# Supporting Information of: On-surface nickel porphyrin mimics reactive center of enzyme cofactor

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## **Experimental Methods**

**XPS and NEXAFS**: The XPS and NEXAFS experiments were performed at the ALOISA beamline situated at the Elettra synchrotron radiation facility in Trieste.<sup>1</sup> XPS data were collected using linearly p-polarized light at grazing incidence of 4° with the sample surface while keeping the hemispherical electron energy analyzer in normal emission geometry. The Ni 2*p* photoemission spectra were measured with a photon energy of 515 and 1000 eV, with a total energy resolution of 240 and 450 meV, respectively. The binding energies (BE) in the XPS data were referred to the Fermi level of the Cu(100) substrate. NEXAFS spectra across the N K-edge were taken in partial electron yield using a channeltron multiplier.<sup>2</sup> The filtering out of the low-energy secondary electrons was achieved by a negatively polarized grid mounted in front of the channeltron detector. The orientation of the surface with respect to the linear polarization (*s* and *p*) of the synchrotron beam was changed by rotating the sample around the beam axis while keeping the incident angle (6°) of light fixed. The photon flux normalization and the energy calibration of the NEXAFS data have been performed following the procedure described in ref.<sup>2</sup> All measurements were carried out in UHV experimental chambers with a base pressure better than 5  $\cdot 10^{-10}$  mbar.

**Sample preparation**: The clean Cu(100) surface was prepared by cycles of  $Ar^+$  ion sputtering at 2.0 keV, followed by annealing at 800 K. The absence of contaminants on the surfaces was checked by XPS. The ordering of the surface and molecular layer was monitored using a reflective high-energy electron diffraction (RHEED) apparatus.

A few dozens of mg of NiTPP powder (Porphyrin Systems) were loaded into a quartz crucible of a home-made Knudsen cell type evaporator. Before the experiments, the molecules were carefully outgassed at 480 K for several days while the UHV system base pressure was monitored. The molecules were thermally evaporated at 520 K onto the copper substrate kept at room temperature. The molecular coverage has been calibrated with a quartz microbalance, the resulting deposition rate was 15 min/ML. The nominal coverage for all the experiments presented here is 1 ML, otherwise stated.

Since the organic molecules have a tendency to dissociate when exposed to ionizing radiation, the XPS spectra have been monitored over the time in order to exclude any possible induced radiation damage. No spectral changes were observed after 1 h, suggesting that NiTPP is reasonably stable under our experimental conditions. Furthermore, since the sublimation process may thermally decompose the NiTPP molecules already in the crucible, the stoichiometry of the different carbon species of the molecule has been verified by XPS (see supporting info) immediately after deposition.

**DFT**: Unoccupied molecular orbitals are calculated from the Kohn-Sham eigenstates of a gas phase molecule using the NWCHEM<sup>3</sup> DFT code, utilizing an optimally tuned rangeseparated hydrid functional<sup>4</sup> for exchange-correlation effects. Additionally, calculations for monolayers of NiTPP adsorbed on the Cu(100) surface have been performed using the VASP code.<sup>5,6</sup> In the latter case a repeated slab approach has been employed: the metallic substrate was modelled by four metallic layers, and a vacuum layer of ~ 15 Å was added between the slabs. To avoid spurious electrical fields, a dipole layer was inserted in the vacuum region.<sup>7</sup> The general gradient approximation (GGA) and HSE functional approach have been used in order to account for the exchange-correlation effects. The super cell geometry has been constructed according to the experimental LEED structure shown in Ref.<sup>8</sup> During the geometry optimization, the atomic positions of the molecular and the first metallic layer were allowed to relax, and the vdW-surf method<sup>9</sup> has been employed in order to account for van-der-Waals interactions.

## Ni 2p core level



Figure S 1: Ni  $2p_{3/2}$  core level photoemission spectra of NiTPP/Cu(100) for mono- (bottom) and multilayer (nominal coverage ~ 8 ML) (top) coverages, experimental data and fit. The spectra are collected in normal emission geometry with photon energy of 1000 eV.

