On-Surface coordination chemistry: Direct imaging of the conformational freedom of an axial ligand at room-temperature

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

The on-surface ligation of nitric oxide (NO) with Co-tetraphenylporphyrin (CoTPP) sublimed onto oxygen-reconstructed Ni(001) is studied by room-temperature scanning tunneling microscopy (STM) and complementary photoemission spectroscopies. On the oxygen-reconstructed substrates, the porphyrines are observed to form well-ordered, self-assembled layers. STM directly images the NO ligand as a characteristic feature in the center of the molecule. At certain STM imaging conditions the dynamicity of this feature can be related to the temperature-activated conformational flexibility of the NO ligand. This provides an indirect confirmation for the bending of the Co-NO bond, as predicted from coordination chemistry.

On-surface coordination-chemistry involves the study of metal coordination at the surface which provides an environment which is at times modifying at other times not. For the reason of these differences and for the fact that on the surface many experiments – in particular by imaging or addressing of single reactants – are possible which are not possible in the liquid or gas phase – this field is rapidly emerging. Apart from the now well-established use of coordinative-bonds to form stable 2D metal-organic layers¹ and on-surface synthesis^{2–4}, the axial-coordination of a ligand onto the free site of square-planar complexes is of great interest: axial coordination allows to control the electronic^{5,6} and magnetic properties^{7–9} of single transition-metal ions as well as to control chemical reactivity as used in catalysis¹⁰ and – embedded in protein architectures – in biochemistry¹¹.

In this report we present studies about the on-surface coordination of nitric oxide (NO) with Co-tetraphenylporphyrin (CoTPP). In contrast to other work^{5,12}, we study the on-surface coordination chemistry on oxygen-reconstructed (O-c(2x2)) nickel films (Ni(001)) grown on copper (Cu(001)) single crystals (cf. illustration in Fig. 1a). This setup is motivated by the modified physical and chemical interaction between the surface support and the ad-molecule. We here focus on the on-surface coordination-chemistry while in earlier studies we reported on the modification of the exchange coupling between CoTPP and magnetic substrates. The axial ligation of CoTPP (one unpaired electron in d_z^2) with NO (one unpaired electron in π^*) has been studied in bulk / solution^{13,14} as well as in the on-surface

environment.^{5,7,8,12} For the σ -type overlap between the d_z^2 orbital of Co and the π^* of NO molecular orbital (MO) theory predicts a $\sim 120^\circ$ Co-NO bond-angle. The coordination of NO-ligands onto CoTPP on Ag(111) has been studied earlier by low-temperature STM at 6K and has been compared with CO exposed CoTPP – where cis-(CO)₂-CoTPP is observed.^{12,15} In our study, the CoTPP-nitrosyl complexes are imaged at room-temperature, in contrast. This allows us to directly observe the conformational libration of the $\sim 120^\circ$ -bent NO-ligand, which is imaged as streaks surrounding the binding site in the center of the porphyrins (vide infra). Furthermore, CoTPP/Ag(111)¹⁶ is in the saddle-shape conformation, whereas the molecule is adsorbed in flat geometry on O/Ni (vide infra).

The substrate preparation is analogous to oxygen reconstructed cobalt films and is described elsewhere.¹⁷ The scanning tunneling microscopy (STM) data presented here is acquired at room temperature (RT). Positive bias voltages result in electron tunneling from the tip into unoccupied states of the sample. In previous studies, we have observed that porphyrines / phthalocyanines form self-assembled layers on oxygen-reconstructed Cu(001) and Co(001) substrates. In contrast these molecules appear randomly arranged when adsorbed on native (clean) Cu(001) and Co(001) substrates.^{17,18,7–9,4} This reflects that self-assembly is facilitated by the lower chemical reactivity of the oxygen-reconstructed substrate which allows for the necessary molecular diffusion. The fact that phthalocyanines on O/Co(001) were imaged with very high intra-molecular resolution⁹ suggests the oxygen-reconstruction serves a similar – even though maybe weaker than alkali-halide carpet layers – role in decoupling the molecular adsorbates and their orbitals from metallic substrates.¹⁹

