

OBSERVING AND STEERING THE FORMATION OF COORDINATION COMPOUNDS ON SURFACES AT THE SINGLE-MOLECULE LEVEL

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Towards the end of the 19th century Alfred Werner formulated the basics of coordination theory, which describes how a central transition metal atom interacts with a set of surrounding molecular ligands. Coordination compounds are of high scientific interest: they play an important role in many biological processes and are employed in the synthesis of novel supramolecular architectures and materials. A rich variety of three-dimensional molecular nanostructures and architectures with well-defined shape and geometry have been obtained using transition metal centers and concepts from coordination chemistry. However, efforts to implement this concept to low-dimensional systems are scarce. In order to gain direct insight into the nature of coordination compounds at surfaces, we have carried out single-molecule level investigations using scanning tunneling microscopy (STM) to analyse compound formation and structure, and to develop recipes for controlled metal-organic assembly.

In our studies both molecular ligands and metal centers are provided by vacuum deposition of organic molecules/metals from molecular beam evaporators onto an atomically clean single crystal Cu(100) surface, giving precise control of both absolute and relative concentrations of the respective constituents. Also the substrate temperature is well defined by a cooling/heating stage to control of reaction kinetics and to achieve thermodynamic equilibrium. STM characterization was performed in situ under ultra-high vacuum conditions to avoid contaminations from ambient gases or dusts.

Dynamics of single chemical reactions and quantification of reaction energetics. When 1,3,5-tricarboxylic acid (tma) molecules are deposited on the substrate held at room-temperature, their carboxylic groups are deprotonated. The resulting reactive molecular ligands readily interact with naturally occurring Cu adatoms (under the employed conditions there is a gas of highly mobile Cu adatoms on the surface which are evaporated from atomic steps). In sequences

of STM images the process of individual complexation reactions could be monitored. Fig. 1 shows the displacements and rotations of single molecules and records how a Cu atom (red dot) is trapped by four tma molecules and subsequently released again. Thus single events of association and dissociation of cloverleaf-shaped $\text{Cu}(\text{tma})_4$ coordination compounds were directly observed.

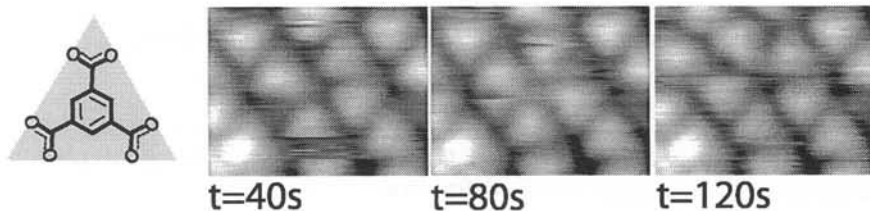


Figure 1: *tma*-molecules bond in a flat adsorption geometry at a $\text{Cu}(100)$ surface and are resolved as equilateral triangles in STM. The sequence of STM images reveals how the thermal motion of molecules at the surface proceeds. Following rotational motions and displacements a Cu adatom (red dot) is captured whereupon a cloverleaf-shaped $\text{Cu}(\text{tma})_4$ coordination compound evolves (second image for $t = 80$ s; see also http://www.mpi-stuttgart.mpg.de/kern/Res_act/supmat_2.html).

From an analysis of STM image sequences recorded with high scanning velocities (9 seconds per frame) at various temperatures, the temperature-dependent average lifetimes of isolated cloverleaves are determined. The inversion of these values provides the mean dissociation rates. These rates obey an Arrhenius law from which an energy barrier of 0.31 ± 0.08 eV for the dissociation reaction is deduced. Note that this value is smaller than typical binding energies of related compounds in the gas phase.

Furthermore it turned out that the lifetime of the compounds depends crucially on the local chemical environment. For instance, with two compounds neighboring each other the average lifetime is typically more than three times longer than that of an isolated species. This suggests different reactivity, i.e., two neighboring species are more stable than isolated ones. Similarly increased lifetimes were observed for compounds at step edges. Since all measurements were made at the same temperature, this variation of reactivity is associated with steric effects depending on the specific local conditions of individual reactions.

It is important to note that the nature of the coordination bond is expected to be modified in the presence of the electrons from the Cu conduction band. Therefore, it is important to note that the $\text{Cu}(\text{tma})_4$ compound cannot be regarded as an isolated entity as the coordination bonding and the electronic states of both Cu and tma are affected by the presence of the metal surface electrons effectively screening charged adsorbates. Thus an isolated

deprotonated tma molecule should not be considered as $(\text{tma}_{\text{ad}})^{3-}$, but rather as neutral $\text{tma}/\text{Cu}(100)$ configuration. As a consequence the oxidation state of the Cu in the $\text{Cu}(\text{tma})_4/\text{Cu}(100)$ compound cannot be determined unambiguously.

