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Mediating Stochastic Switching of Single Molecules Using Chemical Functionality

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Molecules based on oligo(phenylene-ethynylene)s (OPEs) have been proposed as molecular device components because they are fully conjugated along the backbone and have shown interesting electronic characteristics individually,[1−4] in small numbers, and in groups of thousands.[5−7] To date, many studies have examined their electronic and physical properties; however, control of their behavior remains elusive. Toward this end, we have designed a system that mediates stochastic switching of OPE using localized electric fields and hydrogen bonding between the inserted OPE and its host matrix.

In previous work, we showed that single OPE molecules can be inserted into alkanethiol self-assembled monolayers (SAMs) deposited on Au{111} and their electronic and physical properties can be probed using scanning tunneling microscopy (STM).[1−3,8] An insertion strategy ensures that the guest OPE molecules are isolated within the host SAM with a well-defined adsorption geometry.[1,2,8] The structural and electronic properties of the guest molecules can then be examined with STM on an individual basis. In addition, it is possible to monitor the effects of localized electric fields applied by the STM tip on individual molecules. We have shown that the surrounding host matrix order greatly affects the amount of stochastic switching for single OPE molecules and that the observed switching is due to molecular motion since it can be controlled by changing the conformational freedom of the inserted molecules.[2,3] In these studies, the chemical functionality of the inserted molecule did not affect the switching activity.

Herein, we report a method to mediate the switching of inserted OPE molecules by varying their local *chemical* environment. We have inserted 4-(2′-nitro-4′-phenylethynyl-phenylethynyl)-benzenethiol (NPPB) into host amide-containing alkanethiol SAMs that are composed of 3-mercapto-*N*-nonyl-propionamide (1ATC9) (Figure 1, see Supporting Information for sample preparation[2]).[9−11] The embedded amide moiety in 1ATC9 leads to extended hydrogen bonding throughout the monolayer matrix,[9,10,12,13] thereby increasing the crystallinity of the film and limiting the conformational motion of inserted NPPBs. The internal amide group can also hydrogen bond with the $-NO_2$ substituent of inserted NPPBs, resulting in bias-dependent switching (shown below).

The NPPB molecule inserts at defect sites and domain boundaries and appears as a protrusion in STM images since it is both more conductive[14] and physically higher than its surrounding 1ATC9 matrix by ∼4 Å (assuming a tilt angle of 30° for 1ATC9 and 0° for NPPB with respect to normal). In 1ATC9 SAMs, NPPB is stable in at least two states, manifested in STM by a change in apparent topographic height of the molecules, a high conductance (ON) state, and a low conductance (OFF) state.

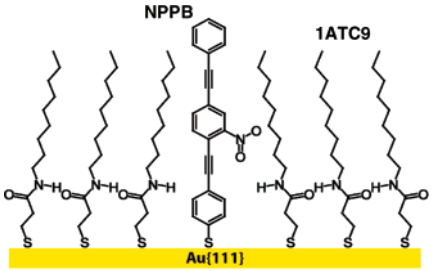

Figure 1. Schematic showing NPPB inserted into 1ATC9 SAM matrix.

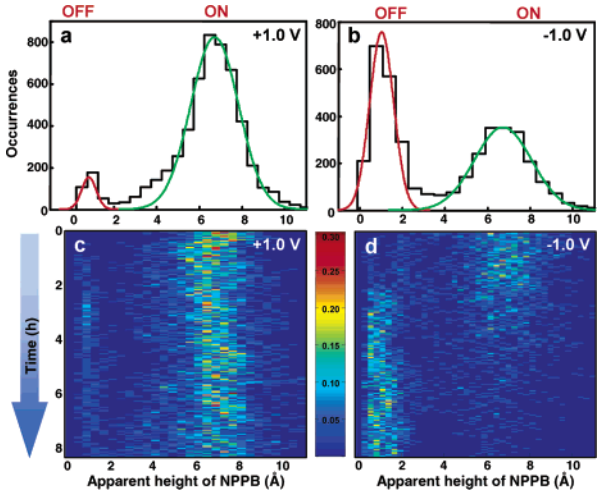

Figure 2. Apparent height distribution of NPPB in a 1500 Å × 1500 Å representative area of 1ATC9/NPPB showing the occurrences at ON and OFF peak heights taken over ∼8.25 h at (a) +1.0 V sample bias and (b) −1.0 V sample bias. (c,d) Apparent height distributions for the same series of STM images, including time information taken at (c) +1.0 V sample bias and (d) −1.0 V sample bias. The intensity indicates the relative number of occurrences at each height for each frame in the series of images.

Since STM measurements represent a convolution of electronic and topographic information, this change in apparent topographic height can be due to a change in conductance, a change in physical height, or both. We have previously introduced a method to track molecules in a time-lapse imaging sequence over an area of the sample to monitor their switching or motion using STM.[2,3,15] We track the behavior of all the inserted molecules in the imaging field of view and then generate a height distribution to determine the relative number of individual molecules in the ON and OFF states.