The consequences of the charge transfer to the molecule on the Ni ion the Ni ion have been investigated by measuring the Ni  $2p_{3/2}$  core level XPS profile on both mono- and multilayer NiTPP coverages, blue and red curves in figure S1, respectively. For the multilayer, we see only one XPS component at 855.95 eV, which is in good agreement with previous measurements for similar systems.<sup>10</sup> This peak shifts by 2.8 eV towards lower binding energy at the monolayer coverage, with a BE of 853.15 eV. The binding energy of the peak was determined using a standard fitting procedure with a Doniach-Sunjic lineshape (Lorentzian width: 1.02 eV). This value agrees well with the ones reported for monolayer NiTPP deposited on other reactive surfaces, such as Cu(111)<sup>10</sup>and fcc Co(100)/Cu(100).<sup>11</sup> This binding energy is typical of metallic nickel,<sup>12</sup> suggesting the reduction of the Ni atom in NiTPP upon adsorption on a copper surface. A similar shift has been also reported for the Co  $2p_{3/2}$  core level of CoTPP adsorbed on the Ag(111)<sup>13</sup> and Ag(100)<sup>14</sup> surfaces. On the contrary, when NiTPP is deposited on a weakly reactive surfaces, such as Au(111), the Ni  $2p_{3/2}$  core level displays a BE similar to the multilayer one, which corresponds to a Ni ion in a formal 2<sup>+</sup> (II) oxidation state coordinated with the four nitrogens of the macrocycle.<sup>15</sup> In the present case, the large charge transfer from the copper substrate to the Ni ion is facilitated by the very short Cu-Ni distance and results in a reduction of the nickel oxidation state. This is in agreement with the partial filling of the unoccupied MOs from the LUMO to the LUMO+3 observed in the NEXAFS spectra and in ref.<sup>8</sup>

## Best fitting parameters of Ni L-edge spectra in fig.2

Table 1: Best fitting parameters of the main spectral features of Ni *L*-edge spectra shown in Fig. 2. The resonance peaks have been fitted to Voigt profiles with a constant gaussian broadening (0.3 eV). The total number of peaks have been fixed, but the fitting parameters have been left free to vary.

	polarization	neak/IP	hų (eV)	FWHM (lor) (eV)	neak area/IP height
	polarization	peak/11	$\Pi \nu (CV)$		peak area/11 height
Multilayer	p	$A_{Ni}$	854.01	0.98	2.710
		$B_{Ni}$	856.03	1.17	0.401
		IP	854.13	_	0.135
Monolayer	p	$A_{Ni}$	_	_	_
		$B_{Ni}$	853.16	0.57	0.053
		IP	852.42	_	0.024
	s	$A_{Ni}$	852.32	0.70	0.261
		$B_{Ni}$	853.26	0.57	0.013
		$C_{Ni}$	854.74	1.43	0.035
		IP	852.50	_	0.021

## NEXAFS at the C K-edge



Figure S 2: Carbon K-edge adsorption spectrum of NiTPP/Cu(100) taken with s and p polarized light. Nominal coverage 1 ML. The main resonances, related to specific transitions to unoccupied states are marked by the dashed lines and labeled, starting from the pre-edge.

The NEXAFS spectra taken at the carbon K-edge are shown in Figure S2. We identify five features related to the  $1s \rightarrow \pi^*$  (A<sub>C</sub> – E<sub>C</sub>) transitions and two associated with  $1s \rightarrow \sigma^*$  (F<sub>C</sub> and G<sub>C</sub>).<sup>16,17</sup> All the  $\pi^*$  resonances show a strong dependence on the polarization orientation: while A<sub>C</sub>, C<sub>C</sub> and D<sub>C</sub> are stronger for *p*-pol than for *s*-pol, B<sub>C</sub> and E<sub>C</sub> exhibit the opposite trend. A<sub>C</sub> (283.9 eV) is entirely associated with carbon atoms belonging to the tetrapyrrolic macrocycle, while B<sub>C</sub> (~285 eV) is dominated from the contribution of the phenyl rings.<sup>16,18</sup> Therefore, the specific polarization-dependent behaviour suggests that the NiTPP macrocycle is oriented parallel to the Cu(100) surface, while the phenyl groups are strongly tilted off the surface plane. The averaged tilt angle  $\gamma$  of the phenyl groups with respect to the surface can be quantitatively determined from the intensity ratio of the corresponding B<sub>C</sub> NEXAFS resonance measured in *p*- and *s*-polarization using the following equation (for the given  $\pi^*$  molecular orbital and four-fold substrate symmetry):

