Supporting Information

Insight into intramolecular chemical structure modifications by on-surface reaction using photoemission tomography

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Computation details

Theoretical photoemission tomography simulations have been obtained within the framework of DFT. The calculations of the gas phase CoOEP and CoTBP have been performed with the NWCHEM[1] code. All calculations used the Becke three-parameter Lee–Yang–Parr (B3LYP)[2–5] hybrid functional. Geometry optimization was done with the 6-31G* basis set followed by single point calculations with def2-TZVPD basis set. The thereafter obtained Kohn-Sham orbitals were used to obtain kmaps[6]. All mentioned energies were obtained from the single point calculations. The known orientation of the molecule allows to determine the experimental orientation see below.

The optimized geometries are online available in mol file format.

Experimental methods

The XPS and NEXAFS measurements were carried out at the ALOISA beamline situated at the Elettra synchrotron radiation facility in Trieste[7].

The NEXAFS spectra across the N K-edge and Co L-edge were taken with the surface oriented either in *s*- or close to *p*-polarization at a constant grazing angle of 6˚. We collected partial electron yield, PEY, data by means of a channeltron multiplier equipped with a negatively biased grid in order to reject low energy secondary electrons. The NEXAFS resonances have been calibrated in enargy and normalized to the signal from the clean substrate using procedures described elsewhere[8]. The XPS measurements have been performed in normal emission with the sample at grazing incidence (4˚) in p-polarization. We

used a photon energy of 515 eV (N1s and C1s) and 910 eV (Co 2p) with an overall energy resolution of 240 and 310 meV, respectively.

The valence band photoemission spectra and work function scans were acquired at the NanoESCA beamline of Elettra, using an electrostatic photoemission electron microscope (PEEM) set-up described in detail in Ref. 9. The data were collected with a photon energy of 30 eV and a total energy resolution of 100 meV, using p-linearly polarized light.

The clean Ag(100) surface was prepared by a standard procedure, cycles of Ar+ ion sputtering at 2.0 keV followed by annealing at 800 K.

CoOEP molecules (Porphyrin system, ≥95% purity) were thermally sublimated at 550 K from a home-made Knudsen cell type evaporator onto the silver substrate kept at room temperature. The coverage has been calibrated with a quartz micro-balance, the resulting deposition rate was 15 min/ML. The nominal coverage for all the experiments presented here is monolayer coverage.

The experimental pattern shown on Fig. 1, in addition to the features originating from the molecular states, also contains sharp sp-band contributions from the Ag(100) surface (visible at $|k| \approx 1.2$ $Å^{-1}$). Exploiting these features of the Ag substrate in the momentum maps (see Figure S1), the orientation of the molecule with respect to the substrate high symmetry directions can be determined. The comparison between the calculated FTs from the gas phase molecular orbitals and the experimental momentum maps shows that the molecules are adsorbed with certain azimuthal angles against substrates high symmetry directions. Indeed, the symmetry of the Ag(100) substrate leads to two mirror domains with opposite tilt azimuthal angles of the molecules. The electron photoemission signal from both domains contributes to the experimental maps and, as a consequence, both of them must be taken into account for the simulated patterns. The best agreement between all experimental and corresponding simulated momentum maps is for an azimuthal orientation of CoOEP and CoTBP of ±21° and ±6° with respect to the [011] direction of the substrate, respectively. Note the gradient in the intensity resulting from the polarization $\mathbf{A} \cdot \mathbf{k}$ factor[6,10] of p-polarized incident light well-reproduced in the simulated data reported on Figure 1.
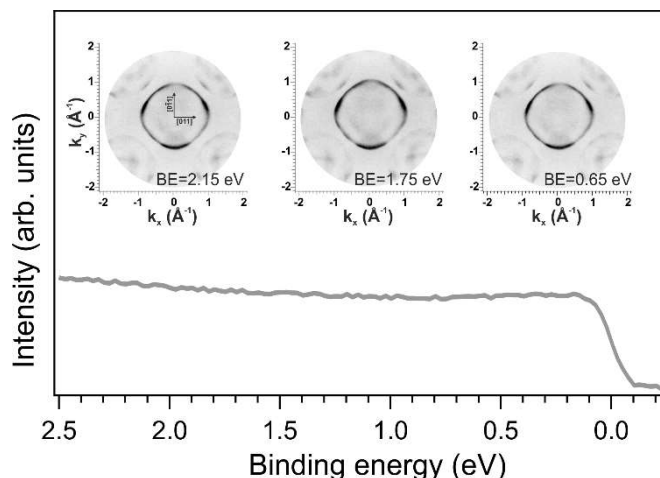

Figure S1. Angle integrated valence band spectrum and momentum maps taken at the BE corresponding to the molecular features reported in Fig 1 of the clean Ag(100) substrate. The substrate orientation is indicated.

