

Steering Two-Dimensional Molecular Growth via Dipolar Interaction

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The growth of self-organized molecular networks is recognized as a nature-given, potential bottom-up solution for further miniaturization of electronic devices into the nanometer regime.^[1] With self-assembling processes being fully parallelized rather than sequential as in conventional top-down approaches as e-beam writing, molecule-based devices gain their potential from a rational design of the fundamental molecular building blocks for controlled bond formation. Relevant aspects are bonding directions and bonding mechanisms. Several different bonding mechanisms are established for network formation as hydrogen bonding,^[2] covalent bonding,^[3] or even metal–organic coordination.^[4] Although the impact of dipole–dipole interaction on network formation is reported^[5] the design of molecular dipole fields is so far not further exploited. Here we report for the first time on such an approach and switch by synthetic means between dominating repulsive and attractive forces among metal–organic complexes. The effect is demonstrated for Co(5,5'-X₂-Salen) complexes, X=H (1), Me (2), and Cl (3) locally monitored in ultra-high vacuum (UHV) by scanning tunneling microscopy (STM).

Salen complexes of transition metals are versatile and easily modified to tailor electronic, magnetic,^[6] and structural bulk properties. Salen complexes are present in a variety of applications in material chemistry and catalysis.^[7] Moreover, most complexes are volatile in UHV which enable local studies in a well-defined nanoscopic environment. In Salen complexes the metal center is surrounded by two nitrogen and oxygen donor atoms, which can lead to complexes in quite high oxidation states. The hydrogen atoms at the 5,5'-positions can be substituted by CH₃, F, Cl, Br, I, NO₂, etc. via the respective salicylaldehyde precursor. Here, individual Co-salen complexes adsorbed on a surface are studied for the first time by STM and reveal an insight into the mechanism of intermolecular coupling.

The experiments are performed in a variable temperature STM operated at ~25 K.^[8] Tips and Cu(111) surfaces are prepared by standard procedures with molecules sublimed from homebuilt Knudsen cells. Voltages refer to the potential of the tip relative to the sample. Positive voltages refer to tunneling into unoccupied sample states and negative voltages to tun-

neling out of occupied sample states. We focus on the analysis of STM images as acquired at -1.4 V, -0.1 V, and +1.4 V which are referred as 'at large negative bias', 'at low bias', and 'at elevated positive bias' throughout the text. Images at these biases show characteristic features as discussed below and are representative for images as acquired within a larger bias interval (~±0.5 V) with only gradual changes in between.

The chemical structures of the complexes used herein are presented in Figure 1 along with corresponding, equally scaled STM images at low bias of isolated molecules adsorbed on a Cu(111) surface. For visualization a scaled model of the structure is superimposed. For complex 1 the appearance of the complex in the STM image perfectly fits to the structure. Due to different substituents the apparent size of 2 and 3 varies in the topographic images. We will first focus on the appearance and adsorption of isolated molecules of complex 1, that is, after low temperature preparation which hinders thermally induced mobility and therefore self-assembling on Cu(111).

Figures 2b–2d show the same isolated molecule of complex 1 but as imaged at different energies. Imaged at low bias (Figure 2c), the molecule nicely fits to the molecular structure and exhibits a maximum in the apparent height at a location between the cobalt center and the top C₂H₄ bridge. Imaged at a large negative energy a pronounced topographic maximum at the site of the Co ion dominates the overall molecular appearance (Figure 2b). We interpret this as resulting from occupied Co 3d orbitals perpendicular to the molecular plane similar to the case of other metal-organic complexes.^[9] A significant change can be observed when tunneling through unoccupied molecular states at elevated positive bias: molecules become asymmetric and the maximum in the apparent height is shifted towards one side of the C₂H₄ bridge (Figure 2d). A first interpretation is suggested by results of DFT calculations for the free complex. In Figure 2a an optimized structure of complex 1 is depicted. The side view clarifies a C₂ symmetry due to a deformation of the C₂H₄-bridge which implies chirality.

