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Published in:
Journal of the American Chemical Society

DOI:
[10.1021/jacs.8b06765](https://doi.org/10.1021/jacs.8b06765)

Published: 17/09/2018

Document Version
Peer reviewed version

Please cite the original version:
Queck, F., Krejčí, O., Scheuerer, P., Bolland, F., Otyepka, M., Jelínek, P., & Repp, J. (2018). Bonding Motifs in Metal-Organic Compounds on Surfaces. *Journal of the American Chemical Society*, 140, 12884-12889. [40].
<https://doi.org/10.1021/jacs.8b06765>

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Bonding Motifs in Metal-Organic Compounds on Surfaces

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KEYWORDS: *atomic force microscopy · scanning tunneling microscopy · metal-organic frameworks · self-assembly · lateral manipulation*

ABSTRACT: The bonds in metal organic networks on surfaces govern the resulting geometry as well as the electronic properties. Here we study the nature of these bonds by forming phenazine-copper complexes on a copper surface by means of atomic manipulation. The structures are characterized by a combination of scanning probe microscopy and density functional theory calculations. We observed an increase of the molecule-substrate distance upon covalent bond formation and an out-of-plane geometry that is in direct contradiction with the common expectation that these networks are steered by coordination bonds. Instead, we find that a complex energy balance of hybridization with the substrate, inhomogeneous Pauli-repulsion as well as elastic deformation drives the phenazine-copper interaction. Most remarkably, this attractive interaction is not driven by electron acceptor properties of copper but is of completely different donation/back-donation mechanism between molecular π -like orbitals and sp -like metal states. Our findings show that the nature of bonds between constituents adsorbed on surfaces does not have to follow the common categories.

INTRODUCTION

Two-dimensional metal-organic networks (MONs) on surfaces represent a versatile platform to pattern metal-organic interfaces and to tailor their properties.^{1–4} As MONs can be controlled by rational design of its constituents, they are envisioned to be applicable in very different fields ranging from catalysis over nanoelectronics to memory devices.^{5–9}

MONs are usually obtained from self-assembly on metal surfaces. While suitable precursor molecules are deposited from gas phase,¹⁰ the metal atoms involved can be either co-deposited or provided by substrate atoms.¹¹ The self-assembly in MONs is most often steered by the introduction of nitrogen atoms in cyano linkers or other end groups in the organic precursors.^{12–18} These nitrogen atoms are observed to strongly link to metal atoms. The so formed bonds therefore govern both, the geometry as well as the electronic properties of the MONs rendering a detailed understanding of these bonds of crucial importance.

From analogy to their three-dimensional counterparts^{1,19–21} MONs are also called coordination networks, implying implicitly or even explicitly^{11–18,22–31} a coordination bond (also called coordinate bond) between the aforementioned constituents. Coordination bonds are covalent bonds in which the two electrons derive from the very

Figure 1. Sample overview and complex formation. (a) Constant-current STM overview [100 mV; 1 pA] of the sample with Cu adatoms (yellow), CO (green) and Ph molecules (blue). Scale bar 50 Å. The inset sketches the Ph molecule with carbon (black), hydrogen (white) and nitrogen atoms (blue). (b-e) Constant-current STM images [300 mV; 5 pA] of a Cu adatom and a Ph molecule on Cu(111) showing the sequence of lateral manipulation (white arrows) of the Cu adatom. In (e) the CuPh complex was formed. Scale bar 10 Å.

same atom (dative bond).^{32,33} However, in solution a coordination bond is usually formed with metal cations that accept the electrons in the bond from the ligand. In contrast, transition metal adatoms on metal surfaces – although they may carry a fractional positive net charge – are far from being fully ionized.^{34,35} This alone raises considerable doubt about the nature of the bond in the case of on-surface MONs. Surprisingly, despite the wide interest in MONs, the knowledge of the bond itself is rather scarce.^{15,18,35,36} In particular, there were indications for other contributions to the bond, namely from a donation/back-donation mechanism,^{18,36} as well as to a charge transfer opposite to what would be expected for such a coordination bond.^{15,18}

The bond between metal and the nitrogen of the organic linker is commonly believed to involve the nitrogen's lone electron pair. The latter protrudes in the plane of the heterocycle for sp^2 -hybridized nitrogen or extending the C-N bond for cyano-groups. The directionality of the formed bond is observed to compete with the adsorption height of the linker and metal atom and their interaction with the surface. In many cases, the adsorption height of metal atoms is smaller than the one for organic compounds, such that the metal can be pulled away from the surface^{22,26,31,37} or the ligand can be pulled towards the surface^{23,24,27,28,38–40} or both^{25,29,41–44}.

