Design of Extended Surface-Supported Chiral Metal-Organic Arrays Comprising Mononuclear Iron Centers

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A design strategy for fabricating a surface-supported chiral metal-organic system comprising a regular arrangement of mononuclear iron centers and nanocavities is presented. By sequential deposition of 1,2,4-benzenetricarboxylic acid (tmla) molecules and iron atoms on a Cu(100) surface under ultrahigh vacuum conditions, chiral square-planar Fe(tmla)₄ metal-organic complexes are generated, which order in extended homochiral arrays. Structure formation and envisioned functionality of such metal-organic architectures are discussed.

Complexes comprising mononuclear transition-metal centers with catalytic activity are a recurrent theme in chemistry and biology[1,2] and have been used in industrial asymmetric synthesis for decades.[3,4] Such species can be anchored at adequate supports by means of surface chemical methods, which represents a promising approach to materials combining advantages of both homogeneous and heterogeneous catalysis.[5,6] An important feature is the control of the chiral signature of such systems—asymmetric heterogeneous catalysis requires asymmetric active substrates.[7−10] Both fields were recently stimulated by scanning tunneling microscopy (STM) studies, which allow one to address molecular chirality and organization phenomena at surfaces at the level of single molecules.[11−18]

In this letter, we report the use of a two-dimensional trimellitic acid (1,2,4-benzenetricarboxylic acid, tmla) molecular precursor layer to fabricate extended enantiopure arrays of mononuclear chiral Fe−tmla complexes on an atomically clean Cu(100) substrate. Our results exploit a methodology introduced in previous studies, where we demonstrated how metal-organic complexation can be conducted at well-defined surfaces under ultrahigh vacuum (UHV) conditions using polytopic carboxylate linker molecules and transition-metal centers. Using this approach, protocols for the modular assembly of distinct low-dimensional metallosupramolecular architectures including nanoporous phases were obtained.[19−24]

The experiments were performed in a UHV chamber equipped with surface preparation and analysis tools and a variable-temperature scanning tunneling microscope. Preparation of Cu(100) and deposition of tmla molecules (powder form, Sigma-Aldrich, 99%) and Fe followed procedures outlined in earlier publications.[19−24] Both tmla and Fe were dosed with the substrate held at elevated temperatures (400−450 K) to increase the mobility and reactivity of the adsorbates and thus to drive the formation of well-ordered structures. STM experiments were subsequently performed in situ following cool-down to room temperature.

With appreciable tmla concentrations (coverage exceeding 0.6 monolayers (MLs); 1 ML corresponds to a close-packed organic layer), regular molecular layers inducing large substrate terraces extending in the 100 nm range are formed.[23] Typically, wide terraces alternate with bunches of narrow ones. The step-terrace reconstruction of the surface covered with the organic layer is clearly distinct from that of the pristine surface.[23] This well-ordered phase is the decisive precursor for the formation