Figures 1b&c show STM images of the oxygen reconstructed Ni (O/Ni(001)) substrate. The O/Ni(001) adlayer reconstructs the surface to form terraces with rectangular edges running exactly along the Cu(001) principal directions (see Fig. 1b).²⁰ This topography is characteristically different from the pure metallic Ni(001) film^{20,7} and resembles oxygen reconstructed Co(001).¹⁷ In Fig. 1c a step edge of the O/Ni(001) film is shown with atomic resolution. It is important to note that one should take special care while assigning the molecular features in an STM image: in Supporting Information we present STM data where the molecules resemble stars and their lobe assignment is compromised by a tip-artifact.

Fig. 1 (a) Molecular scheme of Co-tetraphenylporphyrin (CoTPP) and sketch of the sample composition: CoTPP is sublimed onto an oxygen-reconstructed Ni thin film grown on a Cu(001) single crystal. (b) and (c) STM data of the oxygen-reconstructed Ni film (denoted O/Ni(001)): an overview and atomic resolution, respectively. The arrows indicate Cu(001) principal directions. All experiments are performed at room temperature.

Fig. 2 STM data of ~ 1 ML of CoTPP on O/Ni(001). (a) An overview of the molecular lattice. The dotted rectangle marks the unit-cell of the lattice. A set of molecular schemes is superimposed onto part of the lattice to guide the eye. (b) High resolution image of a phase shift domain boundary between two supramolecular islands. (c) CoTPP molecule imaged by STM in the second monolayer. The detailed analysis of the registry reveals that the 2nd layer molecules stack in the 'on-top' position.

The such prepared surface serves as a substrate for the second step of the experiment, the CoTPP evaporation. The evaporation was performed from a home-built evaporator onto the O/Ni(001) substrate kept at RT. The molecular coverage was monitored by quartz crystal microbalance and cross-checked by X-ray photoelectron spectroscopy (XPS) and STM. Fig. 2a shows an STM image of a CoTPP monolayer with some symbolic molecules superimposed onto the data. The molecules on O/Ni(001) assemble in a chiral arrangement similar to the one presented on O/Co(001).¹⁷ The observed flat conformation is consistent with reports on metal-TPPs on other square metal(001) surfaces.^{21,17} Two mirror domains taking an angle of 28° with respect to each other can be found in large-scale STM images (data not shown). The self-assembled layer is formed by intermolecular interactions between the phenyl residues and the porphyrin macrocycle. This supramolecular arrangement exhibits a square unit-cell of ~ 1.29 nm, similarly to other poprhyrins on fcc(001) substrates¹⁷. In the middle of the molecules, several darker spots are visible (Fig. 2a). Tentatively we associate these defects to a minority component in the crucible: metal-free H2TPP, which, upon reaction with oxygen reconstructed substrate at RT, have self-metalated to form NiTPP.⁴ Fig. 2b shows a phase shift domain boundary between two domains of the 2D self-assembled layers. Here, the distance between two molecules is increased and the intermolecular interaction occurs between the phenyl rings of the neighbouring molecules. Additionally, two molecules of a second layer can be distinguished in Fig. 2a (cf. zoom-in in Fig. 2c). Interestingly, they appear in the flat conformation and lie exactly on top²² of the molecule of the first layer.