Irrespective of the reported geometries, the bond appeared to favor a trigonal-planar geometry at the bonding nitrogen atom in heterocycles, consistent with the common assumption of a coordination bond.^{12–15,17,24,29,40,43,45}

Here, we study the bonding between one and two copper adatoms to a phenazine (Ph) molecule on a Cu(111) surface. Our findings are based on scanning probe microscopy experiments with sub-molecular resolution complemented by density functional theory (DFT) calculations. The structures were built step-by-step by means of atomic manipulation, leading to an atomistic picture of the bonding geometry.

In stark contrast to the aforementioned common expectation, we observe that bonding to adatoms lifts Ph away from the surface, even though the copper adsorption height is clearly below the molecular plane. The DFT calculations reproduce the experimental observations and provide strong evidence that the bonding cannot be interpreted in terms of a coordination bond between the nitrogen's lone pair and the metal atom. Instead, the binding mechanism can be understood as a complex interplay between Pauli repulsion and covalent donation/back-donation bonding involving frontier molecular π -like orbitals and sp -like metallic states.

METHOD DESCRIPTION

All experiments were conducted on a home-built combined scanning tunneling (STM) and non-contact (nc) atomic force microscope (AFM) with a base temperature of 6.8 K at pressures better than $2 \cdot 10^{-10}$ mbar. The qPlus sensor ($k \cong 1800$ N/m, $f_{\text{resonance}} \cong 29$ kHz, $Q \cong 30\,000$) is operated in frequency-modulation mode and at oscillation

amplitudes of 0.5 Å.^{46,47} The bias voltage is applied to the sample with respect to the tip. All adsorbates (CO molecules and Ph, Cu adatoms) were deposited from the gas-phase with the clean Cu(111) sample held at a temperature below 10 K. All AFM images were taken with CO-functionalized tip in constant-height mode. All constant height offsets given in the AFM images are with respect to a constant current set-point of 100 mV, 8.7 pA where positive Δz corresponds to a decrease in tip height.

The FHI-AIMS package^{48–51} was used for DFT slab calculations including van der Waals interaction⁵² using the hybrid HSE03 exchange-correlation functional because standard GGA DFT functionals failed to reproduce the correct order of molecular orbitals.^{53,54} The nature of Cu-phenazine interaction was also analyzed by cluster models using perturbation theory MP2 and coupled-cluster calculations with perturbative triple excitations CCSD(T).^{55,56} The initial geometries were based on the experimental observations on a $6 \times 6 \times 3$ Cu(111) slab with the two bottommost layers fixed and > 25 Å of vacuum between the slabs. Image simulations were performed in the probe-particle model^{57,58} with a quadrupole ($q = 0.025 \text{ e} \cdot \text{Å}^2$) electrostatic field mimicking a CO tip.⁵⁹

RESULTS AND DISCUSSION

Figure 1a shows an STM image of the prepared sample. Phenazine ($\text{C}_{12}\text{H}_8\text{N}_2$, see inset in Figure 1a) has two nitrogen atoms in a pyrazine heterocycle which exhibit an affinity towards metal atoms.⁶⁰

Instead of temperature-assisted self-assembly, we use atomic lateral manipulation in order to have control over

Figure 2. AFM imaging of complexes. The use of atomic manipulation allows a direct assignment of atomic arrangements (a, b) of the structures formed and imaged with AFM (c, d). The latter reveal a surprising lifting of the molecule from the surface upon bond formation with one and two copper adatoms. The simulated AFM images (e-h) reproduce the observed contrast in great detail. Image conditions: (c) $\Delta z = 0.9$ Å. (d) $\Delta z = 0.7$ Å. The arrows in (b) denote two close-packed directions of the Cu(111) surface. (e,f) $\Delta z = 1.0$ Å. (g,h) $\Delta z = 0.7$ Å. Scale bars 10 Å.

where metal atoms are linked to molecules.^{61,62} We selectively form Cu-phenazine (**CuPh**) and Cu-phenazine-Cu (**Cu₂Ph**) complexes by attaching Cu adatoms to Ph at the position of nitrogen atoms, see Figure 1b-e. We observe that already bringing the adatom in few-Å proximity to the molecule results in a spontaneous formation of CuPh or Cu₂Ph, respectively, indicating a bond formation of the constituents. Further, lateral manipulation of the formed complexes resulted in the movement of the entire structure and no bond cleavage could be observed. Figure 2 depicts AFM images of single Ph molecules and complexes. Ph and CuPh adsorb with its long axis parallel to a close-packed direction of the Cu(111) surface, whereas Cu₂Ph is rotated by an azimuthal angle of $\approx 25^\circ$ relative to the high-symmetry direction of the substrate.

