

## Molecular Wires Self-Assembled on a Graphite Surface

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We report a scanning tunneling microscopy study of the amino acid L-methionine on highly ordered pyrolytic graphite deposited under ambient conditions. Our experiments demonstrate the ability of L-methionine to form highly regular structures on the surface of the graphite template. By means of self-assembly, the amino acid arranges itself into an array of molecular wires, i.e., well-ordered stripes of uniform width and separation. The spacing of these wires can be controlled with the deposition amount of the amino acid, whereas the width stays constant. The width of the wires is determined by two methionine molecules arranged with their carboxyl group facing each other. The regular separation of individual wires suggest a long-range interaction among them. Molecular mechanics calculations are used to compare the experimental results with a basic model for the methionine configuration on the surface. A model for the adsorption geometry of methionine on graphite is presented.

## Introduction

Materials and devices that can be constructed from molecular components and assemble themselves chemically by virtue of molecular recognition are an important cornerstone in the very popular area of nanotechnology. These self-assembled nanostructures are a promising field for functional architectures where the goal is to create regular structures on the scale of a few nanometers that exhibit new structural and/or electronic properties.<sup>1</sup> It has been shown that this can be achieved for a wide variety of material combinations, e.g., quantum dots on semiconductor materials,<sup>2</sup> two-dimensional facet structures, where the surface is modulated in its chemical behavior as a result of two different facet structures, i.e., insulator-covered and metal facets,<sup>3</sup> or molecular wires on a metal template.<sup>4</sup> One subfield of nanotechnology, molecular electronics, has been the interest of increasing research in the last couple of years.<sup>5</sup> The self-assembly of so-called “molecular wires”, “molecular ribbons”, or “quantum wires”, i.e., one-dimensional molecular rows, are especially interesting with respect to interconnecting electronic devices.<sup>6</sup> Here, a wide variety of molecular species as well as underlying templates can be used. Recent results were reported on molecular wires, where interactions between the molecules, such as hydrogen bonding, dipole–dipole coupling,<sup>7–9</sup> or mole-

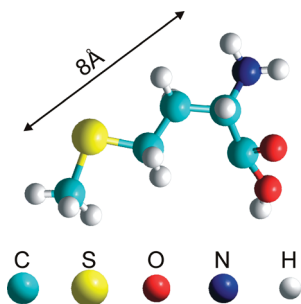
cule–surface interaction with growth along pre-existing template directions,<sup>10</sup> play a role in the molecular self-assembly. Furthermore, the interaction between biologically active molecules such as amino-acids and solid surfaces is relevant in the development of biosensors and other biocompatible materials. To achieve technological applications, it is necessary to investigate the intermolecular and molecule–surface interaction of the self-assembled nanostructures. Scanning tunneling microscopy (STM) is a very powerful method for this kind of research since it yields direct structural information of the molecular structures.

One subclass of these species is sulfur-containing molecules. Since most adsorption studies are carried out under ultrahigh vacuum (UHV) conditions, usually metals are used as substrates. It is by now well established that molecules having thiol (–SH) as endgroups can show strong bonds to surfaces because of the special affinity between sulfur and certain metals, e.g., Au surfaces,<sup>11</sup> Cu surfaces,<sup>12</sup> and Ag surfaces.<sup>13</sup> Furthermore, theoretical studies have shown a strong affinity between transition metals and sulfur.<sup>14</sup> The only two sulfur-containing amino acids are cysteine (COOH–CH(NH<sub>2</sub>)–CH<sub>2</sub>–HS) with a thiol endgroup, and methionine (COOH–CH(NH<sub>2</sub>)–CH<sub>2</sub>–CH<sub>2</sub>–S–CH<sub>3</sub>), where sulfur is incorporated in the side chain (c.f. Figure 1). The former has been the focus of some theoretical studies<sup>15</sup> as well as some experimental research<sup>10,16</sup> on a Au(111) surface under UHV conditions as well as under ambient conditions out of solutions,<sup>17,18</sup>

