

## Direct Observation of Chiral Metal–Organic Complexes Assembled on a Cu(100) Surface

Paolo Messina,<sup>†</sup> Alexandre Dmitriev,<sup>†</sup> Nian Lin,<sup>\*,†</sup> Hannes Spillmann,<sup>†</sup> Mathieu Abel,<sup>†</sup> Johannes V. Barth,<sup>‡</sup> and Klaus Kern<sup>†,‡</sup>

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany, and Institut de Physique des Nanostructures, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

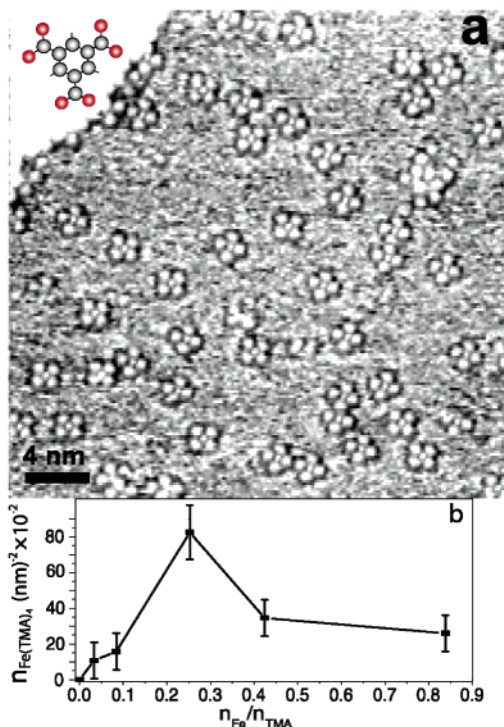
Received September 16, 2002

Chirality is a topic extensively studied in chemistry, biology, and pharmacology. It is encountered at different levels, from single molecules and supramolecular assemblies to living organisms.<sup>1–4</sup> Besides organic molecules, coordination compounds offer a rich variety of chiral species attracting strong current interest.<sup>5,6</sup> Recent studies revealed that by scanning tunneling microscopy (STM), detailed insight into chirality phenomena at surfaces can be gained, including chiral recognition and chirality determination of single molecules, supramolecular assemblies, and extended enantiomerically pure overlayers.<sup>7–15</sup> Many of these studies have shown that surfaces can be used as a symmetry breaking agent to induce enantiomeric separation or enantiomorphic ordering in supramolecular assemblies produced by deposition of a racemate, prochiral, or even achiral molecules.<sup>10–17</sup>

Here we report single-molecule level STM observations of chiral complexes generated by the assembly of achiral components and metal centers at a metal surface. Following co-deposition of iron atoms and 1,3,5-tricarboxylic benzoic acid (trimesic acid, TMA) on Cu(100), we have found that the molecules react with the metal centers to chiral complexes stabilized by metal–ligand interactions. To our knowledge, this represents the first direct observation of a chiral coordination compound on surfaces.

Iron atoms and TMA were co-deposited on a Cu(100) surface under ultrahigh vacuum conditions.<sup>18</sup> The resulting structural arrangements were probed in situ at the single-molecule level by STM. The atomically clean Cu(100) clean surface was prepared by standard cycles of sputtering with Ar and annealing to 800 K. TMA molecules were evaporated from a Knudsen type evaporator at a temperature of 463 K. Fe atoms were evaporated from an e-beam heating evaporator. Both TMA and Fe deposition were performed with the temperature of the substrate at about 100 K, which ensures immobile adsorbates residing on the surface (note that Fe deposition at ambient temperature leads to Fe–Cu atom exchange).<sup>19</sup> The sample was subsequently annealed to room temperature to induce chemical reaction and to perform STM measurements. Our previous studies revealed that the annealing accounts for deprotonation of carboxylic groups of TMA molecules, which provides three carboxylate ligands per molecule. TMA molecules lie flat on the surface and are resolved as equilateral triangles in STM data.<sup>20</sup>

As shown in Figure 1a, flower-shaped arrangements where a central protrusion is decorated by four TMA molecules were fabricated by co-deposition of Fe and TMA at low concentrations.



