



Scanning tunneling microscopy of a disordered Alq3–metal interface

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ABSTRACT

Scanning tunneling microscopy is used to observe the structure of the first monolayer of Alq3 on Cu(1 1 0). Individual molecules can be resolved at very low coverage where there is also evidence of significant surface mobility. As Alq3 surface coverage increases, molecules aggregate by forming pairs and chain-like structures without ever establishing long range order. Interfacial disorder is maintained even after annealing to 590 K. The tendency to form chain-like aggregates is attributed to anisotropic intermolecular interactions. Anisotropies in these interactions are implicated in chain formation by illustrative density functional theory calculations and the role of direct dipolar interactions, anisotropic van der Waals interactions, and substrate-mediated interactions is discussed.

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1. Introduction

The demonstration of an organic light emitting diode (OLED) in 1987 by Tang and van Slyke [1] was a major driving force in creating the intense modern interest in organic materials for electronics and optoelectronic applications. Organic device materials have already made a commercial impact in displays and show significant promise to expand into large area lighting and photovoltaic applications [2]. The emissive materials used in Tang's and van Slyke's original OLED was tris-(8-hydroxyquinoline) aluminum or "Alq3" for short. In the past 20 years, its basic interfacial properties have been characterized extensively [3,4] and it remains a very common emissive layer in state-of-the-art OLED's [5].

Single crystals of Alq3 can be grown by vapor transport methods and show a number of polymorphic structures all driven to a large extent by van der Waals interactions between the π electrons on hydroxyquinolato ligands on adjacent molecules [6]. In contrast, thin films relevant to layered OLED's are structurally disordered and often referred to as "amorphous". For example, an X-ray diffraction study by Brinkmann et al. showed no sign of order in vapor deposited

films [6]. This disorder is crucial to properly modeling thin film device operation [7]. It impacts the voltage and temperature dependence of carrier mobility in space charge limited transport [7] and can modify injection-limited current as described below [8–10]. Strong disorder is likely to be a common feature of organic molecular films in which molecules (such as Alq3) have non-planar 3D structures. For example, a recent scanning tunneling microscopy (STM) study of rubrene on Au(1 1 1) [11] reported disorder due to coexisting 3D conformations of this important molecule.

Electrical transport in thin films of Alq3 contacted by electrodes with high to moderate work functions have often been found to be injection limited [8,12,13] due to the large energy difference between electrode Fermi levels and molecular orbital-derived transport levels. Disorder has been demonstrated to quantitatively modify the current-voltage (I/V) characteristics of injection limited devices. Burin and Ratner derived a simple analytical model for the impact of disorder on charge injection that illustrated how the usual Richardson–Schottky formula for injection-limited current could be altered [9,10]. A clear consequence of this model is that the injection limited current in a device increases as the width of the Gaussian distribution of transport levels increase. A broader distribution has a greater number of energetically accessible states in its tails that enhance injection.

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For Alq3 thin films sandwiched between Mg:Ag and either Al or Mg:Ag electrodes, Baldo and Forrest [8] observed very unique temperature and thickness dependent I/V characteristics that required implementation of a new model of injection into a disordered solid [8]. In the Baldo and Forrest model, it was hypothesized that disorder was enhanced near the metal–organic interface in such a way that the limiting charge injection process was not direct injection from the metal electrode into the disordered Alq3 film but rather injection from a highly disordered interfacial molecular layer into the somewhat less disordered bulk film. A possible physical origin of the interfacial disorder was suggested to be random variations in orientations of Alq3 molecules that result in strongly varying local interfacial dipoles [14] in the plane of the metal–organic interface.

Only a few scanned probe experiments directed at visualizing Alq3 film structure at the molecular level have been attempted. Alvarado and co-workers found that Alq3 diffused too rapidly on the surface to image by scanning tunneling microscopy (STM) at room temperature on Au(1 1 1) [15]. However, they were able to estimate the transport gap for Alq3/Au(1 1 1) using tip distance-versus-voltage spectroscopy [15,16]. More recently, linear Alq3 nanostructures were observed on ultrathin KBr films, but intermolecular distances were not reported [17]. Numerous studies have used atomic force microscopy to image the nanometer scale morphology of thick Alq3 films [18–20].

