

# Squaring the Interface: “Surface-Assisted” Coordination Chemistry

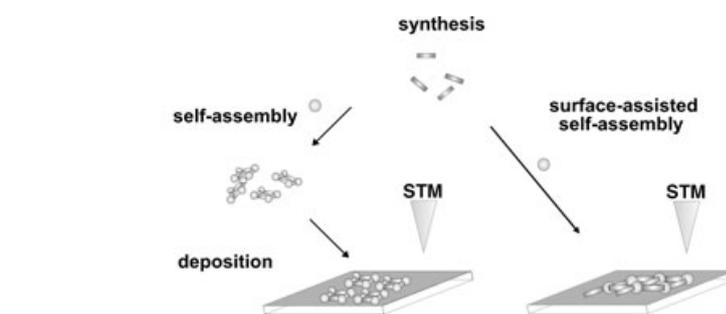
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The potential of highly ordered metal-ion arrays to be used in molecular information storage and processing devices was recently highlighted.<sup>[1]</sup> Among the set of possible architectures, two-dimensional (2D) gridlike arrays of ion-based switchable elements have attracted particular interest due to their structural similarity to components of some of the newest information processing concepts.<sup>[2,3]</sup> So far, the investigation of metal-ion arrays within the nanometer regime has comprised the following steps: the synthesis of the ligand molecules, the self-assembly into supra-molecular entities, and the controlled deposition or anchoring of the supra-molecules on or at surfaces (Figure 1, left), where the metal-ion arrays can be addressed by state-of-the-art single-molecule techniques (generally AFM- and STM-based).<sup>[4]</sup> However, this sequence of synthesis, self-assembly, and deposition is not merely a scientifically necessity, since it also reflects, at least partially, the historic background of an evolving interdisciplinary collaboration of scientific groups anchored in chemistry and physics.

A conceptually alternative route towards nanosized metal-ion arrays on surfaces was developed recently (Figure 1, right). This straightforward self-assembly protocol is based on the near-surface metal-ion coordination of simple ligand systems.<sup>[5,7]</sup> Using such approach,



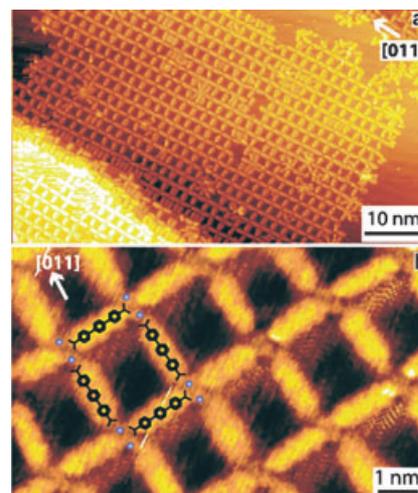
**Figure 1.** Schematic representation of two approaches for the construction of molecular structures on surfaces. Left: the sequence of synthesis, self-assembly, and deposition. Right: surface-assisted self-assembly.

the groups led by K. Kern, J. V. Barth, and N. Lin at the Max-Planck-Institut für Festkörperforschung in Stuttgart and at the École Polytechnique Fédérale in Lausanne generated a variety of infinite metal-ion arrays just by controlling the codeposition parameters for organic dicarboxylic acid derivatives such as terephthalic acid and iron(0) atoms on Cu(100) surfaces under ultra-high-vacuum (UHV) conditions.<sup>[5]</sup>

In the first step the organic ligand was deposited by organic molecular beam epitaxy (OMBE) onto the Cu(100) surface. Subsequently, the metal atoms were deposited on top of the formed (and more or less complete) organic monolayer by electron beam evaporation. After a short annealing period (5 min at  $T=450$  K), during which self-assembly was initiated by the increased mobility of the molecular and ionic components on the surface, well-ordered regular structures emerged readily in domains of up to 50 nm in size (Figure 2).

