Electronic Supplementary Information

Non-innocent Adsorption of Co-Pyrphyrin on Rutile(110)

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1 Surface Energy Calculations of Rutile(110)

In Figure S1, the computed surface energies obtained with slab models of increasing number of O-Ti-O layers are plotted. We compare the values obtained by keeping all the coordinates fixed in the bulk positions (black symbols in the figure) to those obtained by relaxing the outermost layers of the slab (green for 1 layer and red for two layers), and keeping fixed at bulk coordinates the innermost ones. For the rigid slab model, the surface energy is largely independent from thickness and amounts to 1.75 J/m². By relaxing the outermost or the two outermost layers on both sides of the slab, the surface energies are significantly reduced to around 1.21 and 0.69 J/m², respectively.

We also computed the electronic properties for slabs of different size, with particular attention at the electronic states distribution at the surface, where it is most important for the interactions with the adsorbates. We compare 3 × 3 slabs of 5, 6, 7, and 8 layers, always fully relaxing the two outermost O–Ti–O layers on both sides and keeping fixed the innermost ones.

In particular, we observe that with the 5-layers model, and by keeping the atoms of the middle layer of the slab fixed in the bulk positions, the two exposed surfaces are decoupled and their electronic structure does not depend significantly on the thickness.
Figure S1: Surface energy of rutile (110) plotted vs the number of O-Ti-O layers of the slab model. Values obtained for rigid slab are in black (bulk coordinates), values obtained relaxing the outermost layer on both sides are in green, and relaxing two two O-Ti-O layers on both sides are in red.

The HSE06 band gaps obtained from the optimized geometries are 3.18 eV for 5 layers, 3.29 eV for 6 layers, 3.13 eV for 7 layers, and 3.07 eV for 8 layers. The PDOS obtained from the first two relaxed layers for each of the tested models are reported in Figure S2.

For the simulation of the adsorption, we used a 5-layers slab where only the two O–Ti–O layers on the adsorption site have been relaxed, while the rest of the slab has been kept fixed in the bulk position. This set up does not affect the electronic structure at the surface and the adsorption, as demonstrated from the discussion above. For the simulation of the adsorption processes we choose the 3x3x5 slab.

2 Initial Configurations of CoPy Adsorbed on Rutile(110)

Different initial configurations of CoPy adsorbed on rutile (110) are shown in Figure S3. CoPy in the gas phase is flat, hence we start always the optimization with a flat molecule at few Å
Figure S2: PDOS on top two O-Ti-O layers of rutile slabs. a) PDOS of symmetrically relaxed slabs. Black solid line represents PDOS of 5 layer, red 6 layer, magenta 7 layer, and blue 8 layer. Alignment is done with respect to valence band maximum of each slab. b) PDOS of 5 layer slab where only the top two O-Ti-O layers have been relaxed, the one that is used in our calculations. PDOS is aligned with respect to first occupied peak of symmetrically relaxed 8 layer slab.

3 Optimized Configurations of CoPy@rutile

Figure S4 shows configurations of several CoPy@rutile systems after geometry optimization. According to the results, CoPy finds many local minima on potential energy surface that trap the molecule, even if the adsorption energy is low. In the case of model-f, even starting from a slightly different configuration, the structure is minimized to model-a (see Figure S3 and main text). Hence, starting the geometry optimization with a small perturbation results in the same favorable configuration. This stable configuration is only obtained when two N\textsubscript{CN} atoms are close to Ti\textsubscript{5c}. Instead, when only one N\textsubscript{CN} interacts with surface Ti\textsubscript{5c}, as in the case of model-e and model-i, the adsorption energy is weaker. In model-k, Co(II) shows attractive interaction with O\textsubscript{2c}, however the interaction is repulsive for N\textsubscript{CN}, which are pushed away from the surface. The initial geometries of models g and j are slightly different from each other but are minimized...
Figure S3: Initial configurations of CoPy@rutile complex. Color code: brown: C, light blue: N, light pink: H, dark blue: Co, light green: O, grey: Ti.

to the same final model-j, which is similar to model-g, where N_CN adsorbed between O_{3c} and Ti_{5c} atoms, and Co(II) adsorbed on top of O_{2c}. In model-h, we may expect rotation of N_CN towards Ti_{5c}, however the hydrogen atoms coordinated with O_{2c} prevent it.