In Figure 2c (left molecule), the nitrogen atoms of Ph appear to be more attractive (with more negative frequency shift) compared to the outer carbon rings. This is in agreement with a simulated AFM image using the DFT-optimized adsorption geometry, see Fig 2e. In accordance with the literature,^{60,63} we attribute this contrast to a geometric bending of the molecule at the nitrogen atoms.

We now turn to the metal-molecule complexes. As mentioned above, a coordination bond between the adatom and Ph should slightly pull the molecule towards the surface, since the molecular plane should be above the adsorption height of copper. Surprisingly, the Ph molecule in CuPh appears lifted in AFM images, indicating that the part of the molecule that binds to the Cu adatom has moved away from the surface, see right molecule in Figure 2c. After attaching a second copper adatom, we observe that the Ph molecule in the Cu₂Ph complex appears completely flat in AFM and lifted even *further* from the surface; compare the left (Cu₂Ph) and the right molecule (CuPh) in Figure 2d. Such lifting of molecules upon bond formation, as observed here and also for other networks,⁶⁴ raises considerable questions about the nature of the bond.

To elucidate the bond mechanism, we study the different complexes by DFT calculations revealing dominant interaction of substrate with two nitrogen atoms. The observed slight bending of adsorbed isolated Ph is well reproduced (Figures 3a-c), with the nitrogen atoms being approx. 0.3 Å closer to the surface than the outer carbon atoms. In excellent agreement to the experiments, the calculations reveal an adsorption of Ph and CuPh with 0° and Cu₂Ph with 27° to one of the close-packed Cu(111) directions, respectively, see Figure 3a-h. Most importantly, according to the calculations Ph is lifted by approximately 0.7 Å (CuPh) and 1.0 Å (Cu₂Ph) upon binding to Cu adatoms as also observed in the experiments. The very good agreement between the experimental and simulated AFM images (see Figures 2c-h) strongly supports that the bonding geometry is correctly captured by the DFT calculations.

Inspecting the side view of the bonded configurations (Figure 3e, f and h) reveals that the bond angles are incompatible with an in-plane coordination bond. Analysis of calculated densities reveals negligible net charge

transfer between molecule and metallic substrate. This is also in open contradiction to the coordination bond mechanism, which requires strong charge transfer from nitrogen to copper. Further, the charge density redistribution upon bond formation (Figures 3k and l) is also irreconcilable with a coordination bond. Gas-phase calculations further indicate that a coordination bond only occurs for binding of Ph to cationic Cu atoms (see the Supporting Information for details).

Figure 3. Geometry of the complexes, orbital density imaging and calculated charge-density differences. Top- and different side-views of Ph (a-c), Cu₂Ph (d-f), and CuPh (g, h) on Cu(111). Ph is strongly bent due to Pauli repulsion (c). Upon binding to adatoms the molecule is lifted and flattened. Cu adatoms are depicted in yellow. (j) Experimental constant-height STM image [$\Delta z = 1.3$ Å from 100 mV, 2 pA] of Cu₂Ph acquired at low bias exhibits the LUMO density contour of Cu₂Ph, which is well reproduced by a corresponding simulated STM image (inset). (k,l) Side- and top-view of the charge density difference contours of Cu₂Ph, exhibiting electron accumulation (green) in the LUMO and electron depletion (blue) in the HOMO, respectively. (m) HOMO and LUMO calculated contours of gas-phase phenazine for comparison. Scale bars 5 Å. (a-h) was illustrated using Avogadro.^{70,71}

From inspection and comparison of all three configurations Ph, CuPh and Cu₂Ph in terms of geometry, energy and electron density the following picture of bond formation emerges.