C 1s and N K-edge spectra

The C 1s core level spectra reported on Fig.S2 fully support the CoOEP → CoTBP on-surface transformation. Indeed, the feature at low binding energy (BE) of as deposited CoOEP molecules at 284.1 eV, which is mainly associated with the ethyl groups, is shifted to higher BE upon formation of the six-membered carbon rings in CoTBP. The other features in the C 1s spectrum of CoTBP on Ag(100) substrate undergo a shift to lower BE, consistent with the change in the work function (-0.2 eV). Complementary information of the molecular structural changes and formation of new bonds can be obtained by performing NEXAFS measurement. The sensitivity of NEXAFS transitions to the chemical nature and environment of the atoms present in a material provides a unique method to probe the molecular structure. In addition, NEXAFS can reveal the average molecular orientation by probing element-specific electronic transitions of core level electrons to unoccupied molecular orbitals[11]. The N K-edge spectra of as deposited CoOEP onto Ag(100) surface and after annealing of the sample to the high temperature are reported on Fig.2a.
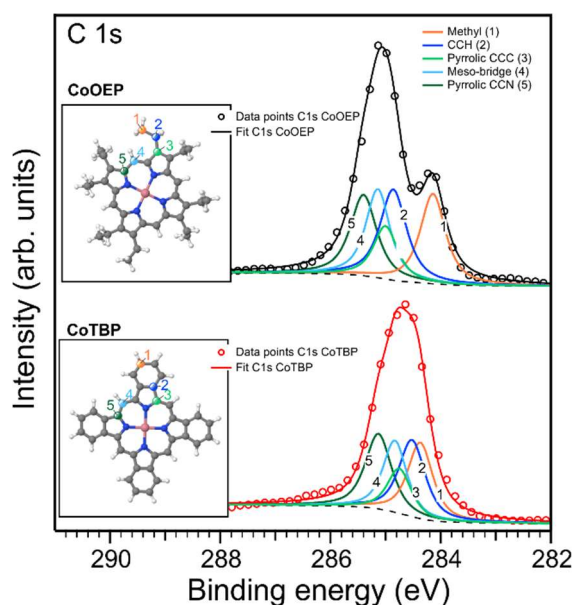

Figure S2. C 1s XPS spectra of CoOEP and CoTBP on Ag(100).

The overall differences in the line shape and energy position of the observed resonances in the NEXAFS spectra measured in p-polarization across the N K-edge before and after annealing process supports the changes in bonding environment in the adsorbed molecules. In particular, while the low energy peak at 398.8 eV display almost no change, the second main peak of the π* orbital region in CoOEP, at ~ 401.4 eV, after annealing is splitted in two features peaked up at 400.15 and 402.0 eV of photon energy. This spectral changes are a fingerprint of the on-surface ring closure reaction, meaning that CoOEP transforms to CoTBP[12,13]. Notably, both new resonances observed at higher photon energy of CoTBP maintain the π*-symmetry character. As a rule of thumb, the N 1s ionization threshold separates the region of π*-symmetry resonance from that of σ*-symmetry ones. Accordingly, the observed linear dichroism points to an adsorption orientation of the porphyrin macrocycle parallel or almost parallel to the surface in both CoOEP and CoTBP arrays supported by Ag(100) substrate. Moreover, the low energy features in the N K-edge spectra measured in *s*-polarization at 399.0 eV observed for both CoOEP and CoTBP molecules are associated with the transition from N $1s$ to a mixed ligands $2p_{x,y}$ - Co $3d_{x^2-y^2}$ orbital with the σ^* symmetry[14].
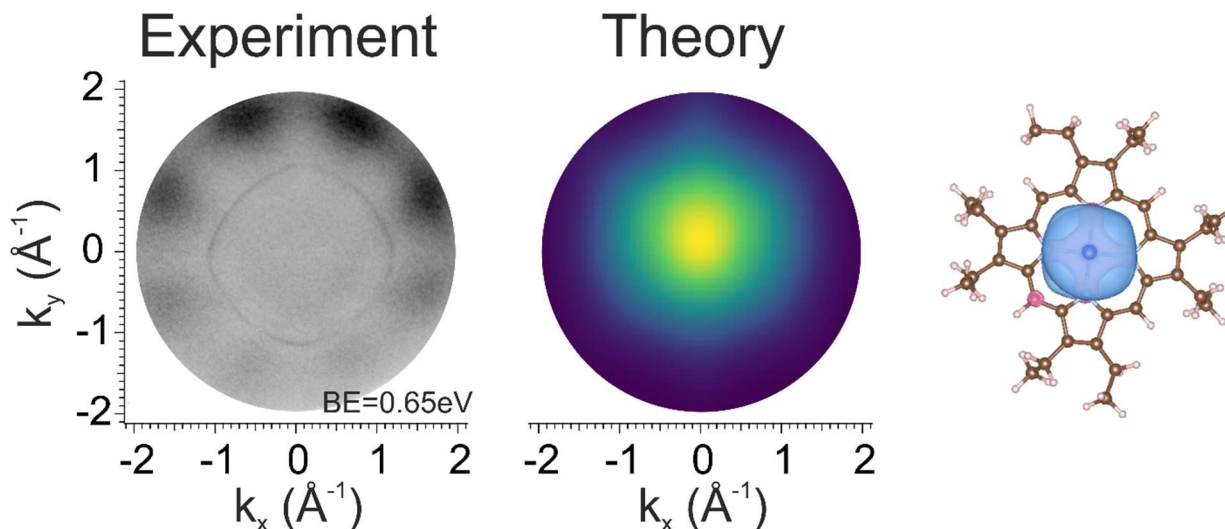
PT simulation: CoOEP gas-phase LUMO+2

Figure S3. Comparison between the experimental feature peaked at 0.65 eV in BE and the charge plots of the atomic like dz^2 state (LUMO+2) and its corresponding FT.

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