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- (1) Rosei, F. J. *Phys.: Condens. Matter* **2004**, *16*, S1373.
- (2) Teichert, C.; Bean, J. C.; Lagally, M. G. *Appl. Phys. A: Mater. Sci. Process.* **1998**, *67*, 675.
- (3) Fölsch, S.; Riemann, A.; Repp, J.; Meyer, G.; Rieder, K. H. *Phys. Rev. B* **2002**, *66*, 161409(R).
- (4) Weckesser, J.; Vita, A. D.; Barth, J. V.; Cai, C.; Kern, K. *Phys. Rev. Lett.* **2001**, *87*, 096101.
- (5) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2000**, *408*, 541.
- (6) Datta, S.; Janes, D. B.; Andres, R. P.; Kubiak, C. P.; Reifenberger, R. G. *Semicond. Sci. Technol.* **1998**, *13*, 1347.
- (7) Böhringer, M.; Morgenstern, K.; Schneider, W.-D.; Berndt, R.; Mauri, F.; Vita, A. D.; Car, R. *Phys. Rev. Lett.* **1999**, *83*, 324.
- (8) Barth, J. V.; Weckesser, J.; Cai, C.; Günter, P.; Burgi, L.; Jeandupeux, O.; Kern, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 1230.
- (9) Yokoyama, T.; Yokoyama, S.; Kamikado, T.; Okuno, Y.; Mashiko, S. *Nature* **2001**, *413*, 619.
- (10) Kühnle, A.; Molina, L. M.; Linderth, T. R.; Hammer, B.; Besenbacher, F. *Phys. Rev. Lett.* **2002**, *93*, 086101.

- (11) Honda, M.; Baba, Y.; Hirao, N.; Sekiguchi, T. *J. Phys.: Conf. Ser.* **2008**, *100*, 052071.
- (12) Barlow, S. M.; Raval, R. *Surf. Sci. Rep.* **2003**, *50*, 201.
- (13) Sardar, S. A.; Syed, J. A.; Yagi, S.; Tanaka, K. *Surf. Interface Anal.* **2003**, *35*, 1055.
- (14) Raybaud, P.; Hafner, J.; Kresse, G.; Toulhoat, H. *J. Phys.: Condens. Matter* **1997**, *9*, 11107.
- (15) Felice, R. D.; Selloni, A.; Molinari, E. *J. Phys. Chem. B* **2003**, *107*, 1151.
- (16) Kühnle, A.; Linderth, T. R.; Hammer, B.; Besenbacher, F. *Nature* **2002**, *415*, 891.
- (17) Dakkouri, A. S.; Kolb, D. M.; Edelstein-Shima, R.; Mandler, D. *Langmuir* **1996**, *12*, 2849.
- (18) Xu, Q.-M.; Wan, L.-J.; Wang, C.; Bai, C.-L.; Wang, Z.-Y.; Nozawa, T. *Langmuir* **2001**, *17*, 6203.



**Figure 1.** Schematic view of L-methionine with color-coded atom species. We call the carboxylic endgroup the “head” and the  $-S-CH_3$  endgroup the “tail”.

but the bigger molecule methionine has only been investigated toward its potential for supramolecular architecture under UHV conditions.<sup>19,20</sup>

