Structure controlled self-assembly of Cu(II) salicylic aldehyde and aldimine derivative complexes

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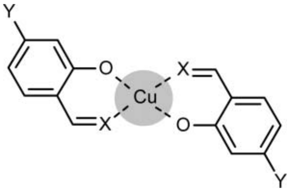
Received (in Cambridge, UK) 2nd September 2004, Accepted 17th November 2004
First published as an Advance Article on the web 25th January 2005
DOI: 10.1039/b413477j

The order of self-assembled monolayers of Cu(II) salicylic aldehyde and aldimine complexes has been gradually changed by ligand substitution and the resulting nanostructures have been studied at the graphite/liquid interface using scanning tunneling microscopy.

In the last few years there has been increased interest in the preparation of nanostructures as highly ordered monolayers on solid surfaces by self-assembly of metal complexes.[1] One major aim herein is the control of the relative metal positions. Some investigations have been performed *e.g.* in the field of phthalocyanine and porphyrin complexes, where the distances between the individual metal centers were controlled by insertion of alkyl side chains.[2] Suzuki *et al.* observed a Cu(II) "*in situ* complexation" of *n*-octadecyl salicylic imine ligands by a characteristic change of the molecular order.[3] Hipps *et al.* could even distinguish between separated metal ions by their characteristic brightness in the STM-image.[4] One important goal is the generation of functional surfaces for applications in fields such as electronics, sensors and catalysis, most probably through metal–metal interaction. In the present communication, we report on ligand design as a tool to control relative distances between Cu(II) ions within highly ordered monolayers of salicylic aldehyde and imine derived complexes.

The presented Cu(II) complexes (Scheme 1) were synthesised and characterised prior to the STM experiments. The free ligands were obtained following general methodologies previously reported in the literature.[5] The conversion to the desired complexes **1–3** was performed subsequently in one further step.†

STM measurements were carried out in the constant current mode under ambient conditions, using a low current RHK scanning tunneling microscope. STM tips were mechanically sharpened from Pt/Ir (90 : 10) wire. HOPG was used as substrate for the ad-layers. The complexes were dissolved in 1,2,4-trichlorobenzene and a droplet of the saturated solution (**1**: 6–7 mmol l^{-1}; **2**: 8–10 mmol l^{-1}; **3**: 22–24 mmol l^{-1}) was placed on freshly cleaved HOPG. The physisorbed monolayer of each complex was formed spontaneously at the graphite/liquid interface (within 5 min). During the STM experiments, the tip was immersed in the supernatant solution. The experiments were repeated in several sessions using different tips to confirm the reproducibility of the highly ordered assemblies. The brighter regions in the reported STM images correspond to ligand π-orbitals and related orbitals of the metal ions, whereas the interacting alkyl chains occur as darker areas. For the presented complexes **1–3**, it can be excluded that the images (Fig. 1–3) exhibit the free ligands.[6]



Scheme 1 Chemical structure of the Cu(II) complexes: **1**, X = O, Y = O–$C_{12}H_{25}$; **2**, X = N–H, Y = O–$C_{12}H_{25}$; **3**, X = N–$C_{12}H_{25}$, Y = O–$C_{16}H_{33}$.

Fig. 1(a) shows the STM image of the self-assembled monolayer of the salicylic aldehyde Cu(II) complex **1**, bearing C_{12}-alkyl chains (Scheme 1, **1**). Metal–metal distances of approximately 7 Å occur within each lamella (Fig. 1(b)). The alkyl substituents arrange with an angle of 42 ± 2° with respect to the main lamella axis. Thus, their periodicity is about 4.5 Å, as expected for densely packed alkyl chains.[8] According to the model (Fig. 1(b)), relatively short distances between adjacent aldehyde functions (2.8 ± 0.2 Å) are observed. Thus, attractive intermolecular interactions through double hydrogen bonds between the carbonyl O and H atoms combined with dipole–dipole interactions are proposed (Scheme 2).[9] The STM investigation of the corresponding C_8-substituted complex reveals a similar pattern, however with a reduced periodicity between the lamellae (C_8: 26 Å relative to C_{12}: 32 Å in the case of **1**) according to the shorter alkyl chains.

