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Atomic Force Microscopy of the Electrochemical Nucleation and Growth of Molecular Crystals

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Introduction

Molecular crystals containing organic components exhibit a variety of interesting and potentially useful electronic properties, including electrical conductivity, superconductivity, non-linear optical behavior, and ferromagnetism,¹ and also comprise the majority of pharmaceutical reagents.² Much of the interest in these materials stems from the ability to employ molecular-level "crystal engineering" strategies³ to control solid state intermolecular interactions in order to rationally manipulate crystal packing and, consequently, influence bulk physical and electronic properties. While these strategies have been employed in the design and synthesis of many organic crystals, the self-assembly, nucleation, and crystallization processes that are responsible for their formation are not well understood, particularly at the molecular and nanoscale level. This understanding is crucial if important crystal characteristics such as polymorphism, habit, morphology, inclusion formation, and defect density are to be controlled.

Recent developments in atomic force microscopy (AFM),⁴ however, now provide for *in situ* visualization of the early stages of growth of organic crystals in liquids, as evidenced by recent reports for these and other materials.^{5,6} This capability provides for dynamic observation of nucleation events, and the determination, at small length scales, of the distribution of topographic features (i.e. terraces, ledges and kinks) that play an important role in crystal growth.⁷ We herein report *in situ* AFM observations of the nanoscale morphology, surface topography, and growth and dissolution characteristics of single crystals of a series of organic charge transfer salts, specifically those comprising the tetracyanoquinodimethane (TCNQ) acceptor and tetrathiafulvalene (TTF), tetramethyltetraselenafulvalene (TMTSF), and bis-(ethylenedithio)tetrathiafulvalene (BEDT-TTF) donors with a variety of counter-ions.

Experimental

Atomic force microscopy (AFM) experiments were performed with a Digital Instruments Nanoscope III scanning probe microscope. *In situ* studies were accomplished with an AFM electrochemical fluid cell (Digital Instruments) in a three-electrode configuration. The working electrode consisted of either graphite or a mature single crystal surface while platinum and silver wires served as counter and quasi-reference electrodes, respectively. The counter and reference electrodes were placed in the outlet port of the fluid cell. Experiments were then performed in organic solutions of ethanol, propylene carbonate, or acetonitrile containing millimolar concentrations of the donor/acceptor and high concentrations of the counterion in a tetrabutylammonium salt, which also served as the supporting electrolyte.

Results and Discussion

A variety of conductive and insulating salts were examined with a range of bonding properties. The low-dimensional conductors typically exhibited one dominant bonding interaction. A strong preference for [100] ledges on the (001) face of the low-dimensional organic superconductor (TMTSF)₂ClO₄ is a consequence of strong intermolecular charge transfer interactions between TMTSF molecules stacked along this direction (Figure 1). The (001) face of (TMTSF)₂ClO₄ exhibits layer-by-layer growth and etching, in which the layers correspond to single unit cell heights of 13.3 Å. A terrace-ledge-kink mechanism⁸ is observed, with the direction of fastest growth and etching oriented along the TMTSF stacking axis.

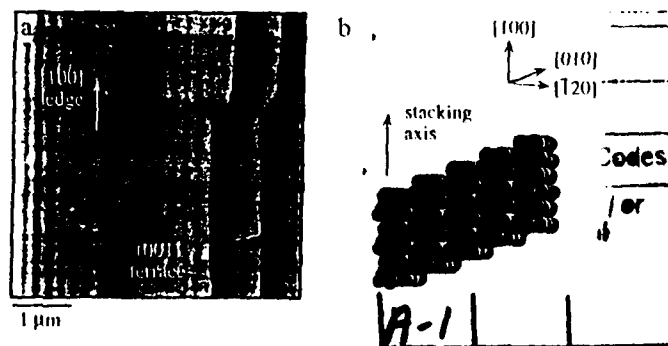


Figure 1: Molecular packing of the (001) plane of (TMTSF)₂ClO₄ and an AFM image of this face on a mature crystal showing (001) terraces bounded by [100] ledges. The [100] direction corresponds to the crystal stacking axis and is the direction of strongest intermolecular solid state bonding.

Crystals of the low dimensional organic conductor (TTF)₂TCNQ have also been imaged *in situ* following nucleation on a highly oriented pyrolytic graphite (HOPG) surface. These crystals exhibit a habit similar to that of the mature crystal and can be indexed using "AFM goniometry." The exposed crystal faces consist of low energy planes, as derived from the crystal structure, while the microscopic surface structure reflects solid state bonding. The observed growth mode varies with the particular crystal face examined. However, the [001] charge transfer axis manifests in the form of oriented topographical structures, namely dominant [001] ledges.

Several two dimensional salts were examined. The insulating salt, (Cp*₂Ru)₂(Cyclophane) (ICNQ)₂, exhibits two dominant bonding interactions, one electrostatic and the other van der Waals in nature, while a significant charge transfer interaction is absent. The resulting growth mode is clearly more two dimensional and exhibits a layer by layer evolution in the [110] direction. However, the presence of anisotropic electrostatic and van der Waals interactions in the plane of this face contributes to the formation of dominant ledge and kink structures (Figure 2). These ledges orient in the [110] and [111] directions. The two dimensional organic conductor α-(BEDT-TTF)₂I₃ exhibits a similar layered growth mode with two dominant ledge directions.

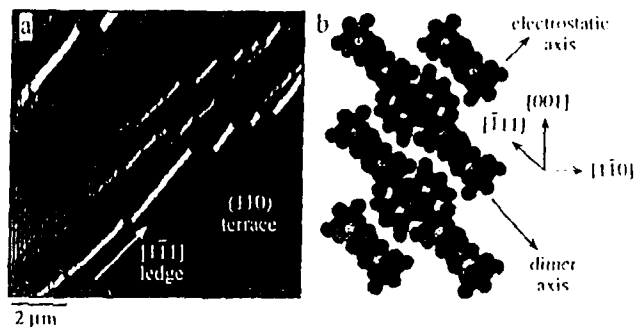


Figure 2: Layered growth of the (110) face of (Cp*₂Ru)₂(Cyclophane) (ICNQ)₂ that results from the two dominant bonding directions. (a) molecular packing of (011) face and (b) AFM image of growth. The [111] ledges are moving in the [111] direction.

Conclusions

These studies illustrate that anisotropic solid state intermolecular forces play a dominant role in defining the nanoscale topography, etching and growth characteristics of molecular single crystal faces. In several examples described here, the behavior is dominated by nanoscale ledge structure that is coincident with directions of strong intermolecular electrostatic and charge transfer interactions. The role of excess interfacial energy during crystal growth is evident from the distribution of terraces, ledges, and kinks that differs from that observed under equilibrium conditions. These observations indicate that the surface topography is related to the morphology of macroscopic crystals, suggesting self-similarity of morphology during the crystal growth process.

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