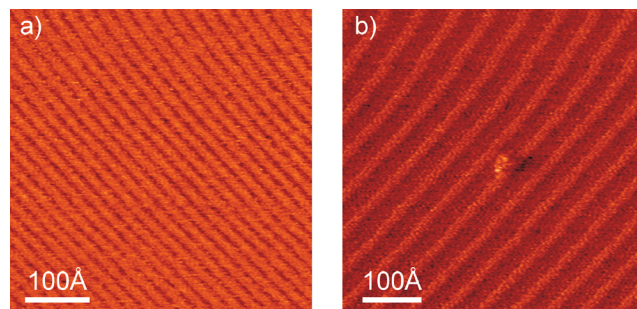
Here, we report the self-assembly of the amino acid L-methionine on the surface of highly ordered pyrolytic graphite (HOPG) under ambient conditions. Previous theoretical and experimental studies have shown surface ordering of proteins on graphite.<sup>21,22</sup> But in our study, the observed structures consist of long molecular wires with tunable separation depending on the amount of deposited material. Usually these kind of structures are achieved under UHV conditions,<sup>4,19</sup> but remarkably the self-assembled structures reported here were achieved at room temperature and at the liquid/solid interface.

### Experimental Section

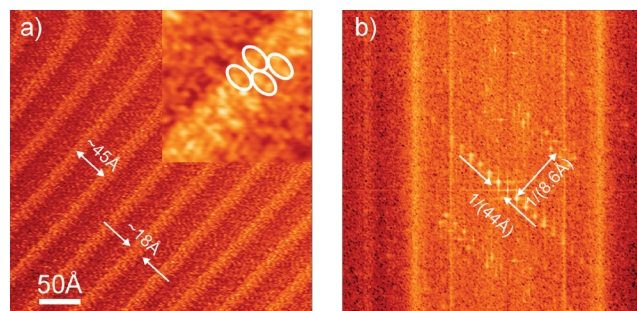
The experiments for the present work were performed with an STM working under ambient conditions using a 0.25 mm PtIr wire as scanning tip. All experiments were carried out at room temperature. Prior to sample preparation, L-methionine was mixed with 1-octanol at various concentrations ranging from 0.28 mg of L-methionine for 1 g of 1-octanol up to 1.9 mg/g. To ensure even concentration throughout the mixed liquid, the solutions were put in an ultrasonic bath for 5 min. HOPG was washed in acetone, baked in an open-air tube furnace for 2–5 min at 700 °C to remove residual organic impurities, and cleaved immediately prior to the application of 20  $\mu$ L of methionine/octanol solution. All STM images were taken at room temperatures using tunneling currents of 1–5 nA and bias voltages of 0.2–0.5 V applied to the STM tip. In the system studied here, the STM tip plunged through the covering octanol solution (which is electrically insulating) to image the structures adsorbed on the graphite substrate. The STM images were processed using the software package WSXM.<sup>23</sup> The topographic images were smoothed out by low-pass filtering to remove noise created by external vibrations.

### STM Results

Upon deposition of the methionine/octanol solution on the graphite surface, a uniformly distributed coverage on the surface can be observed. Methionine builds up structures of dimer rows. The width of the row is determined by the size of



**Figure 2.** STM images of methionine on HOPG: (a) high coverage of about 80% (methionine/octanol concentration: 1.1 mg/g) with row spacings of about 18 Å; (b) low coverage of about 40% (methionine/octanol concentration: 0.4 mg/g) with row spacing of around 45 Å.



**Figure 3.** STM image and Fourier transform of STM image for low coverage case: (a) low coverage of about 40% with row spacings of about 45 Å and row width of 18 Å (methionine/octanol concentration: 0.35 mg/g); inset shows individual methionine molecules imaged as elliptical features; (b) Fourier transform of the sample in panel a with resolved periodicity of about 44 Å perpendicular to the methionine rows (= spacing of methionine rows) and 8.6 Å within the row (= spacing of individual methionine molecules).

the molecule, and the spacing of these rows depends on the overall methionine coverage on the surface. Figure 2a shows the graphite surface with about 80% methionine coverage. The domain consists of molecular rows that are about 20 Å wide (dimer rows) and separated by about 25 Å.

An example of lower coverage (~40%) can be seen in Figure 2b. Here, the width of the methionine rows is again about 18 Å, consistent with the idea of dimer rows, but the rows are separated by about 45 Å. As mentioned above, the spacing between the molecular rows is entirely determined by the overall coverage, which depends on the original solution concentration of the methionine/octanol mixture.