The rectangular molecular assemblies shown were obtained on the copper(100) surface at an Fe/ligand ratio

of about 0.5:1. Structurally, they consist of dimeric  $\text{Fe}_2$  nodes connected by an organic backbone of orthogonally arranged ligand linkers to form an infinite



**Figure 2.** a) STM image showing the 2D topography of the extended gridlike Fe-ligand network; b) high-resolution image of the same network indicating the positions of the organic ligands backbone (Fe atoms of the interconnecting  $\text{Fe}_2$  nodes are represented as blue spheres).<sup>[5]</sup>

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network. The observed Fe pairs in the cross positions of the network deserve some attention due to their coordination characteristics: The two Fe centers are surrounded by two sets of two differently coordinating carboxylate groups; two of these are in a monodentate  $\mu^2$ -bridging mode and two in an apparently bidentate chelating mode (Figure 2b and Figure 3, MOCN-II). Overall, the coordination geometry of each of metal center is square-planar. However, since the resolution limits of the present STM data prevent clear distinction between the mono- and bidentate coordination modes of the two chelating carboxylate groups, the exact determination of the coordination geometry is not possible in all cases.

The Fe–O bond lengths estimated from the STM data are close to that in bulk materials ( $d(\text{Fe–O}) = 1.9\text{--}2.3 \text{ \AA}$ ),<sup>[6]</sup> and the metal–metal distance  $d(\text{Fe–Fe})$  is about  $5 \text{ \AA}$ . However, the observation of sometimes elongated Fe–O bonds might be indicative of a situation, in which both ligand and metal centers are in close contact with the Cu(100) surface, which is then apparently acting a template. Thus, the underlying crystal lattice along with the conduction band of the substrate might interfere structurally as well as electronically in the final positioning of the involved metal atoms relative to the organic ligands.

With regards to the ligands, near-edge X-ray adsorption fine structure (NEXAFS) studies have revealed that the ligand molecules are adsorbed with their phenyl rings almost parallel to the Cu(100) surface plane.<sup>[5]</sup> This kind of metal–ligand contact is reminiscent of the donor–acceptor interaction of neutral arene rings and electron-rich metal centers, a classical coordination motif in coordination chemistry.<sup>[8]</sup>

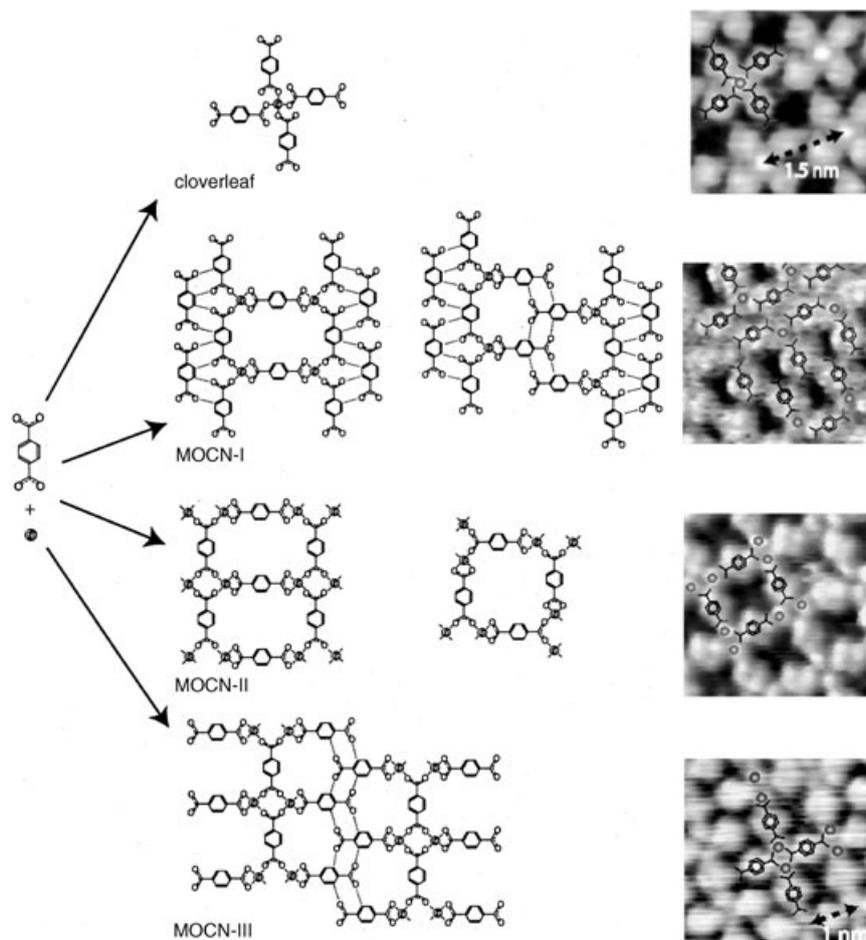
Since a strong interaction with the surface cannot be excluded, at least not at this stage, the discussion of the electronic properties (e.g. oxidation and spin states) of the coordination network components must involve rather unusual contributions like the electronic coupling of the metal centers to the substrate or possible counterbalancing of complex charges by mirror charges within the upper layers of the substrate. Only additional experimental data will clarify the picture and possibly

support alternative interpretations such as the formation of neutral precomplexes composed of the ligand and the Cu(100) mentioned by the same authors in two previous articles.<sup>[9]</sup>