STM measurements identified complexes adsorbed in 12 different configurations on the Cu(111) surface. Figure 2e shows all 12 configurations as imaged at low bias. The observable asymmetry at elevated positive energies (Figure 2f) unambiguously reveals two mirror symmetric (*R* vs *L*) sets of 6 molecules each rotated in steps of 60°. With the exact crystallographic axes determined from atomically resolved images of the bare substrate, two mirror symmetric enantiomers can be attributed to each crystallographic direction. Molecules denoted with *R* are rotated clockwise by +11°±3° relative to the substrate axes and with *L* anticlockwise by -8°±3°. This is schematically illustrated in Figure 2g.

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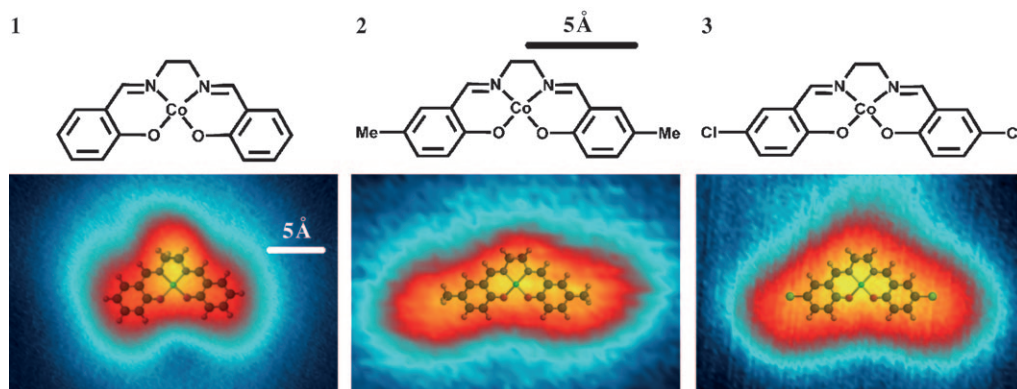


Figure 1. Chemical structures of Co(5,5'-X₂-Salen), X=H (1), Me (2), and Cl (3) along with equally scaled STM images which are superimposed by a scaled model (STM images 3×2 nm², -0.1 V).