Highly resolved STM images (Figure 3a) reveal the internal structure of the molecular rows. Single molecules are imaged as elliptical features of about 8 Å length, which corresponds to the length of a methionine molecule (see inset in Figure 3a). To get more precise data about the separation of the rows as well as spacing of the molecules within each row, a Fourier transformation of the STM image was used (c.f. Figure 3b). Here, we found that along the direction of the molecular rows the distance between neighboring methionine molecules was determined to be twice the distance of equivalent points on the graphite surface of about 8.6 Å. Previous studies of methionine molecules<sup>19,20</sup> as well as molecular mechanics calculations (which will be explained in the next section) were used to develop a model of the methionine configuration on the graphite surface.

(19) Schiffrin, A.; Riemann, A.; Auwärter, W.; Pennec, Y.; Weber-Bargioni, A.; Ceveto, D.; Cossaro, A.; Morgante, A.; Barth, J. V. *Proc. Natl. Acad. Sci.* **2007**, *104*, 5279.

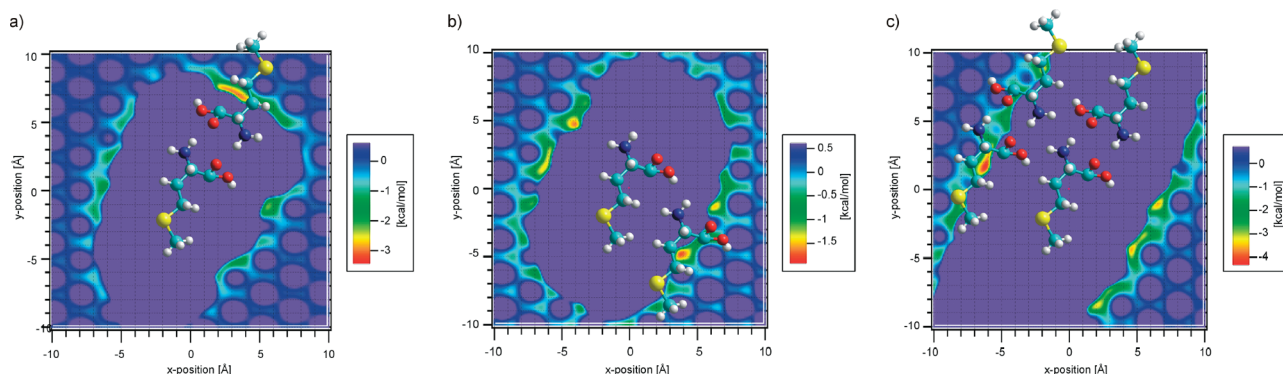
(20) Pennec, Y.; Auwärter, W.; Schiffrin, A.; Weber-Bargioni, A.; Riemann, A.; Barth, J. V. *Nat. Nanotechnol.* **2007**, *2*, 99.

(21) Raffaini, G.; Ganazzoli, F. *J. Phys. Chem. B* **2004**, *108*, 13850.

(22) Svaldo-Lanero, T.; Penco, A.; Prato, M.; Canepa, M.; Rolandi, R.; Cavalleri, O. *Soft Matter* **2008**, *4*, 965.

(23) Horas, I.; Fernandez, R.; Gomez-Rodriguez, J. M.; Colchero, J.; Gomez-Herrero, J.; Baro, A. M. *Rev. Sci. Instrum.* **2007**, *78*, 013705.





**Figure 4.** Total energy map of methionine molecules on a graphite surface: (a) two methionine molecules oriented in antiparallel configuration; the optimal configuration leads to close proximity of the carboxyl and ammonium group; (b) two methionine molecules oriented in parallel configuration; the optimal distance was found to be 6.3 Å, which corresponds to the separation of two methionine molecules along the direction of the molecular rows; (c) two methionine dimers oriented parallel with intradimer configuration according to results from panel a; the optimal distance between two dimers was found to be 6.4 Å.