$$\gamma = \frac{1}{2} \arctan^2(I_p/I_s) \tag{1}$$

where  $I_p$  and  $I_s$  are the intensities of the  $B_C$  resonance in p- and s- polarisation, respectively, while assuming the x-ray beam to be 100% linearly polarized. The present analysis leads to a  $\gamma$  value of 68°± 5°, in excellent agreement with the predicted DFT adsorption model calculated in ref.<sup>8</sup> Finally, the vanishing intensity of the  $A_C$  resonance in the s-pol spectrum suggests a planar geometry of a porphyrin macrocycle, rather than a saddle-shape conformation previously observed for other adsorbed metal-TPPs on Ag(111) and Cu(111) surface.<sup>19,20</sup> The adsorption geometry of the macrocycle and phenyls of NiTPP is similar to that of a CoTPP monolayer on Cu(110), where the CoTPP molecules within the selfassembled structure maintained planarity of the core macrocycle and consequently induced significant tilt of phenyl moieties, while the isolated CoTPP adopts a saddle-shaped conformation.<sup>21</sup>

## NiTPP film exposed to Nitric Oxide



Figure S 3: NEXAFS spectrum at the Ni  $L_3$ -edge acquired for (bottom) for the NiTPP monolayer deposited on Cu(100) and (top) for the NiTPP monolayer exposed to 4000 L of NO with *s*-polarized light.

The effective reactivity of the Ni(I)TPP overlayer was tested by exposing the organic film to 4000 L of nitric oxide (1 L =  $1 \cdot 10^{-6}$  torr·1 s), using a partial pressures of  $5 \cdot 10^{-7}$  mbar, while keeping the sample at room temperature (RT). The combined shift to higher energy of both the main peak A<sub>Ni</sub> and, to a larger extent, of its satellite B<sub>Ni</sub> demonstrate that NO coordinates with the Ni(I) ion (see figure S3). The resulting shape of the NEXAFS spectrum upon NO exposure now closely resembles the one of Ni(II)TPP multilayer, apart from a residual shift of ~ 1 eV that is partially originated by the metal surface screening of the monolayer phase. Overall, the energy shift and the increased separation of the satellite feature is consistent with an effective re-oxidation of the Ni(I) active site. This ligation mechanism is in agreement with the one proposed for other metal-porphyrins deposited on different substrates.<sup>22,23</sup> In the latter cases, the metal-porphyrin films were exposed to smaller NO doses, but at cryogenic temperature, whereas thousands of Langmuir are required to saturate a monolayer of CoTTP at RT.<sup>24</sup> For comparison, NO molecular adsorption on Ni films takes place at low temperatures, while its dissociation starts at 200 K.<sup>25</sup>

As a final comment, we remarke that our NEXAFS measurements of the Ni L<sub>3</sub>-edge exclude the possible exchange of the nickel atom with a Cu one from the substrate (transmetalation). This phenomenon has been claimed to take place for different metallo-porphyrins<sup>26</sup> and phthalocyanines<sup>27</sup> on reactive metallic substrates, even if the hierarchy of metal reactivity would exclude the Ni replacement by a Cu atom, as unequivocally demonstrated for Fe and Ni pyrphyrin compounds on copper.<sup>28</sup> Our conclusion is experimentally supported by i) the dichroism of the two main spectral features at the Ni  $L_3$ -edge, which confirms the coordination of Ni to the nitrogen ligands, and ii) the specific lineshape of the NEXAFS spectra, which is very different from that of bulk nickel,<sup>29,30</sup> Ni films on Cu<sup>31</sup> and Ni-Cu alloys.<sup>32</sup> In fact, the latter spectra are characterized by the appearance of a satellite peak at  $\sim 6.3$  eV higher photon energy from the main peak  $A_{Ni}$ ,<sup>33</sup> which stems from multiple (electron) scattering events from the neighbour metal atoms<sup>30,31</sup> and is clearly absent in our monolayer NEXAFS spectra. These spectroscopic fingerprints of bulk (metallic) nickel are observed also in low coverage Ni films on Cu(100),<sup>34</sup> because nickel grows by nucleation <sup>35</sup> of 2D islands pseudomorphic to Cu(100),<sup>36</sup> whereas they are clearly absent in our NiTPP monolayer NEXAFS spectra.

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