Stacking Phenomenon of Self-assembled Monolayers and Bilayers of Thioalkyl-substituted Tetrathiafulvalene

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The self-assembled monolayer and bilayer of tetrakis (octadecylthio)tetrathiafulvalene (TODT-TTF) on highly orientated pyrolytic graphite (HOPG) surface were studied by scanning tunneling microscope (STM). Direct observation of the dimer of TODT-TTF formed by π-π interaction was achieved.

The past three decades have witnessed continued interest in the synthesis and characterization of organic charge-transfer (CT) salts that display unusual solid-state properties. This is a multi-disciplinary field that involves synthetic chemistry and crystallography etc.[1] The vast majority of the work in this area has involved studies on single crystals. However, currently there is growing interest, from both scientific and application viewpoints, in producing self-assembled and Langmuir–Blodgett ultra-thin films of CT salts.[2] These films offer the possibility for preparing organic structures with a greater level of control over the molecular architecture in addition to the single crystal materials. Thin films of CT salts should be far easier to fabricate into electronic devices than the frail single crystals of CT salts. The techniques of making thin films of organic molecules on solid surface have provided novel advanced technological applications.[3]

STM with its atom-scale resolution ability has been used successfully to image a number of adsorbed organic molecular films on various surfaces.[4] These observations have provided important new information on the binding sites of individual molecules with respect to the substrate lattice, conformational states of individual molecules, periodicity of ordered molecular surface structures that are present in ordered structures.

Tetrathiafulvalene (TTF) and its derivatives belong to reversible and stable electron donors whose cation radical salts represent an important class of conducting molecular materials. In this paper we present the STM observations of the self-assembled mono- and bi-layers of TODT-TTF and the study of its stacking behavior on HOPG surface.

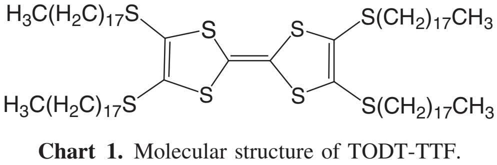

Chart 1. Molecular structure of TODT-TTF.

TODT-TTF (purity: >95%) was obtained from TCI and used without further purification. The solvent used in the STM experiments is toluene (HPLC-grade, Aldrich). The concentrations of all the solutions used are less than 1 mM. Experiment was carried out in two different concentrations (low concentration of the solution was about 0.01 mM, while the high concentration of the solution was about 0.1 mM). Samples were prepared by depositing a drop of the above solution on freshly cleaved HOPG. Experiments were performed with a NanoScope IIIA system (Digital Instrument, Santa Barbara, CA) operating under ambient conditions. STM tips were mechanically formed Pt/Ir wires (90/10). All the STM images were recorded using the constant current mode of operation.

Presented in Figure 1a is a large scale STM image of TODT-TTF molecules adsorbed on HOPG surface when experiment was carried out in low concentration. It can be seen that TODT-TTF molecules form well-ordered two-dimensional arrays, with sporadic molecular defects. The image illustrates bands of well ordered bright spots separated by low contrast regions. As it is well known in STM studies, the bright spots can be attributed to the conjugated π-electron systems of TTF nuclei and the shaded zigzag lines interconnecting the bright spots correspond to the long alkyl chains. The bright spots appear in Figure 1a clearly display two types of brightness. A cross section was performed along the line shown in Figure 1a. The difference in height suggests that both mono- and bi-layer of TODT-TTF were formed. It can be seen from the section anal-

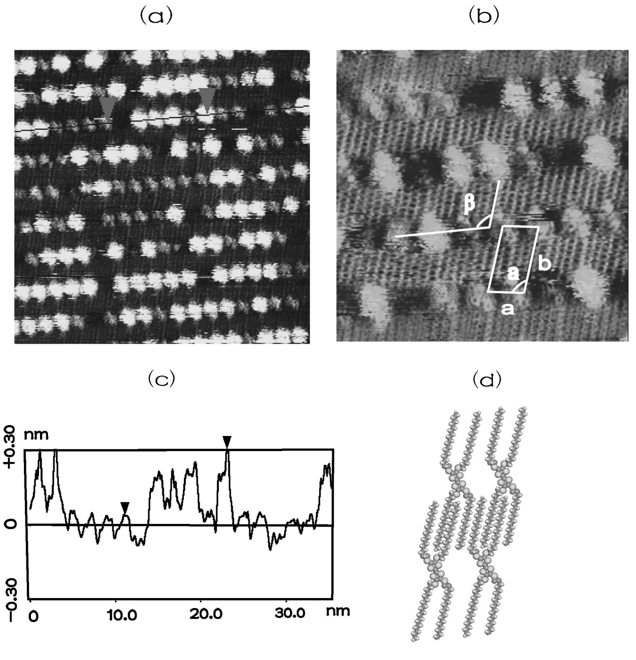

Figure 1. a) STM image (35.4 × 35.4 nm^2) of a self-assembled monolayer and multilayer of TODT-TTF of type I assembly pattern on a HOPG surface. The imaging conditions are $I = 897$ pA and $V = -800$ mV. The z-axis is 0.6 nm. b). A higher resolution STM image (16.1 × 16.1 nm^2) of type I assembly pattern. The imaging conditions are $I = 897$ pA and $V = -800$ mV. The z-axis is 0.6 nm. c) A section analysis of Figure 1a. d) Molecular models of the adsorbed structure of TODT-TTF of type I assembly pattern.