We observe in all these structures a hybridization of the molecular frontier π -like orbitals with the sp -like states of the metal adatoms and the substrate emerging in a strong broadening of HOMO and LUMO, while the metal's d-orbitals remain largely unperturbed upon bonding (see the Supporting Information for details). As the molecule's HOMO and LUMO smear over the chemical potential of the respective structure, this leads to a partial population of the LUMO and (to a much lower degree) to a depopulation of the HOMO, as captured by the common donation/back-donation picture.^{65–67} Interestingly, the same mechanism works also for isolated Cu₂Ph without substrate exhibiting a bond of similar strength based on donation/back-donation between Cu and Ph (see the Supporting Information for details). In all cases, the bonding occurs almost exclusively between metal and nitrogen atom, while benzene rings remain almost intact trying to maintain the aromatic character.

This is evidenced, for example, by the charge accumulation in the charge density redistribution plot (Figures 3k,l) showing the same nodal plane structure as the LUMO density of the free molecule, see Figure 3m. The charge density redistribution for the isolated Cu₂Ph looks very similar. We therefore identify this as the main driving force for the strong attractive interaction between molecule and substrate in all adsorbed cases. A constant-height STM image recorded at very low bias voltage of the Cu₂Ph-complex, exhibiting the symmetry of the LUMO density (see Figure 3j) verifies the smearing of the LUMO over the substrate's chemical potential also experimentally and thereby supports the applicability of the donation/backdonation picture in our case. Ph without adatoms is attracted to the surface by the above mechanism until the attractive force is compensated by Pauli repulsion. The latter leads to a strong charge depletion directly between the molecule and the substrate (pillow effect)^{68,69} as can be seen in charge difference plots (see the Supporting Information for details). Most probable, this repulsion is also the driving force for the observed V-shaped geometry of the molecule. From gas phase calculations we quantified the energy cost of such a bending to be on the order of 1 eV ($\approx$ 23 kcal/mol).

Importantly, we observe that the bonding to copper adatoms in CuPh and Cu₂Ph maintains a similarly strong hybridization between molecule and copper sp -like states for a large molecule-substrate distance. In fact, this seems to be the key for the bonding mechanism: The presence of adatoms allows to increase the molecule-substrate distance and thereby reduces the Pauli repulsion, diminishing the energy cost of bending, while otherwise preserving the energy gain in the framework of donation/back-donation. In general, the bond strength between an adatom and an adsorbed molecule is characterized by the energy gain of the entire structure over the separately adsorbed species. Hence, since the hybridization of

molecular π -like orbitals does not significantly change upon bond formation, the avoidance of Pauli repulsion has a significant contribution to the large bond strength in CuPh and Cu₂Ph.

Specifically, we obtain an adsorption energy of 1.7 eV (39 kcal/mol) for isolated Ph, and a bond strength of 0.8 and 1.0 eV (19 and 23 kcal/mol) for the first and second bond to adatoms, respectively. These observations highlight the striking difference of bonding between different adsorbates in an on-surface geometry as compared to solution chemistry. In this context we reiterate that copper adatoms are almost charge neutral – in strong contrast to the usual charge state of copper (Cu^I/Cu^{II}) undergoing a coordination bond in solution. This opens up the possibility to study bonding mechanisms that are not accessible in solution chemistry. Instead, here the constrained geometry arising from the rigidity of the surface plays a most important role in the bonding.

CONCLUSION

In this article we presented unexpected bonding mechanisms between phenazine molecules and Cu adatoms on a Cu(111) surface based on scanning probe measurements and DFT calculations. Our results show that the bonding is not provided by a coordination bond, but by a covalent bonding including donation and backdonation of π -like orbitals of the molecule and sp -like metallic states. These observations should not be limited to the specific bonding partners studied here. Our results shed new light onto bonding mechanisms in on-surface geometries in general with implications for the field of catalysis involving on-surface reactions in UHV conditions.

ASSOCIATED CONTENT

Supporting Information.

Charge redistribution plots; calculated molecular orbitals; projected densities of states; cluster calculations in the gas phase; geometries used for calculations; experimental STM-images; dI/dV-data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENTS

Fruitful discussions with Laerte L. Patera, Florian Albrecht and Sophia Sokolov as well as financial support from the Graduiertenkolleg “GRK1570” and the German-Czech bilateral project Nos. RE2669/4; 14-16963J are gratefully acknowledged. P.J. acknowledges support from Praemium Academie of the CAS, MEYS LM2015087 and GACR 18-09914S. M.O. thanks LO1305 by MEYS and Miro Medved' for help.

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