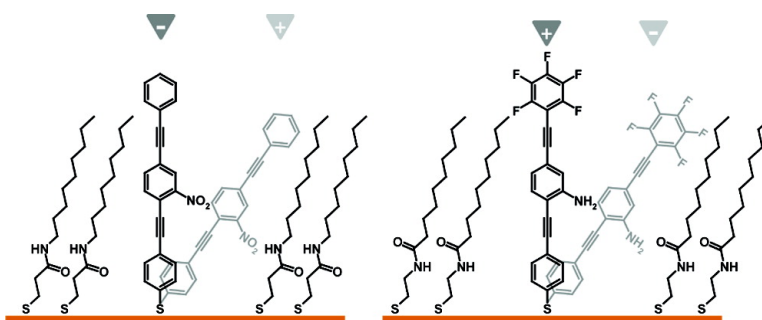**Article**

Molecular Engineering of the Polarity and Interactions of Molecular Electronic Switches

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Molecular Engineering of the Polarity and Interactions of Molecular Electronic Switches

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Abstract: We have investigated and learned to control switching of oligo(phenylene ethynylene)s embedded
in amide-containing alkanethiol self-assembled monolayers on Au{111}. We demonstrate bias-dependent
switching of the oligo(phenylene ethynylene)s as a function of the interaction between the dipole moment
of the oligo(phenylene ethynylene)s and the electric field applied between the scanning tunneling microscope
tip and the substrate. We are able to invert the polarity of the switches by altering their design—inverting
their dipole moments. For appropriately designed switches and matrix molecules, the conductance states
are stabilized by intermolecular hydrogen bonding. These results further support the hypothesis that
conductance switching in these molecules is due to hybridization changes at the molecule—substrate bonds
due to tilting of the switch molecules.

Introduction

Since the advent of solid-state technology, there has been a desire to produce ever smaller, faster, and cheaper device components. This has been achieved largely by improving upon device fabrication technology in order to allow for the continued miniaturization of solid-state devices. Current fabrication technology is limited to the production of device components that are on the order of tens to hundreds of nanometers and may reach fundamental limitations. Thus, there has been a drive toward designing electronic device components out of molecules or atoms, a field known as molecular electronics.[1−3]

A number of designs have been proposed and investigated as possible future devices that implement the use of fullerenes and carbon nanotubes,[4−8] metal or semiconductor nanowires or nanoparticles,[9−11] and conjugated molecular systems.[3,10−13] Despite the accomplishments in this field, much of the observed

phenomena defy simple explanation since atoms and molecules behave very differently when examined individually rather than as ensembles. Therefore, to understand and to predict the behavior of these molecular- and atomic-scale devices, it is necessary to study the intrinsic physical and chemical properties of these systems at the single-molecule level.

Using scanning tunneling microscopy (STM), it is possible to probe molecules on an individual basis and to elucidate their physical and electronic properties. We have studied oligo-(phenylene ethynylene)s (OPEs) at the single-molecule level using STM to examine their potential as molecular electronic device components. Previously, we studied the switching behavior for functionalized and nonfunctionalized OPEs inserted into self-assembled monolayers (SAMs) on Au{111}.[14−17] The OPE molecules are isolated from one another such that they can be addressed on an individual basis.

In alkanethiol SAM matrices, OPEs have shown stability in at least two states, manifested in STM by a change in apparent topographic height of the molecules, a high conductance (ON)

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(1) Mantooth, B. A.; Weiss, P. S. *Proc. IEEE* **2003**, *91*, 1785−1802.
(2) Reed, M. A. *Proc. IEEE* **1999**, *87*, 652−658.
(3) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791−804.
(4) Xie, R. H.; Bryant, G. W.; Zhao, J. J.; Smith, V. H.; Di Carlo, A.; Pecchia, A. *Phys. Rev. Lett.* **2003**, *90*, 206602-1−4.
(5) Yao, Z.; Postma, H. W. C.; Balents, L.; Dekker, C. *Nature* **1999**, *402*, 273−276.
(6) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2000**, *408*, 541−548.
(7) Avouris, P. *Acc. Chem. Res.* **2002**, *35*, 1026−1034.
(8) Avouris, P.; Appenzeller, J.; Martel, R.; Wind, S. J. *Proc. IEEE* **2003**, *91*, 1772−1784.
(9) Bezryadin, A.; Dekker, C.; Schmid, G. *Appl. Phys. Lett.* **1997**, *71*, 1273−1275.
(10) Husband, C. P.; Husband, S. M.; Daniels, J. S.; Tour, J. M. *IEEE Trans. Electron Devices* **2003**, *50*, 1865−1875.