### Molecular Mechanics Calculations

For the present system we carried out some basic molecular mechanics calculations<sup>24</sup> with the software package HyperChem 7.5.<sup>25</sup> The intent is to test whether a very basic approach leads to results similar to those of the experimental findings. To optimize individual molecules and calculate the total energies of different configurations, we used HyperChem's molecular mechanics force field MM+,<sup>26</sup> but one has to be careful with such a “black box” approach for complex systems.<sup>27</sup> All calculations were performed in vacuo and at 0 K. A two-layer graphite slab with dimensions of about 70 Å × 70 Å was used in the calculation. The presented calculations basically yield a comparison of the total energy of different molecule–substrate and/or intermolecular configurations. Previous experiments have shown that the width of the methionine rows is given by a “head-to-head” (antiparallel) configuration, which brings the carboxylic head groups of two methionine molecules in close proximity, and that along the row the methionine molecules are arranged in a parallel configuration.<sup>19</sup> For the case of methionine on HOPG, three calculations were performed, and the results can be seen in the color coded total energy maps of Figure 4. During the first step, one methionine molecule was geometry optimized. The adsorption energy found for one methionine molecule on the graphite surface was 0.5 eV, which is consistent with previous calculations of amino acids on graphite.<sup>28</sup> For the following calculations, this methionine molecule was fixed with its center of mass at the origin of the energy maps. The energy map in Figure 4a shows the results of the total energy of the system of the graphite surface with two methionine molecules: one fixed with its center of mass at the origin and a second methionine molecule in antiparallel configuration positioned according to the *x*- and *y*-coordinates of the graph. In the antiparallel case, the molecule is rotated by 180° on the absorption plane with respect to the stationary molecule at the origin. The zero point energy of the graph corresponds to two noninteracting methionine molecule on the graphite surface. The second graph (cf. Figure 4b) shows the total energy map using the

same approach as for the first, with the only difference being that the methionine molecule, which changes position during the calculation, is in parallel configuration. For the third energy map (cf. Figure 4c), the results from Figure 4a were used as the fixed configuration, i.e., a methionine dimer with one molecule at the origin and the other molecule at the position found in Figure 4a are fixed. A second dimer with fixed intradimer configuration is moved to different positions, with the center of mass of one molecule represented as the *x*- and *y*-coordinates of the graph. Here, the zero point energy corresponds to two noninteracting methionine dimers on the graphite surface.

The energetically most favorable configuration of two methionine molecules can be seen superimposed on the color-coded energy map in Figure 4a. The resulting dimer has a length of approximately 18 Å in very good agreement with the experimentally determined value as the width of the methionine rows. For the next case, where the second methionine molecule is parallel to the fixed molecule at the origin, the energetically most favorable configuration is again superimposed on the energy map (Figure 4b). Here, the distance between the methionine molecules along the row was determined to be 6.3 Å, whereas the experimental finding suggests a distance of 8.4 Å. This discrepancy can be attributed to the shortcomings of the very basic approach in this molecular mechanics calculation (in vacuo, temperature 0 K, no solvent). The effect of surface–methionine interactions is underestimated in our computational model, since the experimental results suggest that methionine molecules try to find a quasi commensurate configuration on the graphite surface. The experimentally found spacing of about 8.4 Å corresponds to 2 times that of the high symmetry surface lattice vector. The third total energy map (Figure 4c) corresponds to a structure where the optimized configuration of two antiparallel methionine molecules (a methionine dimer) deduced from the energy map in Figure 4a is used as the stationary molecules and a second optimized dimer is shifted along the absorption plane. Here, the optimized configuration superimposed on the energy map can be seen in Figure 4c, which yields an optimized spacing of 6.4 Å along the methionine row. This spacing is basically identical to two methionine molecules in parallel configuration (cf. Figure 4b).