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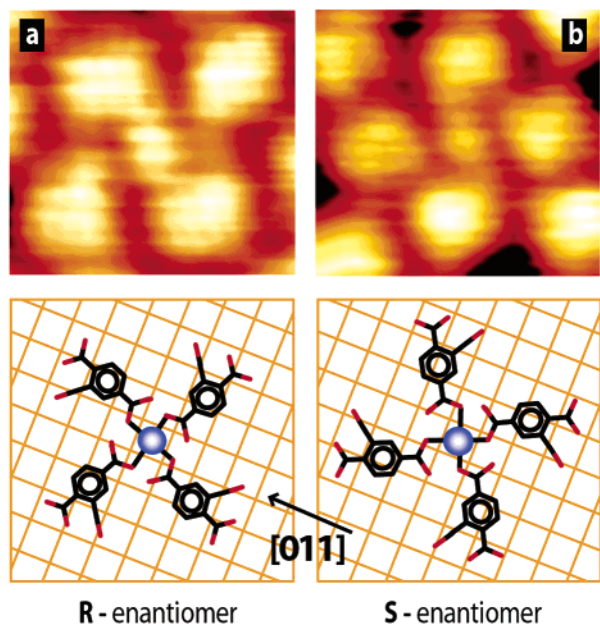(20) Lingenfelder, M.; et al. *Chem.—Eur. J.* **2004**, *10*, 1913.
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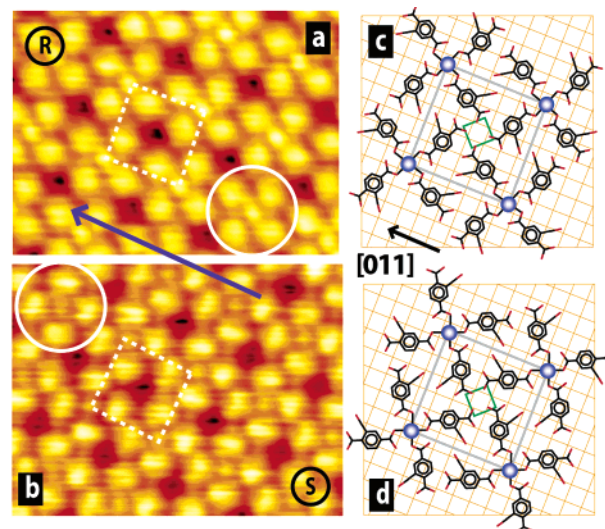(24) Spillmann, H.; Dmitriev, A.; Lin, N.; Messina, P.; Barth, J. V.; Kern, K. *J. Am. Chem. Soc.* **2003**, *125*, 10725.

Figure 1. STM images and modeling of the two mirror-symmetric species of cloverleaf-shaped mononuclear Fe(tmla)$_4$ complexes, denoted as R- and S-enantiomers, which develop upon deposition of small amounts of Fe on preformed tmla organic layers on the Cu(100) square substrate. The chirality of the complexes is a result of the correlated unidentate Fe−carboxylate linkages of tmla molecules to Fe centers. Image size: 20×19.5 Å^2. Details of the molecular arrangement are shown in the corresponding tentative geometric models for each enantiomer (the Fe centers are shown in blue; the underlying grid visualizes the substrate square symmetry). Cu[011] azimuth is indicated.

Figure 2. Packing of metal-organic complexes in arrays comprising a regular positioning of Fe centers and nanocavities. (a and b) STM data of two enantiopure domains with mirror-symmeteric arrangements (the R- and S-enantiomers are shown in parts a and b, respectively). For both cases, a square unit cell is found (dashed in white). Individual mononuclear complexes of each handedness are highlighted by white circles. Image size: 63.4×48.4 Å^2. (c and d) Tentative geometric model for the organization of Fe(tmla)$_4$ in nanoporous arrangements. The carboxylate groups at the *ortho* position of each tmla are presumably rotated out-of-plane to allow for an effective packing of the complexes in arrays and improved substrate coupling. Chiroselective interactions between individual complexes stabilize enantiopure arrays comprising species of exclusively one handedness. Cu[011] mirror-symmetric axis indicated by an arrow. The lattice defined by Fe centers (shown in blue) is represented by a (6×6) unit cell marked in gray. Nanocavities formed by packing of four complexes are indicated by green squares.

of enantiopure extended arrays of densely packed chiral mononuclear metal-organic structures, as it offers pre-organized carboxylic groups which readily react with co-deposited Fe adatoms.[19−24]

Here, we concentrate on the scenario encountered at small Fe concentrations (Fe coverage of ∼0.03 ML). Upon Fe deposition with the substrate held at 450 K, distinct chiral entities evolve in the form of two mirror-symmetric cloverleaf-shaped arrangements, as depicted in Figure 1. Similar to the metal-organic structures described previously, the cloverleaf motif is identified as a mononuclear species reflecting the metal-directed assembly of four tmla molecules in a square-planar fashion around a central Fe atom; that is, mononuclear Fe(tmla)$_4$ complexes are formed. Comparison of parts a and b of Figure 1 evidences the existence of two enantiomeric species, which are nonsuperimposable upon in-plane rotation or translation. The asymmetric molecular structure of tmla prevents the direct identification of the exact coordination geometry of the complex, which was possible for the previously studied Fe−tma (1,3,5-benzenetricarboxylic acid) system, where a straightforward correlation of molecular geometry and STM topography exists. However, it is generally known for the STM imaging mode of small organic adsorbates on metal surfaces that the topography shows specific C−C bonds rather than positions of individual C atoms.[25] By keeping this in mind and relying on our experience from previous studies on similar systems,[19−24] we suggested the tentative geometric models for both Fe(tmla)$_4$ enantiomers reproduced in Figure 1. The chirality of the individual complexes is understood as a consequence of correlated unidentate linkages of tmla carboxylate groups