In the final step of the experiment we have exposed a monolayer of CoTPP/O/Ni(001) to 6000 Langmuir ($p=8 \cdot 10^{-6}$ mbar) of nitric oxide (NO) and recorded a set of STM data (see Figs. 3 and 4). Upon NO exposure, the NO ligand binds to the Co-porphyrin via its open top site.^{5,7,8,12} We were able to image the NO-CoTPP complexes at RT at different bias-voltages. In Fig. 3a ($U_{\text{bias}} = 2.0$ V) the axially bonded NO ligand is imaged as regularly appearing streaky zones in the pattern of the molecules. Note that the porphyrins are a bit tricky to be identified in the patterns: around a molecular vacancy (blue square zoom-in) the imaged features can be assigned to the molecular structure. The molecules' 2D arrangement remains approximately the same after the NO exposure. The size of the squarely symmetric unit cell is ~ 1.30 nm, which is virtually the same as before NO coordination. While there are no indications for a molecular rearrangement upon NO exposure on the oxygen-reconstructed substrate, however this does not exclude the potential presence of NO adsorbed in-between the porphyrines. Notably our result differs from earlier observations: NO exposure to CoTPP on Ag(111) was found to rearrange the unit-cell of the 2D self-assembled layer by being incorporated inbetween the CoTPP molecules.²⁴ It seems possible that this different behaviour is due to the different properties of the substrate-adsorbate systems: i) Ag(111) and O/Ni(001) differ in the symmetry of the surface lattice, i.e. hexagonal vs. quadratic ii) the modified molecule-

substrate interaction; this is reflected in the conformation of the CoTPP, either saddle-shaped or flat on Ag(111) and O/Ni(001), respectively and iii) the lower and higher

electronic corrugation of Ag(111) and O/Ni(001), respectively.

Fig. 3 STM data of the CoTPP monolayer on O/Ni(001) after exposure with NO (6000 Langmuir). (a) The CoTPP molecular lattice image is depicted well in the STM data acquired with $U_{\text{bias}} = 2.0$ V. The dotted square assigns the molecular unit-cell. The streaks appearing regularly at the molecular centers are caused by the NO adsorbed at the Co-center metal atom of CoTPP and by its conformational libration at room temperature. Hollow sites have been assigned to Ni-metalated H2TPP molecules (see text). Single porphyrins can be identified around a molecular vacancy (blue square, cf. zoom-in on the right-hand side). (b) The same molecular lattice recorded with $U_{\text{bias}} = 1.2$ V. The regularly appearing streaks are still distinguishable. Four molecules in the second layer are depicted by blue lines (cf. zoom-in section in the green square).

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Fig. 4 Bias-dependent STM data of NO-exposed CoTPP on O/Ni. All three images display the same area on the sample. (a) $U_{\text{bias}} = 2.0$ V, the protrusions denote phenyl rings, NO visible as streaks in the molecular centres. Hollow sites are either NiTPP, or CoTPP without NO (b) $U_{\text{bias}} = 0.3$ V, the protrusions denote pyrrole rings, the bright stripes (arranged in a windmill-shape) – phenyl rings. Bright molecular centres are NO coordinated Co atoms, semi-dark molecular centres are Co without NO and dark ones NiTPP. The streaks now appear now slightly below the molecular centres. (c) $U_{\text{bias}} = -0.5$ V, bright protrusions indicate phenyl rings, contrasts of molecular centres and NO molecules are the same as in (b). (d) The proposed Co-porphyrin NO σ -bond based on the overlap of the Co d_z^2 and NO π^* orbitals.²⁵ In c), one porphyrin has been removed from the lattice due to the interaction with the STM tip.

When imaging with modified bias voltage (Fig. 2b, $U_{\text{bias}} = 1.2$ V) CoTPP molecules appear differently, due to other molecular orbitals being probed (compare Fig. 4). Also the streaks of the imaged NO-ligands are here much less pronounced. Interestingly, the molecules of the second monolayer (green zoom-in) again adsorb exactly on top of the first-layer, but here they are distorted and are found in the saddle-shape conformation.

The observation of individual ad-molecules with intramolecular resolution at RT is quite remarkable: to the best of our knowledge so far only self-assembled ad-layers and not individual ad-molecules have been imaged by STM.²³

Since we can also image the ad-molecules without the NO ligand, we relate the surprising stability of the ad-molecule with the flat conformation of the underlying first monolayer.