However, considering the distinct  $\text{M}_2\text{L}_4$  stoichiometry of the dimeric  $\text{Fe}_2$  nodes, it seems reasonable to assume that the principle of electroneutrality also persists under near-surface conditions. This assumption would lead to the definition of two  $\text{Fe}^{\text{II}}$  ions surrounded by four deprotonated, negatively charged carboxylate groups. The formation of such electroneutral ( $4+/4-$ ) units will depend critically on the course of the deprotonation reaction, during which four protons are reduced to hydrogen molecules and simultaneously the two iron(0) centers are oxidized. The gaseous hydrogen could easily migrate into the UHV environment, thus driving the redox reaction to completion. The local

electroneutrality around the dimeric  $\text{Fe}_2$  nodes may also explain the high thermal stability of the 2D networks (up to 500 K); however, they are not stable to ambient gases. Obviously, further investigations concerning the electronic nature of the metal centers and ligands are necessary, and the results will be awaited with great interest.<sup>[5]</sup>

How the variation of the deposition parameters (e.g. ligand-to-metal ratio, annealing temperature) influences the formation of a set of different self-assembled modular structures was reported in more detail by the same authors in two further articles.<sup>[7]</sup> Depending on the  $\text{Fe}^0$  concentration, different network structures were formed from the same organic ligand, terephthalic acid, on the Cu(100) surface: these ranged from isolated mononuclear “cloverleaf” complexes to infinite 2D “ladder” coordination polymers to the



**Figure 3.** Structural formulas and STM images of the different network motifs (cloverleaf, MOCN-I–III) obtained on the Cu(100) surfaces by variation of the Fe/L ratio and the annealing temperature.<sup>[7a]</sup>

previously described gridlike 2D coordination polymers (Figure 3).<sup>[7a]</sup>

At lower Fe concentrations the connectivity of the molecular network is achieved in part by additional hydrogen bonds between the aromatic H atoms of the phenyl ring and the oxygen atoms of the carboxylate groups. At higher Fe concentrations the formation of the dimeric Fe<sub>2</sub>-based structures predominates. In general, it was found that the amount of iron used must slightly exceed the theoretical value of the structural motif formed. This effect, which is even more pronounced at higher annealing temperatures, is attributed to the loss of Fe atoms/ions in collateral surface reactions such as decoration of substrate steps, formation of Fe islands, and Fe–Cu intermixing processes.

The further elucidation of the coordination characteristics of metal centers in close contact with metal surfaces (coordination number, redox and spin state, metal–metal interactions, mirror charges, etc.) might mark the beginning of a new branch of “surface-assisted” metal coordination chemistry (maybe as an extension of the more bulk- and solution-based, conventional “Werner-type”<sup>[10]</sup> coordination chemistry). Together with other STM-based single-molecule surface manipulations (e.g. C–C bond formation, generation of surface chirality)<sup>[11,12]</sup> and new approaches towards nanomagnetism (e.g. spin-polarized STM),<sup>[13]</sup> such surface-assisted coordination chemistry might constitute part of the future tool kit needed for the construction and controlled manipulation of functional interfaces and operational surfaces.

Furthermore, the well-defined nanopores in these networks can be loaded with suitable substrates (e.g. C<sub>60</sub>)<sup>[5]</sup> which might be of importance for the design of many surface-dominated processes like heterogeneous catalysis and selective gas adsorption, and even for

the generation of optical metamaterials.<sup>[14–16]</sup> Interestingly, the emergence of dimeric metal units is also strongly reminiscent of structural features observed around the catalytic centers of some types of enzymes.<sup>[17]</sup>

It can be anticipated that the controlled design of functional surfaces by applying the principles of surface-assisted coordination chemistry not only opens new scientific perspectives but will also yield aesthetically appealing structures on surfaces that can be observed in real time.

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