to the central Fe atom, as indicated in the model.[22] In analogy with previously studied systems, the two types of enantiomers are denoted R and S, with the Cu[011] azimuth representing a mirror-symmetric axis (cf. Figure 1). We presume a conformational adaptation of the individual molecules in the form of out-of-plane rotations of the *ortho* carboxylate group which allows the avoidance of a too close rapprochement of negatively charged oxygens of neighboring complexes and a better coupling of the tmla to the underlying substrate (cf. the caption of Figure 2). This is expected to induce distortions and a slight out-of-plane tilt of the molecular plane (geometric modeling suggests that the tilt does not exceed ∼30° in view of the C−O bond length of the rotated carboxylate group). All carboxylic groups are expected to be deprotonated to carboxylate moieties in the course of complexation.[23] The high-resolution STM topographs reveal an asymmetric appearance of tmla in the cloverleafs, whence we assume that the *ortho* carboxylate group is generally positioned away from the Fe centers.

Moreover, a regular ordering of the individual complexes in the form of regular arrays occurs, which are in registry with the underlying substrate atomic lattice. An analysis of corresponding STM data, such as the images shown in Figure 2, demonstrates that the distance between adjacent Fe centers in the arrays amounts to six Cu lattice constants ($a_0 = 2.55$ Å) in both high-symmetry directions of the square substrate. A detailed inspection of the data reveals that this superstructure is present in all cloverleaf superlattices, which can be accordingly described by a (6×6) unit cell, where the central Fe atoms span a square lattice with a 15.3 Å stride both along the [011] and [0$\bar{1}$1]

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directions. Enantiomeric R and S types of Fe(tmla)$_4$ complexes are identified within different arrays. Thus, one type represents the mirror image of its counterpart with respect to the Cu[011] azimuth (shown by the blue arrow in Figure 1a,b). Moreover, because exclusively complexes with a distinct chiral signature are found in a given domain, the cloverleaf array represents a supramolecular homochiral arrangement. The complexes are sterically packed to form an extended regular topology of mononuclear iron centers in a local chiral ligand arrangement.

With the help of the geometric models for the mirror-symmetric arrays presented in Figure 2c,d, insight into the principles underlying the organization of individual complexes in homochiral arrays can be gained. The structure of the molecular templating adlayer, provided by the tmla precursor domains, does not inhibit tmla reorientation processes (flipping) in the elevated-temperature evolution of complexes and arrays. A possible scenario would be that the initial chirality signature of a domain is generated in the folding of an individual complex, which necessarily involves a symmetry break. In the subsequent array evolution, chirality proliferation occurs and as a consequence entire terraces are covered by homochiral arrays. In any case, the homochiral nature of the Fe(tmla)$_4$ arrays implies that chiroselective interactions are decisive in the superstructure formation. At the origin of these interactions are presumably the anionic carboxylate groups at the exterior of the cloverleafs, which can effectively couple laterally to the aromatic rings of adjacent Fe(tmla)$_4$, potentially through hydrogen bonding or weak electrostatic forces. An appealing extension of the present approach is to use appropriate enantiopure 3-D chiral carboxylate linkers in order to obtain an entirely homochiral metal-organic nanostructured surface.

