPP/Cu (111) is in a Co(0) oxidation state.

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[3] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humprheys and A. P. Sutton, Phys. Rev. B **57**, 1505-1509 (1998).

[4] We have taken an effective U value of 2 eV for Co *d* electrons. This value has been estimated for a Co impurity with the partial screening of a nearby Cu (111) surface[5].

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