(11) Tour, J. M.; Cheng, L.; Nackashi, D. P.; Yao, Y. X.; Flatt, A. K.; St. Angelo, S. K.; Mallouk, T. E.; Franzon, P. D. *J. Am. Chem. Soc.* **2003**, *125*, 13279−13283.
(12) Chen, J.; Reed, M. A.; Asplund, C. L.; Cassell, A. M.; Myrick, M. L.; Rawlett, A. M.; Tour, J. M.; Patten, P. G. V. *Appl. Phys. Lett.* **1999**, *75*, 624−626.
(13) Robertson, N.; McGowan, C. A. *Chem. Soc. Rev.* **2003**, *32*, 96−103.
(14) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705−1707.
(15) Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **2001**, *292*, 2303−2307.
(16) Donhauser, Z. J.; Mantooth, B. A.; Pearl, T. P.; Kelly, K. F.; Nanayakkara, S. U.; Weiss, P. S. *Jpn. J. Appl. Phys.* **2002**, *41*, 4871−4877.
(17) Lewis, P. A.; Inman, C. E.; Yao, Y. X.; Tour, J. M.; Hutchison, J. E.; Weiss, P. S. *J. Am. Chem. Soc.* **2004**, *126*, 12214−12215.

state and a low conductance (OFF) state.[15] 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 or a change in physical height, or both. We have shown that the physical environment surrounding the OPE molecules strongly influences the switching between states.[15] In *n*-alkanethiol SAM matrices, the switching activity increased as the SAM crystallinity decreased, indicating that the observed switching of OPE molecules is due to molecular motion since it can be controlled by changing the conformational freedom of the inserted molecules.[15,16] The motion we observe is consistent with tilting of the inserted OPEs, changing the hybridization and thus the contact conductance of the molecule−substrate bond.[18,19]

The chemical environment of the inserted OPE molecules has also been shown to be an important factor in mediating their switching behavior.[17] We have inserted OPEs into host amide-containing alkanethiol SAMs to determine the effect of adding a hydrogen-bonding interaction to the matrix SAM. The buried amide groups in the host SAM can hydrogen bond throughout the monolayer matrix,[20−23] which increases the crystallinity of the film and limits the conformational motion of the film and of the inserted OPEs. The inserted OPE molecules are stable in two conductance states and exhibit less switching activity than previously reported for OPEs inserted into alkanethiol matrices. This can be attributed to the rigidity of the surrounding host environment imparted by the hydrogen-bonding amide groups in the matrix. These results indicated that amide−alkanethiol SAMs can be used as stable insertion matrices for the study of individual OPE molecules.

An additional feature of this system is the ability for hydrogen bonding to occur between inserted OPE molecules and adjacent amide-containing alkanethiols.[17] We have observed bias-dependent switching for nitro-functionalized OPE molecules (4-(2-nitro-4-phenylethynyl phenylethynyl)benzenethiol, or NPPB), inserted into amide-containing alkanethiol SAMs, a phenomenon that was not previously observed for OPE molecules inserted into *n*-alkanethiol SAMs at low bias.[15] Here, we present the results of a systematic study in which the mechanism of this observed bias-dependent switching is investigated by engineering the dipole of the switch molecules and their molecular interactions. The intrinsic dipole moment of the inserted OPEs can interact with the electric field applied by the STM tip, producing bias-dependent switching in which the ON (OFF) state is favored at positive sample bias for OPE dipole moments that are positive (negative) at the film surface. This bias-dependent switching is then stabilized by hydrogen bonding that occurs between the OPE and the amide−alkanethiol matrix.

We have designed, synthesized, and investigated several functionalized OPEs that have been inserted into amide−alkanethiol SAMs. Their intrinsic molecular dipoles as well as

their ability to hydrogen bond with adjacent matrix molecules (also designed and synthesized for this purpose) were selected to test our predictive ability to control switching. These conjugated molecules have the added benefit that they are stable relative to fragmentation when reduced or probed in the STM tunneling junction. Herein, we present the results of five different OPE molecules inserted into amide-containing alkanethiol SAMs: 4-(4-phenylethynyl phenylethynyl)benzenethiol (PPB), 4-(2-nitro-4-phenylethynyl phenylethynyl)-benzenethiol (NPPB), 4-(2-nitro-4-pentafluorophenylethynyl phenylethynyl)benzenethiol (FNPPB), 4-(3-nitro-4-pentafluorophenylethynyl phenylethynyl)benzenethiol (FNPPB-o), and 4-(2-amino-4-pentafluorophenylethynyl phenylethynyl)benzenethiol (FAPPB) (Figure 1). These results provide compelling evidence that the switching of OPE molecules can be controlled by an applied electric field and by intermolecular interactions with their chemical environment.