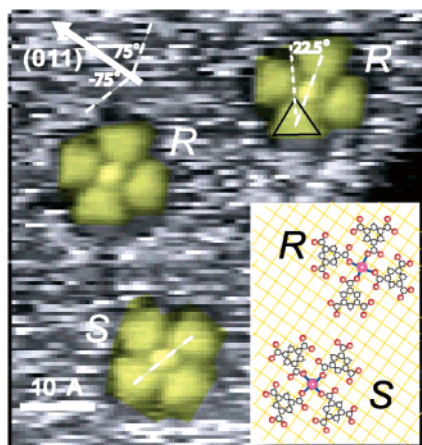
**Figure 1.** (a) Flower-shaped  $\text{Fe}(\text{TMA})_4$  complexes resolved by STM predominate on the Cu(100) surface following co-deposition of Fe and TMA in a 1:4 ratio at low coverages. The inset in the upper left shows a model of the TMA molecule (oxygen in red and carbon in gray; hydrogen omitted for clarity), which is imaged as an equilateral triangle in the STM image. (b) The evolution of the complex concentration as a function of the Fe–TMA concentration ratio (with the TMA coverage constant at 0.63 molecules per  $\text{nm}^2$ ) has a marked peak at the ideal stoichiometry, where about 40% of the available reactants form  $\text{Fe}(\text{TMA})_4$  complexes.

These structures are thermally stable and appear exclusively in the presence of Fe on the surface. Their proportion initially rises for a given TMA coverage with the Fe dose, as illustrated by the plot in Figure 1b. When both reactants are present in a 1 Fe:4 TMA ratio, they almost exclusively assemble in the flower-shaped structures, which are consequently identified as compounds from a central Fe atom surrounded by four TMA molecules (designated  $\text{Fe}(\text{TMA})_4$ ). A further increase of the Fe dose results in the formation of extended Fe–TMA nanostructures which will be reported elsewhere. Figure 1a also reveals that all complexes are aligned exclusively in two orientations at the surface, whereby a statistical analysis demonstrates that the two orientations are equal in occurrence.

\* To whom correspondence should be addressed. E-mail: N.Lin@fkf.mpg.de.

<sup>†</sup> Max-Planck-Institut für Festkörperforschung.

<sup>‡</sup> Institut de Physique des Nanostructures.



**Figure 2.** High-resolution image showing the two  $\text{Fe}(\text{TMA})_4$  stereoisomers, labeled *R* and *S*, representing mirror-symmetric species with respect to the [011] substrate direction. In the inset, a corresponding model is shown. There is a unidentate coordination of the carboxylate ligands to the central Fe atom (placed on the hollow site) with a bond length of about 2 Å (blue lines). The corresponding rotation of the carbon backbone is strictly correlated for all TMA molecules in a given complex. The resulting symmetry break accounts for the chirality of the complexes.

A close inspection of the high-resolution STM image reproduced in Figure 2 reveals that the angle between the high-symmetry [011] direction of the substrate and the principal axis of the complexes (arbitrarily defined from the connection of the centers of two opposing TMA molecules, marked as dashed lines) is  $+75^\circ$  or  $-75^\circ$ . Furthermore, it can be seen that in a complex, the TMA molecules do not point straight toward the center Fe. Rather, their triangular envelope is rotated by  $22.5^\circ$  clockwise or counterclockwise with respect to the principal axes of the compound. 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. Moreover, it is found that there is a strict correlation of the rotation for every TMA molecule in a given complex. In a complex rotated by  $+75^\circ$  ( $-75^\circ$ ) relative to the substrate [011] direction, each individual TMA molecule rotates counterclockwise (clockwise). As a consequence of this symmetry break, the two resulting species, labeled *R* and *S*, 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 Cu(100).

A model for the enantiomers based on high-resolution STM data is depicted in the inset in Figure 2. It reveals that the unidentate bonding in conjunction with the correlated rotation accounts for a compact arrangement of the molecules in the complexes. Possibly, the packing is assisted by hydrogen bond formation between the oxygen atoms of the carboxyl moiety, which do not directly couple to the Fe center, and the phenyl ring of the neighboring molecule. From the modeling, the O–Fe bonding distance is estimated to

fall below 2 Å, which agrees well with the typical value of Fe–carboxylate bonds in three-dimensional compounds.<sup>21</sup> Also, the square-planar geometry is frequently encountered in metal-carboxylates. However, it is important to note that the  $\text{Fe}(\text{TMA})_4$  complex cannot be regarded as an isolated entity as the coordination bonding and the electronic states of both Fe 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 a neutral TMA/Cu(100) configuration. As a consequence, the oxidation state of the Fe in the  $\text{Fe}(\text{TMA})_4/\text{Cu}(100)$  compound cannot be determined unambiguously.

