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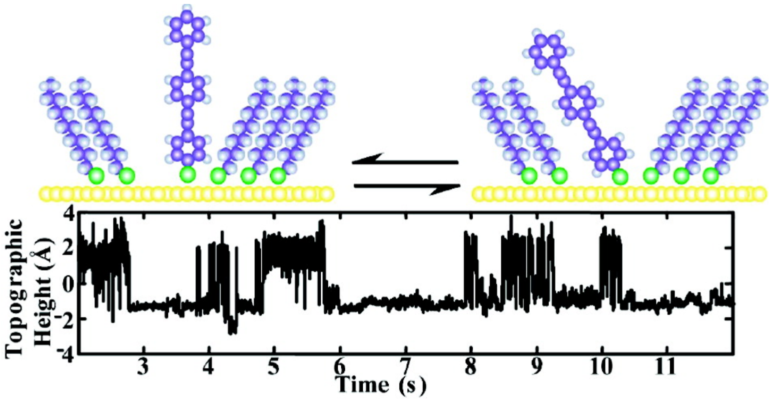

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Real-Time Measurements of Conductance Switching and Motion of Single Oligo(phenylene ethynylene) Molecules

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In order to understand the electronic properties involved in conductance switching of individual molecules, it is important to analyze and to understand the motions of the molecules and the substrate atoms to which they are bound. We and others have studied the conductance switching of oligo(phenylene ethynylene) (OPE) molecules isolated in host self-assembled monolayer (SAM) matrices[1−3] and their place-exchange up and down substrate step edges[4] using scanning tunneling microscopy (STM). Previously, conductance switching and motion of the OPE molecules were analyzed by determining the apparent height of each molecule in each STM frame, allowing us to characterize tens of molecules over hundreds of frames.[4,5] However, on the time scale of imaging, each OPE molecule is imaged for only 1−25 ms per image, depending on the image resolution. To broaden the dynamic range for measuring the switching and motion of OPE molecules and the host SAM, real-time (data obtained at 10 kHz), fixed lateral position topographic measurements have been acquired.

Real-time motions have previously been studied using STM for single atoms and molecules using time-dependent tunneling measurements.[6] These studies, performed in ultrahigh vacuum, analyzed the dynamics of single atoms as they diffused or were laterally manipulated by blanking the STM current feedback loop and recording the tunneling current versus time. Here, we measured the real-time conductance switching and place-exchange for OPE molecules and the host SAM by recording height versus time (z vs. t) with the feedback loop *active*, thereby minimizing drift and recording the topographic height of the molecule, enabling us to perform these measurements in ambient conditions.

Sample preparation has been described previously.[1,2] Briefly, a dodecanethiolate SAM was adsorbed from a 1 mM solution onto a flame-annealed Au{111} substrate for 5 min. This short adsorption time forms SAM matrices containing relatively less order and more defect sites than typical SAMs, ultimately allowing for more stochastic switching and motion.[1] After adsorption, the SAM was rinsed with ethanol and dried under nitrogen. Nitro-functionalized OPE molecules (4-(2-nitro-4-phenylethynyl phenylethynyl)benzenethiol) were inserted for 1 min from a 1 μM solution into the preformed SAM under a nitrogen environment.

During image acquisition, z versus t data were obtained by pausing the tip for 20 s over OPE molecules and the host SAM. Figure 1A displays a 500 Å × 500 Å imaged area of a SAM containing inserted nitro-functionalized OPE molecules that appear as protrusions from the SAM.[7] Several images were obtained over this area with z versus t measurements recorded in each image for each inserted OPE molecule (labeled **1**−**4** in Figure 1A) and over the host SAM (labeled **a**). The labels are offset from each molecule to show each molecule's location within the host SAM displayed between 4 and 5 s and place-exchange up and down the substrate step edge (∼2.3 Å height change), as displayed at several points. By tabulating the occurrences at each apparent height from the time history in Figure 1B, we find three distinct peaks (Figure 1C), in agreement with our previous data where we characterized molecules over a series of STM images at slower time scales, and found place-exchange up and down substrate step edges occurring independently of conductance switching.[4] We assign the peaks as the following: ON for the greatest apparent height, STEP for the middle apparent height, and OFF for the lowest apparent height. Note that we are