It is interesting to compare the present scenario leading to well-ordered domains with metal-organic superstructures occurring with the Fe−tma (1,3,5-benzenetricarboxylic acid) system on the same substrate. While the chemical nature of the employed ligands is in both cases identical, their geometric arrangements are different (tma is a molecule with 3-fold symmetry). Whereas the coordination motif in isolated mononuclear Fe(tma)$_4$ chiral complexes is similar to the one in the Fe(tmla)$_4$ array, the different tma symmetry and substrate lattice match obviously prevent the formation of regular precursor layers and cloverleaf domains with tma.[22,24] Also, at higher coverages, the geometrically simple 1-D and 2-D coordination arrays obtained with Fe and carboxylic acids providing linear linkages (tmla; tpa, 1,4-benzenedicarboxylic acid; and its higher analogues)[20,21,23] contrast the intricate nanoporous open-cavity networks fabricated with tma.[24] These results provide convincing evidence that carboxylate groups in *para* orientations are a decisive ingredient for obtaining well-ordered mononuclear metal-organic arrays with the carboxylate linkers on the Cu(100) square substrate.

Because chiral metal-organic arrays evolve on the basis of ordered tmla domains, they tend to preserve the surface morphology of the precursor layer: wide terraces contain well-ordered structures, while on narrow ones only randomly scattered aggregates are encountered (cf. Figure 3a). The STM image in Figure 3b illustrates the long-range ordering in the homochiral array: the structure is mesoscopically strictly (6 × 6) commensurate with the underlying Cu substrate. In marked contrast to the
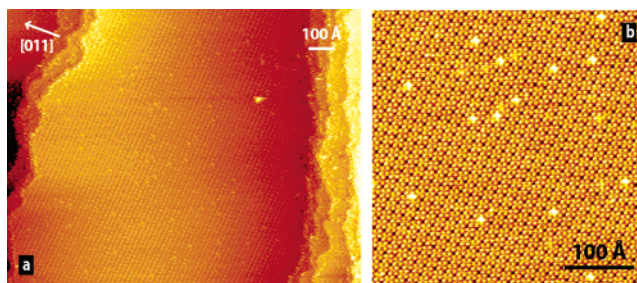
Figure 3. Large-scale view of extended metal-organic arrays. (a) Terraces with very large widths comprising homochiral metal-organic arrays result from the deposition of precursor tmla adlayers on the substrate held at 400 K. The Cu[011] azimuth is indicated. (b) The zoom into the domain shown in part a reveals the high degree of ordering in the metal-organic arrays—homochiral cloverleaf-shaped Fe(tmla)$_4$ complexes cover the entire monatomic terrace. White spots are residual impurities adsorbed in nanocavities.

previously investigated systems, the presence of the precursor layer thus promotes an extended array size comprising regularly arranged Fe(tmla)$_4$ metal-organic complexes. Only monatomic step edges limiting the terraces act as a natural boundary for the domain size, which can effectively extend to several hundred nanometers. Thus, metal-organic layers comprising mononuclear Fe centers in a well-defined environment with a local chiral order of ligands and long-range periodicity approaching the micron scale can be obtained on the Cu(100) substrate.

The openings of the underlying Cu substrate between the complexes in the arrays, imaged in STM as square depressions, represent chiral cavities functionalized by the surrounding tmla ligands. They amount to 4 Å in size and, following the geometric model (cf. Figure 2c,d; the cavities are highlighted in green), are rationalized as Cu(100) substrate hollow-site openings, surrounded by four carboxylate moieties in a chiral geometry. Thus, the well-ordered arrays of chiral Fe(tmla)$_4$ complexes simultaneously provide a system comprising chiral cavities organized in a (6 × 6) superstructure with respect to the Cu(100) substrate. Their functionality as asymmetric hosts for inclusion of small molecules or functional moieties is potentially useful; for instance, a close look at the STM image shown in Figure 3b evidences that the formed cavities readily host residual impurities imaged as white protrusions.

In summary, we succeeded in the design of an extensively ordered surface-supported chiral metal-organic system comprising a regular arrangement of mononuclear iron centers and nanocavities. Individual Fe−tmla complexes develop on the base of precursor tmla adlayers, which change the morphology of the substrate and allow for the formation of large homochiral metal-organic arrays, laterally extending up to 200 nm. It is expected that this unique structural arrangement has specific catalytic functionality due to the availability of mononuclear Fe centers and nanocavities in a regular spacing and correlated chiral environment—first studies to address the reactivity of such systems toward coadsorbed molecular species are currently underway.