ysis (Figure 1c) that the upper layer is about 0.3 nm higher than the lower one, which is close to the interplanar distance (0.34–0.36 nm) in the crystal structure of some TTF derivatives and their CT salts.[5] Figure 1b is a high resolution image on which a unit cell is superposed with $a = 3.9 \pm 0.1\,\text{nm}$, $b = 2.0 \pm 0.1\,\text{nm}$, $\alpha = 111.6^\circ \pm 0.3^\circ$. The TTF nuclei appear to pack with $\beta = 107.2 \pm 0.3^\circ$ between the molecular axis and the alkyl lamellae direction. According to the STM image of Figure 1b, a packing model consisting of four molecules was given in Figure 1d. It can be seen that the four long alkyl chains of a TODT-TTF molecule are divided into two groups, with one group attached to the head of the TTF nuclei and the other group to the end. All alkyl chains are parallel to each other and the chains of neighboring lamellae are interdigitated.

In high concentration, another type of assembly pattern formed with one TODT-TTF molecule laid above the other. Figure 2a is a large scale STM image of TODT-TTF molecules assembled in this type. Just as in Figure 1a, a section analysis was also performed on Figure 2a, with a line drawn parallel to the diagonal. From the section analysis data (Figure 2c), one can easily see that all the peaks are almost of the same height and the height is near the same of that of the second layer in Figure 1a. This indicates that the bright spots, which correspond to the TTF nuclei, are in the same layer and they form a bilayer. Figure 2b is a high resolution image of TODT-TTF in this type of assembly pattern. A unit cell is superposed on Figure 2b. The parameters of the unit cell are $a = 3.9 \pm 0.1\,\text{nm}$, $b = 2.4 \pm 0.1\,\text{nm}$, $\alpha = 126.6^\circ \pm 0.3^\circ$, respectively. The TTF nuclei appear to pack with $\beta = 127.4 \pm 0.3^\circ$ between the molecular axis and the alkyl lamellae direction. An array of four TODT-TTF molecular models was given in Figure 2d. From the models one can also find that the four long alkyl chains of a molecule are also divided into two groups, with one group stretching from one side of the TTF nuclei and the other stretching from the other side.

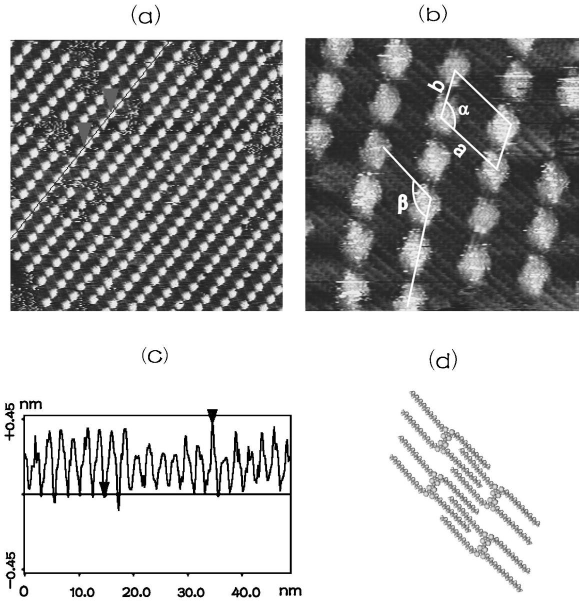

Figure 2. a) STM image ($55.3 \times 55.3\,\text{nm}^2$) of a self-assembled bilayer of TODT-TTF of type II assembly pattern on a HOPG surface. The imaging conditions are $I = 1.43\,\text{nA}$ and $V = -347\,\text{mV}$. The z-axis is 0.9 nm. b) A high resolution STM image ($14.1 \times 14.1\,\text{nm}^2$) of type II assembly pattern. The imaging conditions are $I = 897\,\text{pA}$ and $V = -800\,\text{mV}$. The z-axis is 0.6 nm. c) A section analysis of Figure 2a. d) Molecular models of the adsorbed structure of TODT-TTF of type II assembly pattern.

The π-π interaction exists in diverse phenomena in nature such as double helix of DNA and the packing of aromatic molecules in crystals. It leads to the conclusion that the π systems adopt a coplanar arrangement with their centers offset. Stacking behavior or formation of multilayers of some planar molecules on various surfaces was investigated by STM[6–8] before. In the present systems, the π-π interaction plays a key role in controlling the lattice of the bilayer of TODT-TTF. Because of the strong π-π interaction between the TTF nuclei, when bilayer occurs, one molecule's TTF nucleus is laid above that of other. Because of the thermally activated diffusional motion of the alkyl methylene groups, only the under layer of alkyl chains directly adsorbed on HOPG can be imaged.

In summary, in this work, we studied the self-assembled mono- and bi-layer of TODT-TTF adsorbed on HOPG by STM. This work lays a good foundation for the further study on self-assembly behavior of CT salts on graphite by STM, which is now in progress in our lab.

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