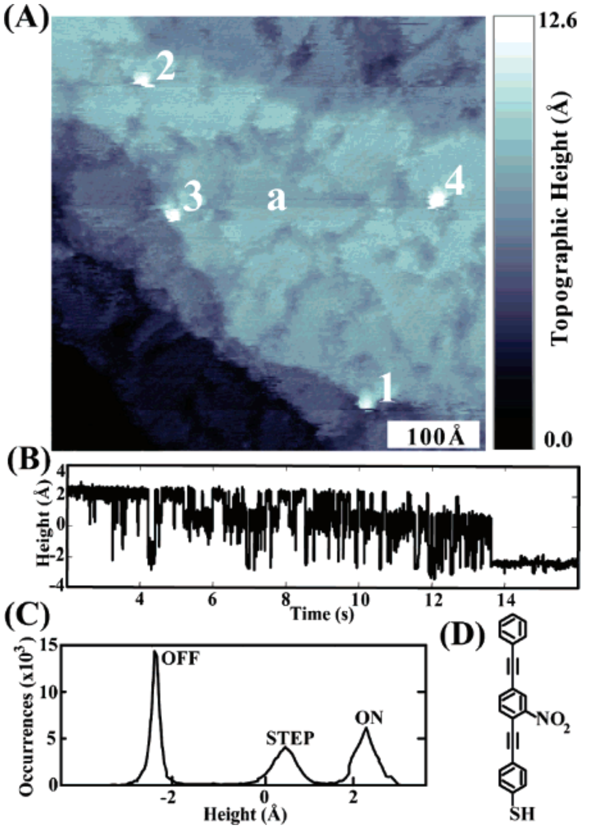

Figure 1. (A) Scanning tunneling microscopy topographic image of nitro-functionalized OPE molecules inserted into a host dodecanethiolate self-assembled monolayer matrix (500 Å × 500 Å; $V_{\text{sample}} = -1$ V; $I_{\text{tunnel}} = 1$ pA). (B) Real-time height versus time measurements for molecule **1**. Height changes indicate the molecule was actively switching conductance and place-exchanging up and down the substrate step edge during the measurement. (C) Occurrences versus height tabulation for real-time measurements in (B) displaying ON, STEP edge, and OFF topographic heights. (D) Nitro-functionalized oligo(phenylene ethynylene) molecule.

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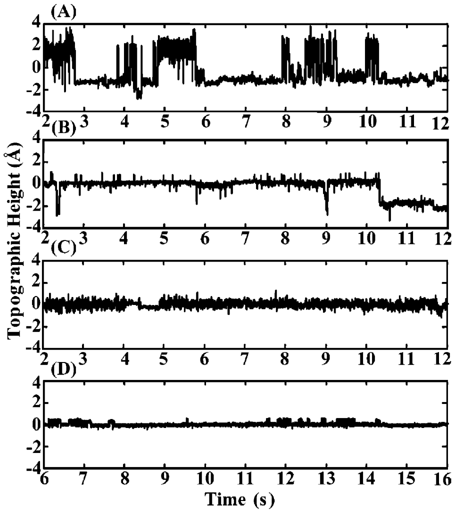

Figure 2. Real-time z versus t measurements obtained for the molecules and the SAM matrix at point **a**, as marked in Figure 1: (A) molecule **2**; (B) molecule **3**; (C) inactive molecule **4**; (D) SAM matrix at point **a**.

unable to distinguish between OFF for molecules at the top or bottom of the substrate step edges because molecules' topographic heights when in the OFF conductance state are indistinguishable from the surrounding host SAM matrix (i.e., the molecule does not appear in the image).[4] Figure 1D is a schematic of the nitro-functionalized OPE molecules used here. As described in ref 7, these OPE molecules are 21 Å long, and, if oriented normal to the surface, physically protrudes 5 Å from the host matrix; measured apparent heights are convolutions of geometric and electronic structure.

Figure 2 displays a few typical time histories as examples of many measurements obtained over OPE molecules and the host SAM, including real-time switching activity, place-exchange up and down the substrate step edge, and inactive molecules from Figure 1. Each was recorded for 20 s; however, only the most active 10 s are displayed here for ease of visualization. Molecule **1** (Figure 1B) displayed both conductance switching and place-exchange at a step edge. Figure 2A presents z versus t for molecule **2**, which exhibited only stochastic conductance switching between ON and OFF states, measured as topographic height changes of ∼4 Å. Only conductance switching was observed since molecule **2** was located within a SAM domain boundary (not at a step edge).

Figure 2B shows z versus t for molecule **3**, which underwent place-exchange up and down a substrate step edge measured as a height change of ∼2.3 Å. This motion is only observed at substrate step edges and substrate vacancy sites where molecules are able to place-exchange up and down a substrate step. The observed height change is equal to that of a step in the Au{111} substrate.[8] Molecule **3** was not active as a switch during this measurement; however, it did exhibit smaller motions, observed as topographic changes of ∼0.5 Å, typical in these z versus t measurements, and far above the noise floor of our measurements. These small topographic height changes were also observed for the host SAM and are discussed further below. Not all OPE molecules exhibit conductance switching or place-exchange during all z versus t measurements. Figure 2C shows a measurement for molecule **4** where the molecule displays no topographic height changes corresponding to conductance switching nor motion at a substrate step edge.

Over the host SAM, we observe small topographic height changes of ∼0.5 Å as displayed in Figure 2D. Our previous data have shown that both OPE molecules and SAM matrices can exhibit motion.[4,9] Experimental and theoretical data for SAMs suggest that the S headgroup of a SAM molecule is bound to a surface Au adatom and that these Au-thiolate species are mobile on the Au{111} surface.[10] We tentatively assign the small ∼0.5 Å topographic height changes observed over the OPE and SAM to substrate or molecule−substrate complex motions.[11] Grazing incidence X-ray diffraction performed on alkanethiolate monolayers found that the topmost layer of Au was distorted from the ideal bulk termination and oscillated between maximum and minimum values with an amplitude of 0.5 Å along the surface normal direction.[12] We expect a 0.5 Å topographic height change for a 0.5 Å physical height change of the substrate.[13]

Our temporal resolution is limited by the bandwidth of the feedback loop; therefore, some conductance switching and motion events may not be observed. This can be improved either by recording tunneling current versus time (the current amplifier bandwidth here is 30 kHz, but can be extended to 1 MHz and above) or by performing frequency-based measurements[14] (to reach on the order of 10 GHz). The real-time measurements presented here show that OPE molecules exhibit conductance switching and place-exchange at substrate step edges faster than the time scale of typical STM image acquisition. Further, we have been able to observe smaller topographic height changes that have not previously been measured in real-time, and that we attribute to substrate and/or molecule−substrate motion.

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