The calculations lead to a good qualitative agreement with the experiments in the relative position of methionine molecules to each other. Nevertheless, the model underestimates

(24) Karplus, M.; McCammon, J. A. *Nat. Struct. Biol.* **2002**, *9*, 646.

(25) *HyperChem Professional 7.51*; Hypercube, Inc.: Gainesville, FL.

(26) Weiner, P. K.; Kollman, P. A. *J. Comput. Chem.* **1981**, *2*, 287.

(27) Harding, J. H.; Duffy, D. M. *J. Mater. Chem.* **2006**, *16*, 1105.

(28) Roman, T.; Dino, W. A.; Nakanishi, H.; Kasai, H. *Eur. Phys. J. D* **2006**, *38*, 117.

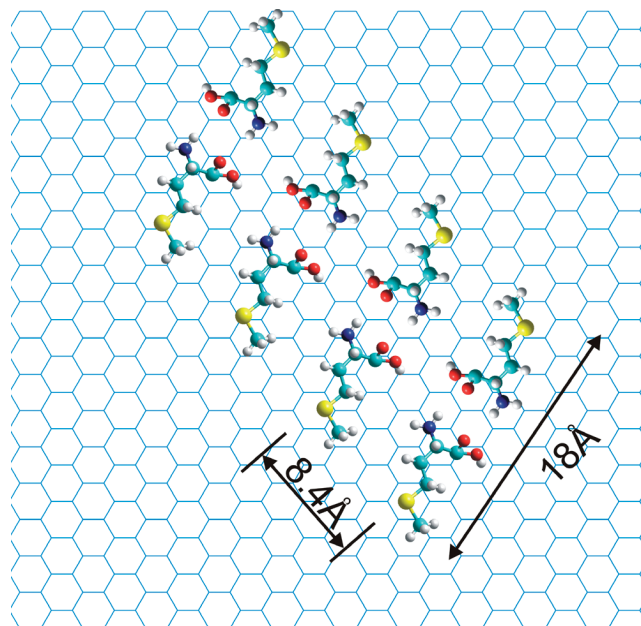
the surface–molecule interactions, which leads to a quantitative discrepancy of the intermolecular distance within the molecular rows between experiment and simulation. To improve the simulation results, one needs to carefully examine the used force fields in greater detail,<sup>27</sup> which also corresponds to a higher computational cost. This kind of work is planned for further theoretical studies of this system and other types amino acid adsorption on graphite.

### Structural Model

With the experimental findings as well as previous results,<sup>19</sup> we suggest the model (c.f. Figure 5) for the methionine adsorption onto the graphite surface. The molecular wires consist of methionine molecules that face each other “head-to-head” to make up the width of the row of about 18 Å. Along the row, methionine molecules are spaced out by 8.4 Å mediated by the underlying substrate periodicity. Neither STM data nor the calculations allow determination of the exact adsorption site of the molecule on the graphite surface; only the surface periodicity corresponds to a periodicity of the molecular structure.

### Summary

Here, we present for the first time a study of the amino acid methionine on HOPG under ambient conditions. This system provides the opportunity to create a regular nanostructure of molecular wires. The spacing of these rows can be tuned by the amount of deposited material. Similar experiments have been carried out under UHV conditions,<sup>19</sup> but remarkably here molecular wires could be manufactured under ambient conditions, which could provide a big step forward in the quest of molecular electronics. The driving force of the observed structures are a combination of intermolecular and molecule–surface interactions. We hope to extend this study to other molecules with interest in molecular engineering appli-



**Figure 5.** Model for the methionine adsorption on a graphite surface; the intermolecular distance along the rows is 8.4 Å, and the row width of about 18 Å is determined by two methionine molecules in antiparallel configuration.

cations. In future experiments, it could be interesting to find out whether similar ordering could be achieved using other amino acids in order to gain additional knowledge about the mechanisms involved in this self-assembly.

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