Substitution of the aldehyde O atom in **1** by an imine group leads to complex **2** (Scheme 1). Interestingly, the NH-function of **2** induces a significant change in the 2D molecular array, affording increased metal–metal distances of about 10 Å within each lamella (Fig. 2). Contrary to **1**, the alkyl chains from neighbouring lamellae of **2** are interdigitating. The angle between the aliphatic chains and the main lamella axis changes to 60 ± 2°, while the

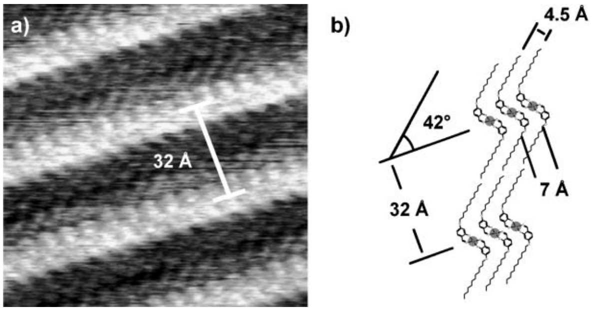


Fig. 1 (a) STM image of a monolayer of the Cu(II) salicylic aldehyde complex **1** physisorbed at the graphite/solution interface. Image area: 10 × 10 nm^2, V_{set} = −660 mV, I_{set} = 20 pA. (b) Molecular model of the monolayer.[7]

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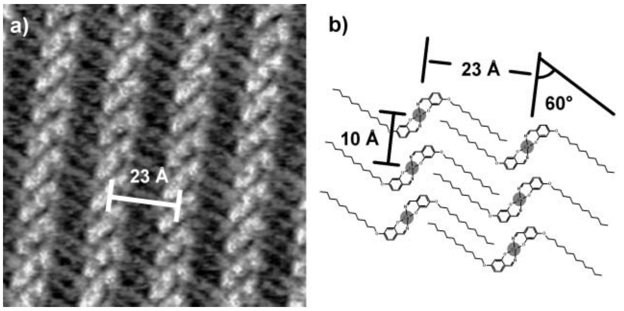


Fig. 2 (a) STM image of a monolayer of the Cu(II) salicylic imine complex **2** physisorbed at the graphite/solution interface. Image area: 10 × 10 nm^2, $V_{set} = -460$ mV, $I_{set} = 30$ pA. (b) Molecular model of the monolayer.[7]

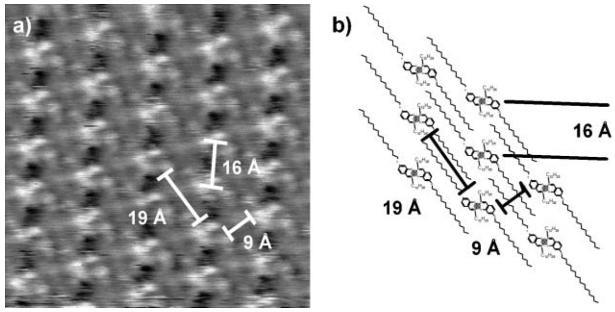
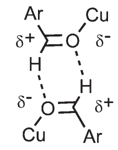


Fig. 3 (a) STM image of a monolayer of the Cu(II) salicylic imine complex **3** physisorbed at the graphite/solution interface. Image area: 10 × 10 nm^2, $V_{set} = -200$ mV, $I_{set} = 22$ pA. (b) Molecular model of the monolayer.[7]



Scheme 2 Proposed double hydrogen bonding and dipole–dipole interactions between the aldehyde groups of adjacent complexes within the 2D assembly of **1**.

typical space demand of approximately 4.5 Å per chain is maintained. Corresponding hydrogen bonds as proposed for the assembly of complex **1** (Scheme 2) cannot occur for complex **2** due to the proton of the NH group which blocks the acceptor function of the hetero atom. Hence, less attractive interactions between adjacent molecules of **2** compared to **1** lead to a less dense packing. The area per molecule increases from 2.1 ± 0.05 nm^2 (**1**) to 2.3 ± 0.05 nm^2 (**2**). Also in the case of **2**, the periodicity of the lamellae can be varied by the alkyl chain length (C_{16}: 27 Å relative to C_{12}: 23 Å for compound **2**).