4 Spin Density of CoPy@rutile

The spin state of Co(II) is doublet, therefore, spin-polarized calculations are carried out for both CoPy in gas phase and CoPy@rutile complex. Figure S5 shows the localization of spin density on Co(II) in CoPy@rutile complex.
5 Effects of Density Functionals on Electronic Properties of CoPy and Py

Standard DFT is often unable to describe electronic localization correctly [1]. The reason is attributed to the incomplete cancellation of the Coulomb self interaction in GGA functionals leading to the stabilization of delocalization [2]. Applying hybrid functionals, like HSE06, removes some of the self-interaction error and favors localized electronic states by reducing the barrier to the localization [3]. Figure S6 shows the comparison between the PDOS computed for CoPy in the gas phase using HSE06 or PBE.

The localization of the electronic states introduced using HSE06 has a clear effect on the
energy distribution of those states with 2p-N\textsubscript{CN} and 3d-Co(II) character. In particular, the highest occupied states at the Co(II) metallic center are stabilized by about 2 eV, while the lowest unoccupied are pushed to higher energies by more than 1 eV. This corresponds to the decoupling of these states from the states on N\textsubscript{p} and C, in particular for what concerns the unoccupied orbitals. With PBE, instead, the unoccupied states projected on C and N\textsubscript{p} are hybridized with the delocalized 3d states of Co at about 2.5 eV. This has a pinning effect that most probably prevents the further relaxation of the energy gap, see also Figure S7.

HSE06 has been considered a good choice also for several porphyrin–derived molecules studied by Han et al. [4]. In this work, the ground state electronic structures and some excitation properties of Zn centered porphyrins, namely YD2 and YD2-o-C8, have been calculated with different density functionals, showing that HSE06 provides the best description of these properties.

6 Density of States Projected on CoPy

Figure S8 shows PDOS projected on optimized CoPy in the gas phase (flat structure) and CoPy in gas phase with the same coordinates as in the complex. Although the geometries of CoPy are different, their PDOS are similar.
Figure S6: PDOS on different species of CoPy calculated using HSE06 (red solid line) and PBE in the gas phase (black solid line). a) PDOS on Co, 3d states. b) PDOS on the central N atoms binding to the pyridine rings (N_p), 2p states. c) PDOS on the external N atoms belonging to the cyano groups (N_CN), 2p states. d) PDOS on all carbon atoms, 2p states.

7 Kohn-Sham Molecular Orbitals of CoPy

Figure S9 shows some selected molecular orbitals of the optimized CoPy in the gas phase. The molecular orbitals are distributed over all pyridine rings. Homo-1 has also contributions located on the N_CN atoms.
Figure S7: PDOS on different species of CoPy (red solid line) and Py (blue solid line) calculated using PBE (left) and HSE06 (right) in the gas phase. 

a) PDOS on Co, $3d$ states. 
b) PDOS on the central N atoms binding to the pyridine rings ($N_p$), $2p$ states. 
c) PDOS on the external N atoms belonging to the cyano groups ($N_{CN}$), $2p$ states. 
d) PDOS on all carbon atoms, $2p$ states.
Figure S8: PDOS related to CoPy optimized flat geometry (blue solid line) and distorted geometry (red solid line) in gas phase are compared. a) TDOS. b) PDOS on Co(II). c) PDOS on the central N atoms binding to the pyridine rings, N_p. d) PDOS on the external N atoms belonging to the cyano groups, N_CN. e) PDOS on C atoms.
Figure S9: Selected molecular orbitals of optimized CoPy in gas phase, a) homo-2, b) homo-1, c) lumo+1, and d) lumo+2. Color code: brown: C, light blue: N, light pink: H, dark blue: Co. Isosurface (orange for positive and green for negative) is set to 0.236 e/Å³.
References