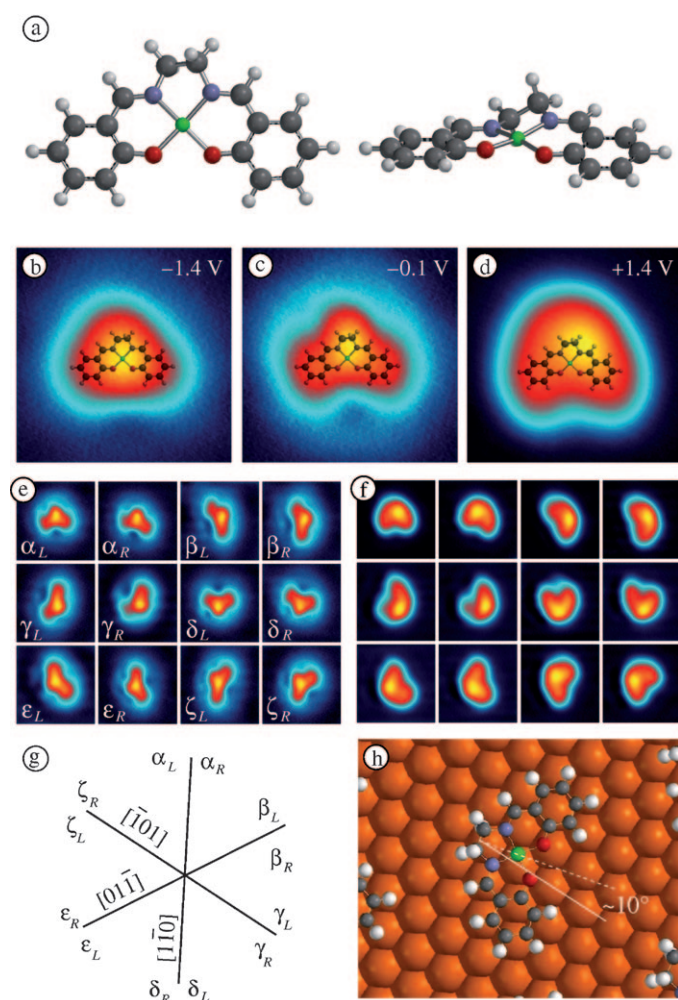


Figure 2. a) Structure of a Co-Salen complex as optimized by DFT methods with C₂ symmetry due to twisting of the C₂H₄-bridge. b)–f) STM images of individual Co-Salen molecules on Cu(111) imaged at b) -1.4 V, c), e) -0.1 V, d), f) +1.4 V (2.5×2.5 nm²). e), f) 12 configurations of Co-Salen are observable, 6 due to substrate symmetry and 2 due to chirality (3×3 nm²). g) Sketch of all 12 configurations with the substrate axes indicated as determined from an atomically resolved image of the bare substrate. h) Optimized complex on a Cu(111) surface corresponding to configuration ζ_L.

DFT calculations for complex 1 adsorbed on the Cu(111) surface were performed,^[10] which reveal the optimized structure in Figure 2h. The C₂ axis as defined for the free molecule is tilted by -10° relative to one of the closed-packed directions of the substrate. Such a molecule corresponds excellently to a left-handed molecule *L* as experimentally observed.

A detailed view on the results of the calculation is presented in Figure 3a. A distance of 325 pm between the Co-center and a best plane spanned by the Cu-surface atoms is found. The Co-center is shifted about 11 pm below the N₂O₂ ligand plane, indicating hybridisation of the Co-orbitals with substrate states. In addition, short distances, $d(\text{H}-\text{Cu})=254$ pm and 260 pm, between one of the C₂H₄-hydrogen atoms and Cu-atoms and distances of $d(\text{C}_6-\text{Cu})=325$ pm and 375 pm between the centroids of the C₆-rings of the salen ligand and the next by Cu-atom complete complex-surface interactions. Compared to the optimized structure in the gas-phase (Figure 2a) Co–O and Co–N distances are extended by 2 pm and 3 pm, respectively upon deposition of complex 1. A stereo inversion of the bridge leads to different H–Cu₂ contacts which result in a rotation of the molecule by about 20°, that is, to +10° relative to one of the closed-packed directions of the substrate.

So far isolated molecules of complex 1 are discussed. Apart from a complete decoration of monoatomic Cu steps (see Supporting Information), which is indicating high mobility during preparation, the deposition on a room temperature sample does not promote self-assembly. Instead, molecules stay fully isolated, which suggests a repulsive molecule–molecule interaction as reported for other planar hydrogen terminated molecules.^[11] An energetically favorable dimerization by a stacking perpendicularly to the molecular plane as in bulk material^[12] is prevented by the strong molecule–substrate coupling and was not observed.^[13] To overcome the present in-plane repulsive steric forces and to artificially equip Salens with the ability to form regular molecular networks, we introduced a substituent bearing a high polarity (Cl, complex 3) to outbalance the molecular charge distribution and induce a local attractive dipole moment (see Figure 3b).

In 3, chlorine serves as such a negative electric pole (–), which positively charges the molecular center (+). Complex 2

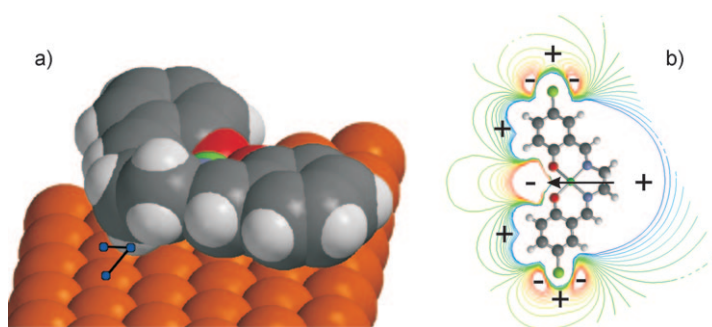


Figure 3. a) Van-der-Waals representation of deposited complexes; close contacts of one of the C_2H_4 -hydrogen atoms with surface Cu atoms (Cu-H = 254 pm, Cu-H = 260 pm) are depicted by blue dots. b) Contour plot of the potential landscape of the free molecule with red indicating locally acting negative poles and blue positive poles for $Co(5,5'-Cl_2-Salen)$. The arrow reflects the resulting total molecular dipole.