Figure 2a shows the height distribution for all NPPB molecules sampled in a 1500 Å × 1500 Å area over ∼8.3 h at a sample bias of +1.0 V. Gaussian peaks were fit to the histogram using least-squares analysis and show the OFF state occurring at 0.8 ± 0.3 Å

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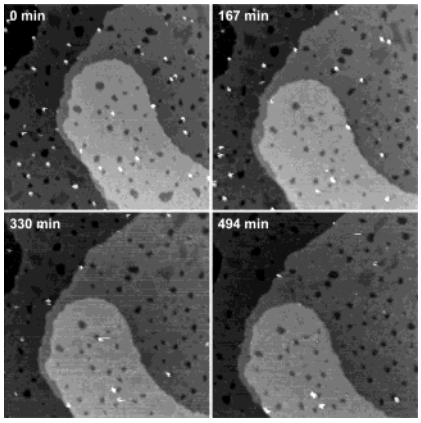

Figure 3. Selected images (1400 Å × 1400 Å) taken at 165-min intervals from a series of time-lapse images at −1.0 V sample bias and 2 pA current.[17] The protrusions are NPPB molecules in the ON state. Depressions are substrate defects from the matrix deposition process.

and the ON state occurring at 6.7 ± 1.1 Å (Δh = 5.9 ± 1.2 Å).[16] The ratio of the ON/OFF peak area is 17.8, indicating that the ON state is highly preferred under these conditions. This is always a biased measurement in our analyses as molecules that remain OFF throughout data acquisition are not included. Nonetheless, the high ON/OFF peak area ratio indicates that hydrogen bonding between amide groups in the 1ATC9 matrix contributes to a more rigid host matrix, which greatly reduces stochastic switching of embedded molecules.

The polarity of the applied electric field between the STM tip and the substrate strongly influences the switching behavior of NPPB and leads to bias-dependent switching. At positive sample bias, NPPB has a preference for the ON state, as evidenced by the histogram shown in Figure 2a and by the large ON/OFF ratio. Conversely, we observe a strong preference for the OFF state at negative sample bias. Figure 2b shows this trend in the height distribution of NPPB for a series of images taken over a 1500 Å × 1500 Å area of NPPB/1ATC9 for ~8.3 h at negative sample bias. The OFF and ON peaks occur at approximately the same apparent topographic heights as at positive sample bias (1.0 ± 0.6 and 6.7 ± 1.3 Å, respectively; Δh = 5.7 ± 1.5 Å). However, it is apparent from the histogram that the OFF state is significantly populated at negative sample bias (ON/OFF peak area ratio of 1.10). This low ratio is indicative of a high number of molecules initially in the ON state switching to the OFF state for the duration of imaging.

It is important to note that the switching *activity* is still limited by the hydrogen-bonded matrix at negative sample bias; that is, molecules typically remain in the OFF state and do not undergo subsequent switching events. This phenomenon is evident in Figure 3, which shows four selected 1400 Å × 1400 Å areas extracted from the images used to generate the histogram in Figure 2b. The images were taken ~165 min apart.[17] In the first image, there are many NPPB molecules in the ON state (indicated as bright spots). As the imaging progressed, the NPPB molecules in the imaging field were affected by the applied electric field for a longer period of time, which resulted in an overall decrease in the number of NPPB molecules in the ON state. At the end of the series of images, almost all of the NPPB molecules initially in the ON state switch to and remain in the OFF state.

These data can be visualized by generating a 3-D histogram that represents the same data as in Figure 2a,b but includes time information (Figure 2c,d). At positive sample bias, there is little activity and most of the switches remain in the ON state (Figure 2c), as indicated by the high intensity for the peak at ~6 Å throughout the series of images. At negative sample bias, there is still little activity, but the majority of the NPPB molecules switch to the OFF state (Figure 2d). We do not observe this bias dependence in studies where the amide groups of the matrix[2,3] or the $-NO_2$ functionality of the OPE are absent. From this we deduce that hydrogen bonding between the amide groups and the $-NO_2$ group is a factor in the observed bias dependence.

The bias dependence observed for NPPB in 1ATC9 SAMs is reversible in that the conductance state of the molecules can be changed by reversing the polarity of the applied bias. Subsequent images acquired after changing to positive sample bias show that it is possible to drive the NPPB molecules back into the ON state (see Supporting Information). The reversible switching of NPPB molecules excludes the possibility that they are removed from the surface by the STM tip. In addition, it further demonstrates control over the state of the inserted NPPB using the applied electric field.

We have demonstrated a method for mediating conformational switching of NPPB by modifying the chemical functionality of the host matrix. Using this strategy, we can induce bias-dependent switching of individual NPPB molecules, which was formerly not possible based on the intrinsic characteristics of NPPB.[2,3] We have shown that the chemical and physical environments of proposed molecular devices are crucial to their function and can be exploited to impart tunable electronic properties. Currently, we are investigating the bias-dependence mechanism by incorporating substituents on the inserted OPE that alter the degree and location of hydrogen bonding between the inserted molecules and the host matrix.

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Supporting Information Available: Sample preparation and STM images showing reversible switching. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) The apparent height difference between NPPB and 1ATC9 (Δh = ~6 Å) is expected to be greater than the physical height difference (Δh = ~4 Å) because of electronic effects, i.e., higher conductance of NPPB.
(17) Thermal fluctuations and piezoelectric creep of the rastering mechanism cause the small amount of drift that is apparent between images.JA038622I

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