Besides the "fine-tuning" of the packing by preventing the hydrogen bonds in **2** by introducing the NH groups, we expect further influence on the assembly by steric effects. Hence, the NH protons were substituted by *N*-alkyl substituents (NR, $R = C_{12}$) resulting in species **3**. Indeed, this change has a substantial impact on the order within the monolayer and suppresses the formation of lamellar structures completely, leading to clearly separated bright areas (Fig. 3 (a)). The complexes in monolayers of **3** now show further increased minimal Cu(II)–Cu(II) distances of approximately 16 Å due to the steric demand of the additional alkyl chains. Unexpectedly, a reasonable model (Fig. 3(b) with interdigitating C_{16} alkyl chains, *cf.* Fig. 1, **3**, $Y = O–C_{16}H_{33}$) which is applied to the STM image reveals that there is not enough space for the extra N–R chains to adsorb fully on the HOPG. Consequently, we suggest that the additional chains interact only partially with the surface pointing their tail into the solution. A further hint for this proposal are the dark spots in the STM image (Fig. 3 (a)) which are attributed to the $N–C_{12}H_{25}$ groups. They cannot be visualized due to their high mobility. The model is further supported by geometric parameters: the distance of 19 Å between the bright areas corresponds to the length of C_{16} O-substituents. The distance of 9 Å is in accordance with the space demand of two alkyl chains (4.5 Å each).

The variation of molecular parameters by complex design allows a well-defined decoration of surfaces. The presented complexes lead to a gradual expansion of metal–metal distances from very short 7 Å in lamellar layers up to 16 Å in structures bearing on separated complex "islands". We suggest that the differences in packing are governed by hydrogen bonding, dipole–dipole interactions and steric effects, respectively. Studies on secondary reactions, like reduction or metal deposition performed on the 2D layers are underway and will show if self-assembled functional surfaces are accessible by this technique.

The authors thank the *Deutsche Forschungsgemeinschaft* DFG through the "*Sonderforschungsbereich*" SFB 569 ("Hierarchic Structure Formation and Function of Organic–Inorganic Nano Systems") for financial support.

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Notes and references

† The complexes **1** and **3** were obtained by conversion of the corresponding free O-protonated ligands with stoichiometric amounts of Cu(II) acetate in ethanol (reflux for 30 min) and purification (filtration, washing with water, ethanol, diethyl ether, drying in vacuum). Complex **2** was obtained in analogy to complex **1**, also using the free salicylic aldehyde ligand, but in the presence of excess of ammonia (added as solution in methanol). This *in situ* formation of the imine complex **2** was followed because the free C=N–H imine ligand cannot be isolated as a pure compound. The complexes were characterised by EA (%) and IR (KBr (cm^{-1})). Supporting analytical data: **1**: Anal. Found: C 67.80, H 8.60; calcd for $C_{38}H_{58}CuO_6$: C 67.68, H 8.67; IR: 1626 (C=O). **2**: Anal. Found: C 67.76, H 9.04, N 3.96; calcd for $C_{38}H_{60}CuN_2O_4$: C 67.87, H 8.99, N 4.17; IR: 1617 (C=N); **3**: Anal. Found: C 74.93, H 11.09, N 2.44; calcd for $C_{70}H_{124}CuN_2O_4$: C 74.98, H 11.15, N 2.50. IR: 1609 (C=N).

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6 The complexation with Cu(II) plays a decisive role for the self-assembly and order of all the presented compounds. The free salicylic aldehyde ligand of **1** cannot be visualised by STM from 1,2,4-trichlorobenzene solution. The ligand of **2** is only stable in the complex and cannot be observed by STM. The free ligand of **3** shows a different order compared to the complex under the same conditions.

7 Molecular dimensions of the complexes **1–3** gained from the STM images correspond to the dimensions of the given models and are in high accordance with crystallographical data of the unsubstituted complexes (A. Elmali and Y. Elerman, *Z. Kristallogr.*, 1995, **210**, 613; B. E. N. Baker, D. Hall and T. N. Waters, *J. Chem. Soc. A*, 1966, 680) and molecular modelling investigations for the alkoxy substituted compounds.

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