serves as an additional reference with a charge distribution close to complex 1. When studied as isolated molecules after low temperature preparation, all complexes share the same properties in terms of appearance, chirality and adsorption geometry.

Concerning self-assembly, the three complexes interact differently. Figure 4 shows representative images of complexes 1 to 3 adsorbed on Cu(111) after room temperature preparation. For complex 1 and 2, no indication for attractive interaction among the molecules is observed (compare Figures 4a and b). Molecules are mobile during preparation and stick to step edges and defects, but stay isolated on flat terraces during low temperature imaging, pointing to a repulsive interaction among molecules. With chlorine as substituent, molecules form peculiar six membered clusters (complex 3, see Figure 4c). Competing structures at lower frequencies are chains and four membered islands. These structures vary in orientation and chirality reflecting the manifold orientations of the single molecules and have a defined internal arrangement of molecules. Increasing the coverage to a full monolayer decoration, a large scale regular self-assembled network structure is observed. The six membered cluster is identified as the building unit of this network (see white circle in Figure 4d). Large domains with different molecular orientations are observed as shown in Figure 4e. A schematic drawing of these domains is plotted in Figure 4f along with their orientations indicated by arrows. Four different orientations (out of six possible) are present in the given example.

Figures 5a and b show two of these fundamental building units as isolated entities imaged at low and elevated positive bias. These two clusters are mirror symmetric to each other, revealing two of the six different orientations. The mirror axis runs along the $[1-\bar{2}1]$ direction of the substrate and is indicated by the white line. The image at elevated positive bias (Figure 5b) reveals the chirality for each individual molecule (*R* or *L*). Each cluster is composed of individuals of both chiral types at a fixed ratio of enantiomers of 4:2. For illustrations Figure 5c presents the internal molecular arrangement of the right cluster (in Figure 5a) as experimentally deduced. Molecules are aligned as ex-

pected from the controlled charge redistribution by the electro-negative chlorine. Oppositely charged sides [Cl(-), H(+)] of the molecule face each other due to attractive Coulomb forces. This results in stabilized molecular units, which overcome the repulsive forces among uncharged molecules. Moreover, due to the symmetric arrangement in six membered clusters the resulting dipole moment is zero. Coulomb forces among molecules are superimposed by local directional molecule-substrate forces, which determine the arrangement of molecules relative to the substrate as for isolated molecules. Nevertheless indications for additional repulsive forces decisive for the actual molecular arrangement in the six membered clusters are present. Homorace clusters as well as clusters with the molecules α_R and δ_R (see Figure 5c)