As the molecular symmetry of the ad-molecules is lowered (2-fold) with respect to the first monolayer (4-fold), they spontaneously arrange in two energetically equivalent directions as indicated by the blue lines (Fig. 4b). The ad-molecules are also NO-ligated. We do not know if the CoTPP-molecule below the ad-molecule is also with NO-ligand, but since NO-ligation has been shown to proceed into molecular multilayers,⁵ this is very plausible. These considerations suggest two possible mechanisms for the observed two-fold

symmetry of the NO-CoTPP ad-molecules: i) due to NO-ligation of the ad-molecule inducing the saddle-shape conformation, ii) due to the (possibly) present NO-ligand in the first layer which lifts up the ad-molecule and which allows for symmetry reduction via electronic / steric effects. In both images (Fig. 3a and 3b) the Ni-metalated H2TPP's are visible with dark spots in the middle.

Fig. 4 displays a set of STM images of the same sample area of the CoTPP monolayer recorded at different bias voltages.

In Fig. 4a ($U_{\text{bias}} = 2.0$ V) phenyl rings appear as bright protrusions and the dark spots are either Ni-metalated H2TPP or non-coordinated CoTPP. Fig 4b recorded at $U_{\text{bias}} = 0.3$ V resolves the former ambiguity. Here we see three different contrasts of molecular centers: bright, semi-dark and dark, which we respectively assign as NO-ligated CoTPP, CoTPP without NO-ligand and Ni-metalated H2TPP. In Fig. 4c acquired at $U_{\text{bias}} = -0.5$ V the centres have similar contrast to Fig. 4b and the phenyl rings appear as bright protrusions, as in Fig 4a. Interestingly, one molecule in Fig. 4c has been removed by an STM tip while scanning, which evidences the previously anticipated low molecule-substrate interaction¹⁸.

Table 1 Peak areas from X-ray photoelectron spectra.

	CoTPP/O/Ni	CoTPP/O/Ni + NO
	peak (kcps eV)	peak (kcps eV)
C1s	11.95	10.7
N1s	3.3	8.5
O1s	15.3	26.4
Cu2p	124	98
Ni2p	1897	1743

Table 1 displays peak areas of X-ray photoelectron spectra. After NO-exposure, the O1s and N1s signals are significantly increased. On the basis of 4 nitrogen atoms per porphyrin, the increased N1s signal corresponds to ~6 additional NO molecules per porphyrin. Tentatively, we ascribe this to 4 NO molecules within the self-assembled CoTPP layer (appearing bright in Fig. 5b) and to one NO acting as axial ligand.

Conclusions

In summary, we have shown that on oxygen-reconstructed Ni(001) substrates CoTPP self-assembles into well-ordered molecular monolayers consisting of molecules in the flat conformation. This is in-contrast to CoTPP on Ag(111)¹⁶, which adsorbs in saddle-shape conformation. We show that the axial-NO ligand can be directly imaged even at room-temperature and not only at 6K.^{12,6} The bias dependent room-temperature images reveal the conformational flexibility of the NO ligand which provides an indirect confirmation for a bent Co-NO bond.^{13,14} Interestingly, the CoTPP ad-molecules observed in the second layer possess a lowered (2-fold) symmetry – however only after NO-ligation. Remarkably the present scanning tunneling microscopy study allows for the analysis of complex on-surface coordination reactions and

monitors conformational and structural issues – even in dependence of first vs. second layer position of the molecules. This brings this method far beyond what has been achieved with spatially averaging spectroscopic methods while the latter method provides higher precision spectroscopic information which motivates further studies, in particular by spectro-microscopy correlation.

Acknowledgements

This work was supported by the Swiss Nanoscience Institute (SNI), National Centre of Competence in Research Nanosciences (NCCR-Nano), Swiss National Science Foundation (SNSF), Holcim Foundation for the Advancement of Scientific Research, Switzerland. The authors sincerely thank Rolf Schellendorfer for technical support.

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