Experimental Section

Commercial Au{111}/mica substrates were annealed with a hydrogen flame and then exposed to a 1 mM ethanolic solution of either 3-mercapto-*N*-nonylpropionamide (1ATC9) or decanoic acid(2-mercaptoethyl)amide (R1ATC9) for 24 h, rinsed thoroughly with ethanol, and dried under nitrogen (Figure 1). STM images of the amide−alkanethiol SAMs were obtained to ensure the SAMs were well-ordered. The fresh amide−alkanethiol monolayers were exposed to ∼1 mL of a ∼0.1 mM THF solution of the OPE molecule of interest for 1−60 s in an inert atmosphere to perform the insertion.[24]

The dipole moments for the OPE molecules were calculated semiempirically using CAChe Worksystem Pro (version 6.1.1) with PM5 parametrization. The values that are given are for the free-thiol OPEs and are presented as a qualitative comparison between the Au-bound OPE thiolate molecules. The dipole magnitudes of the OPE molecules would almost certainly change when adsorbed on a Au surface, but we expect that for qualitative purposes a comparison of the free thiols is relevant.

The OPE/SAM samples were imaged under ambient conditions using a beetle-style STM that has been described in detail previously.[24] Series of time-lapse images were acquired for many hours in the same area of the sample such that changes in apparent height (i.e., changes in conductance) could be monitored for the individual OPE molecules in the field of view over an extended period of time. For the studies detailed here, images were acquired over relatively large areas of the sample (1500−3000 Å^2) for 8−30 h with an individual frame recording interval time of 2.5−6 min. In situ drift correction was employed manually to account for the small drift caused by thermal fluctuations and piezoelectric creep of the raster mechanism.

We used a method that we have previously described to track molecules in time-lapse imaging sequences over areas of the sample, enabling us to monitor their switching or motion.[15,16,25,26] We extracted the conductance of individual molecules in the imaging field of view using a drift track that is calculated by cross-correlation of Fast Fourier Transform spectra of sequential images. Using this drift track, we analyzed the apparent topographic height as a function of time for each molecule in the field of view. The apparent topographic height is indicative of the conductance state of the inserted OPE; thus, by monitoring the apparent topographic height, it was possible to determine whether the inserted OPE was in a high or a low conductance state.

(18) Kornilovitch, P. E.; Bratkovsky, A. M. *Phys. Rev. B* **2001**, *64*, 195413-1−4.
(19) Kornilovitch, P. E.; Bratkovsky, A. M. In *Molecular Electronics*; Annals of the New York Academy of Science, 2002; Vol. 960, pp 193−202.
(20) Smith, R. K.; Reed, S. M.; Lewis, P. A.; Monnell, J. D.; Clegg, R. S.; Kelly, K. F.; Bumm, L. A.; Hutchison, J. E.; Weiss, P. S. *J. Phys. Chem. B* **2001**, *105*, 1119−1122.
(21) Lewis, P. A.; Smith, R. K.; Kelly, K. F.; Bumm, L. A.; Reed, S. M.; Clegg, R. S.; Gunderson, J. D.; Hutchison, J. E.; Weiss, P. S. *J. Phys. Chem. B* **2001**, *105*, 10630−10636.
(22) Clegg, R. S.; Reed, S. M.; Smith, R. K.; Barron, B. L.; Rear, J. A.; Hutchison, J. E. *Langmuir* **1999**, *15*, 8876−8883.
(23) Clegg, R. S.; Hutchison, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 5319−5327.