Our results demonstrate that a square-planar  $\text{ML}_4$  complex can be chiral in two dimensions when symmetric bidentate ligands are employed which link to the metal atom (representing the stereogenic center) in an organized unidentate fashion. In principle, this intriguing example for stereoisomerism can be similarly encountered for three-dimensional octahedral compounds of the general form  $\text{MX}_6\text{L}_4$  when the bidentate ligands lie in the same plane.

## References

- (1) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; John Wiley & Sons: New York, 1994.
- (2) Palyi, G.; Zucchi, C.; Caglioti, L. *Advances in Biochirality*; Elsevier: Oxford, 1999.
- (3) Cline, D. B. *Physical Origin of Homochirality in Life*; AIP Press: Woodbury, New York, 1996.
- (4) Lehn, J.-M. *Supramolecular Chemistry, Concepts, and Perspectives*; VCH: Weinheim, 1995; Vol. 227.
- (5) Buckingham, A. D. In *Inorganic Biochemistry*; Eichhorn, G. L., Ed.; Elsevier: Amsterdam, 1973; Vol. 1, pp 3–62.
- (6) Zelewsky, A. v. *Stereochemistry of Coordination Compounds*; John Wiley & Sons: Chichester, 1996.
- (7) Eckhardt, C. J.; Peachey, N. M.; Swanson, D. R.; Takacs, J. M.; Khan, M. A.; Gong, X.; Kim, J.-H.; Wang, J.; Uphaus, R. A. *Nature* **1993**, *362*, 614–616.
- (8) Lopinski, G. P.; Moffat, D. J.; Wayner, D. D. M.; Wolkow, R. A. *Nature* **1998**, *392*, 909–911.
- (9) Fang, H.; Giancarlo, L. C.; Flynn, G. W. *J. Phys. Chem. B* **1998**, *102*, 7311.
- (10) Böhringer, M.; Morgenstern, K.; Schneider, W.-D.; Berndt, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 821–823.
- (11) Lorenzo, M. O.; Baddeley, C. J.; Muryn, C.; Raval, R. *Nature* **2000**, *404*, 376–379.
- (12) Weckesser, J.; Vita, A. D.; Barth, J. V.; Cai, C.; Kern, K. *Phys. Rev. Lett.* **2001**, *87*, 096101.
- (13) Kühnle, A.; Linderoth, T. R.; Hammer, B.; Besenbacher, F. *Nature* **2002**, *415*, 891–893.
- (14) Chen, Q.; Frankel, D. J.; Richardson, N. V. *Surf. Sci.* **2002**, *497*, 37–46.
- (15) Barth, J. V.; Weckesser, J.; Trimarchi, G.; Vladimirova, M.; Vita, A. D.; Cai, C.; Brune, H.; Günter, P.; Kern, K. *J. Am. Chem. Soc.* **2002**, *124*, 7991.
- (16) Yablon, D. G.; Giancarlo, L. C.; Flynn, G. W. *J. Phys. Chem. B* **2000**, *104*, 7627.
- (17) De Feyter, S.; Grim, P. C.; Rucker, M.; Vanoppen, P.; Meiners, C.; Sieffert, M.; Valiyaveetil, S.; Müllen, K.; Schryver, F. C. *Angew. Chem., Int. Ed.* **1998**, *37*, 1223.
- (18) Dmitriev, A.; Lin, N.; Weckesser, J.; Barth, J. V.; Kern, K. *J. Phys. Chem. B* **2002**, *106*, 6907.
- (19) Chambliss, D. D.; Johnson, K. E. *Phys. Rev. B* **1994**, *50*, 5012.
- (20) Lin, N.; Dmitriev, A.; Weckesser, J.; Barth, J. V.; Kern, K. *Angew. Chem.* **2002**, in press.
- (21) King, R. B., Ed. *Encyclopedia of Inorganic Chemistry*; Wiley: Chichester, 1994.

JA028553S