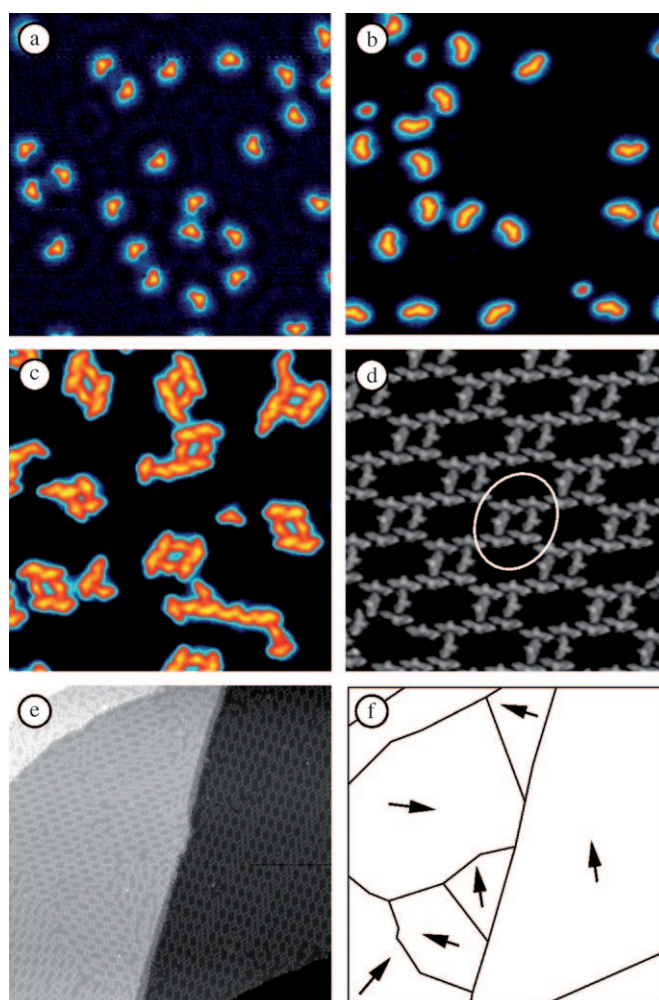


Figure 4. a)–c) $Co(5,5'-X_2-Salen)$, X = H (a), Me (b), Cl (c) after room temperature preparation on Cu(111). Chlorine terminated complexes show self-assembly on the surface (All images $25 \times 25 \text{ nm}^2$, -0.1 V). d) Full monolayer coverage leads to formation of regular network structures revealing the six membered cluster (white circle) as the building unit of the network ($15 \times 15 \text{ nm}^2$, -0.5 V). e) Large scale overview image shows differently oriented domains in the network ($100 \times 100 \text{ nm}^2$, -0.5 V). f) Schematic representation of (e) indicating the directions of the different domains by the black arrows.

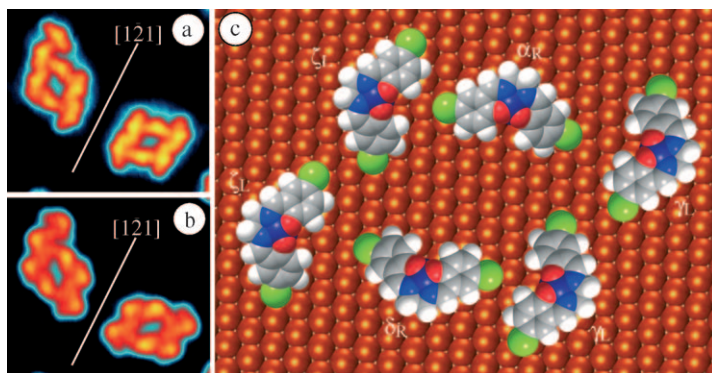


Figure 5. Two self organized Co(5,5'-Cl₂-Salen) clusters on Cu(111) imaged at a) -0.1 V, b) $+1.4$ V. c) Structure of a six membered cluster as deduced from the STM image. The cluster is composed of both enantiomers at a fixed ratio of 4:2 (STM images 12×9 nm²).

pointing inwards would result in a closer arrangement of the cluster. Since this was never observed, it is interpreted as a repulsive interaction among the hydrogen terminated sides. The same interpretation holds for observed chain structures and four membered islands.

Concluding, directional forces between Co(5,5'-X₂-salen) complexes and a Cu(111) surface compete with attractive intermolecular ionic forces and with repulsive forces among hydrogen terminated sides. Tuning the ionic forces by exchange of substituents switches between the ability to form two-dimensional molecular networks (Cl) and being fully repulsive (H, Me). Our results demonstrate a new route to steer directional growth beyond established mechanisms.

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- [13] Up to a coverage of 3ML of complex 1, no regular self-assembly was observed. Beyond 3ML stable imaging became impossible.

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