(24) Cygan, M. T.; Dunbar, T. D.; Arnold, J. J.; Bumm, L. A.; Shedlock, N. F.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *J. Am. Chem. Soc.* **1998**, *120*, 2721−2732.
(25) Mantooth, B. A.; Donhauser, Z. J.; Kelly, K. F.; Weiss, P. S. *Rev. Sci. Instrum.* **2002**, *73*, 313−317.
(26) Moore, A. M.; Mantooth, B. A.; Donhauser, Z. J.; Maya, F.; Yao, Y.; David W. Price, J.; Tour, J. M.; Weiss, P. S. In press.
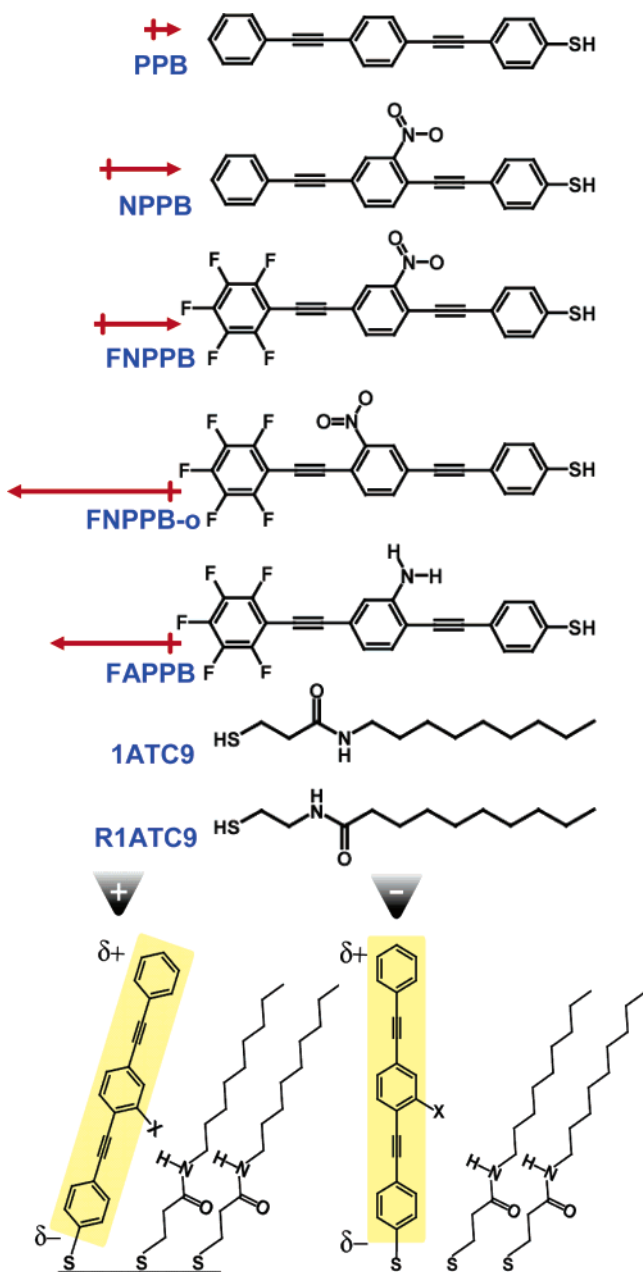
Figure 1. (Top) Structures of the OPE molecules used in this study: PPB, NPPB, FNPPB, FNPPB-o, and FAPPB. (Middle) Amide-containing al-kanethiol matrix molecules used in this study: 1ATC9 and R1ATC9. (Bottom) Schematic showing a hypothesized mechanism for the bias-dependent induced switching. (Bottom left) At negative sample bias, electrostatic repulsion between the positive charge of the STM tip and the positive dipole of the OPE molecule can cause the OPE to tilt into the OFF state, allowing for hydrogen bonding to occur between the substituent of the OPE (−X) and the amide groups of 1ATC9. (Bottom right) At positive sample bias, the electrostatic attraction between the negative tip and the positive dipole explains the preference for the ON state.

From these data, an apparent height distribution was generated for all of the individual molecules to determine the relative number of individual molecules in the ON and OFF states for an entire sequence of images.

Results and Discussion

A hypothesized mechanism for the induced bias-dependent switching is illustrated in Figure 1. The amide-containing alkane-thiols can hydrogen bond with neighboring amides within the matrix as well as with the OPE substituents (−X in Figure 1).

Table 1. Calculated Dipole Moment Components Parallel to the Molecular Axes of the OPE Molecules Used in This Study (the values given are for the free-thiol OPEs)

OPE	NPPB	PPB	FNPPB	FNPPB-o	FAPPB
dipole (total)	+4.6	+1.6	+6.0	−8.1	−4.4
dipole component (parallel to OPE axis)	+2.4	+1.1	+2.6	−5.2	−3.9

If there is a repulsive interaction between the biased STM tip and the inserted OPE based on the orientation of the dipole moment of the OPE, the electrostatic interaction can cause the OPE to tilt into the OFF state (for the dipole orientation shown). In this tilted state, the amide groups of the matrix can hydrogen bond with the substituent on the OPE, stabilizing it in the OFF state. Conversely, if there is an electrostatic attraction between the STM tip and the molecular dipole, the OPE molecule will remain in or be drawn into the ON state (once again for the dipole orientation shown). In both cases, the stability of the matrix imparted by the hydrogen-bonding amide groups con-tributes to reduce the total number of stochastic switching events.