In the present paper we report scanning tunneling microscopy observations of the first layer of Alq3 on a Cu(1 1 0) surface that achieve single molecule resolution. These experiments show a poorly ordered interface that results from growth on a room temperature substrate and that persists after annealing up to about 590 K. While no long range order is observed in this first monolayer, intermolecular interactions are revealed by the formation of randomly-oriented chain-like aggregates of Alq3 molecules. We describe the origin of these disordered chain structures from anisotropic intermolecular interactions using model density functional theory (DFT) calculations.

2. Experimental methods

Experiments were carried out in an ultrahigh vacuum system with two interconnected chambers. One chamber (base pressure $<7 \times 10^{-11}$ torr) houses facilities for substrate cleaning and STM characterization. Another chamber (base pressure $\sim 1 \times 10^{-8}$ torr) is separated from the first by a gate valve and houses home-built organic evaporators and a quartz oscillator for flux monitoring.

The substrate was a Cu(1 1 0) single crystal (Princeton) cleaned by repeated cycles of 1 keV Ar⁺ sputtering following by annealing for 20 min at ~ 700 K. During deposition, the Cu(1 1 0) crystal was held at room temperature. Powdered tris-(8-hydroxyquinoline) – Aluminum (“Alq3”, Sigma–Aldrich – 99.995%) was loaded as received into a degassed quartz crucible that could be heated by a tightly wrapped Tantalum filament coil. The Alq3 was outgassed for several hours in the deposition chamber prior to film

growth. The stability of Alq3 flux was monitored with a quartz oscillator before and after deposition. Absolute flux calibration was carried out by direct STM imaging with molecular resolution.

STM imaging was carried out at room temperature with a commercial instrument (Omicron VT-STM-XA) operated in constant current mode with electrochemically-etched tungsten tips. Annealing experiments after Alq3 deposition were performed by heating the sample in the cleaning/STM chamber manipulator with an integrated PBN heater. Temperature was monitored by a K-type thermocouple attached near the sample and corrected by adding 120 K to estimate the real sample temperature. This correction is based on infrared pyrometry at temperatures greater than 820 K and is expected to be accurate only to about ± 30 K.

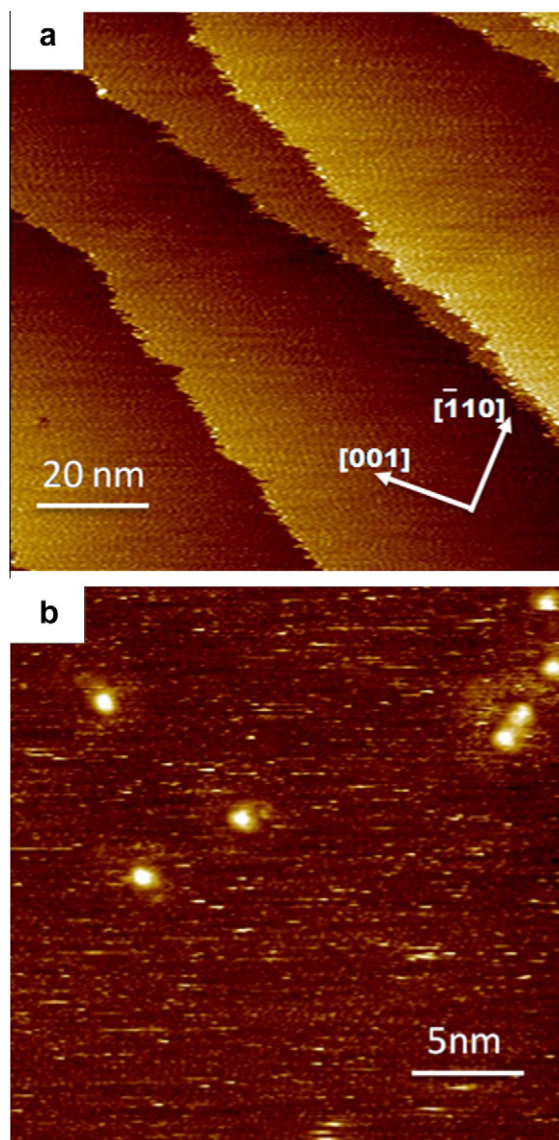


Fig. 1. (a) STM image (100 nm \times 95 nm, -0.8 V, 30 pA) of the clean Cu(1 1 0) substrate; (b) STM image (25 nm \times 25 nm, -1.0 V, 2 pA) after deposition of a small quantity (90 s deposition time) of Alq3. Single molecules are imaged as bright protrusions as indicated by the arrow.

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