Creating chiral compounds out of achiral molecules. A chiral object is not superimposable onto its mirror image. Chirality is encountered at different levels, from single molecules and supramolecular assemblies to living organisms. Chiral molecules play an important role in biology and pharmacology. We succeed in creating chiral coordination compounds from achiral reactants - iron atoms and tma molecules. Again the reaction took place with the constituents adsorbed at the Cu(100) surface where a cloverleaf-shaped $\text{Fe}(\text{tma})_4$ compound evolves. However, a stronger interaction between the central Fe atom and the carboxylato ligands is encountered in this system. As a consequence there is an increased thermal stability and a more compact compound structure.

It can be seen in Fig.2 that in a compound the tma molecules do not point straight towards the center Fe. Rather, their triangular envelope is rotated by 22.5° clockwise or counterclockwise with respect to the principal axes of the compound.

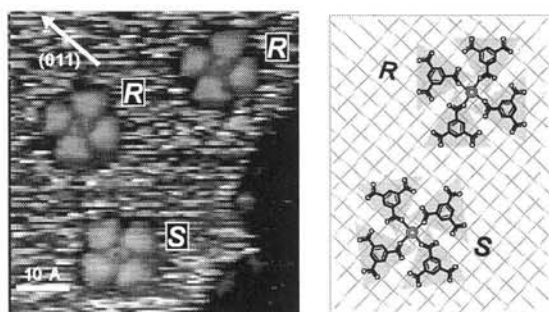


Figure 2: *Synthesis of $\text{Fe}(\text{tma})_4$ compounds at a copper substrate. There is a unidentate bonding and a correlated orientation of the four tma molecules surrounding the central Fe atom. As a consequence two mirror-symmetric compounds can be formed, designated with R and S, i.e., the system is chiral in two dimensions.*

This is associated with a unidentate Fe-carboxylate bond, where one of the oxygen atoms of the carboxylate group involved in the bonding comes significantly closer to the central Fe atom than the other. In addition there is a strict correlation of the rotation in any given complex. As a result of this symmetry breaking two distinct compounds exist (labeled R and S) which cannot be superimposed onto each other by translation or rotation on the surface. They are mirror-symmetric configurations with respect to the [011] direction of

the substrate and thus represent two $\text{Fe}(\text{tma})_4$ enantiomers on $\text{Cu}(100)$. This represents the first observation of a chiral coordination compound at a surface.

Modular assembly of surface-supported coordination networks. For many applications the controlled realization of metal-organic architectures with specific topologies and a high structural stability at well-defined substrates is desirable. We succeeded in developing a new strategy to fabricate surface-supported coordination networks by modular assembly of 1,2,4-benzenetricarboxylic acid molecules (tma) and Fe atoms at a surface. The networks are stabilized by relatively strong lateral metal-organic coordination bonds and consist of regularly spaced nanocavities of identical size and shape. The precise control of the concentration ratio of the components allows for the assembly of distinct architectures. This approach opens up new possibilities for the bottom-up fabrication of low-dimensional functional materials.

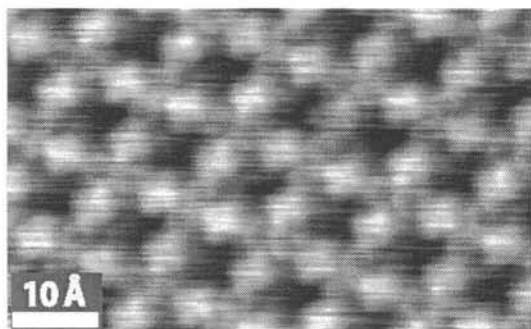


Figure 3: *STM topograph showing a regularly ordered metal-organic network structure comprising nanocavities. Single protrusions (highlighted in green) at the network's points of intersection are associated with Fe atoms, laterally coordinated by tma carboxylato moieties.*

(I guess showing the corresponding model might help to understand what's actually going on)

In the STM image reproduced in Fig. 3 we demonstrate an example of a regular coordination network assembled at the $\text{Cu}(100)$ surface: pairs of Fe atoms (highlighted by green dots) are linked to tma molecules, which gives rise to an extended open network architecture comprising cavities with a well-defined shape. These cavities have a size of $5 \text{ \AA} \times 5 \text{ \AA}$ and are regularly spaced forming an array with a 10 \AA periodicity.

It is interesting to address the potential functionality of the networks. Firstly, the periodically arranged magnetic atoms which are mediated by organic linkers represent a nanoscale magnetic system. On the other hand, the well-defined nanocavities may find an application in selective molecular or ion adsorption.

Finally, the long-range order provides potential templates for three-dimensional molecular architectures, such as nanoporous frameworks.

These research efforts represent first steps in the exploration of the nature and bonding mechanisms in coordination compounds at surfaces, a research field where our current knowledge is rather limited. In view of the remarkable structures obtained such as the chiral cloverleaf compounds and the metal-organic networks, it is expected that a systematic understanding of the underlying chemistry and physics will be of significant value for the deliberate synthesis of surface-supported functional supramolecular architectures and nanostructures.