On the basis of this model, there are two important factors that contribute to bias-dependent switching: (1) the intrinsic dipole moment of the inserted OPE, and (2) hydrogen bonding between the inserted OPE and the amide groups in the 1ATC9 matrix. Both of these aspects were examined to test this hypothesis and are discussed below.

To test our mechanism for bias-dependent switching, we systematically altered the sign and magnitude of the dipole moment of the OPE by designing a series of fluorinated OPEs to control the polarity of the bias dependence. NPPB and PPB have intrinsic dipole moments of +4.6 and +1.6 D, respectively. These dipoles are designated as positive for the purpose of this discussion and indicate that the positive end of the dipole is presented at the outer surface of the film when the OPE molecules are inserted into a SAM. To test the role of the dipole orientation on bias-dependent switching, fluorinated OPE molecules were examined in which the intrinsic dipole moment was opposite that of PPB and NPPB (i.e., the negative end is presented at the outer film surface when the molecules are inserted into a SAM matrix). These fluorinated OPEs were studied to determine whether the polarity of the bias dependence could be reversed from previous studies of NPPB in 1ATC9 SAMs; that is, the OFF state would be favored at positive sample bias, and the ON state would be favored at negative sample bias. Table 1 lists the estimated dipole moments of the OPE molecules used in this study, with the relative directions given in Figure 1. In addition to the total dipole magnitude, the component of the dipole moment along the molecular axis when the inserted OPE molecules are oriented roughly normal to the substrate is also presented. We expect the component of the dipole normal to the surface to have the largest influence on bias-dependent switching because it will be aligned by the electric field between the STM tip and the sample.

The fluorinated analogue of NPPB (FNPPB) has an overall dipole moment of +6.0 D and a dipole component along its molecular axis of +2.6 D (Table 1). The apparent height distributions from a series of time-lapse images taken for the FNPPB/1ATC9 system at positive and negative sample bias show the same bias dependence polarity as the NPPB/1ATC9 system,[17] with ON/OFF peak area ratios of 6.9 and 1.6 for positive and negative sample bias, respectively (Figure 2A,B).
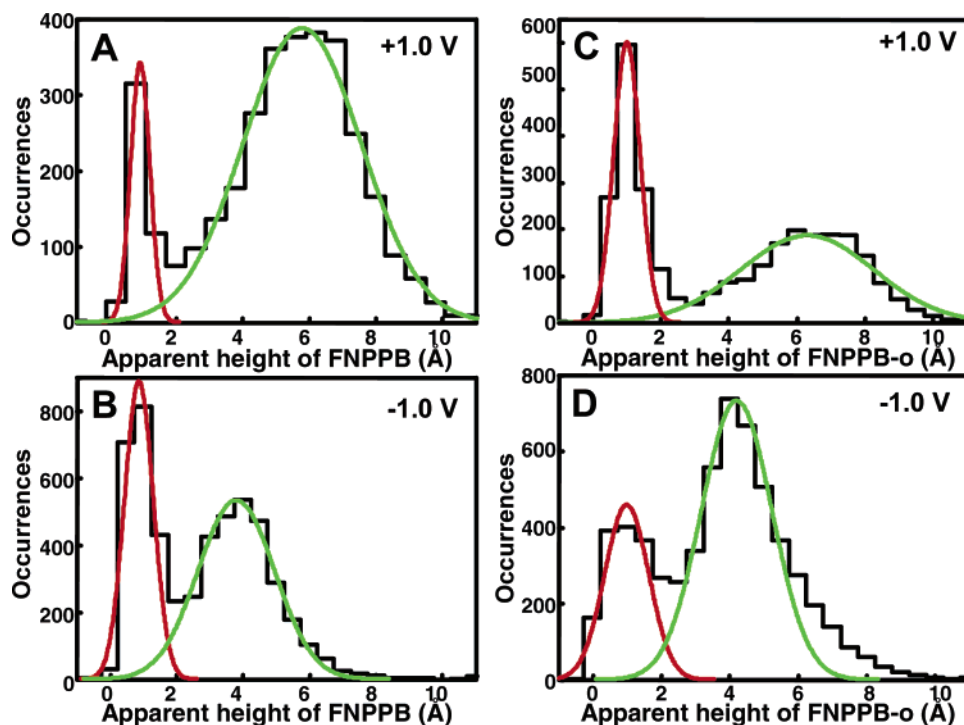
Figure 2. (A and B) Apparent height distributions of FNPPB in 2000 Å × 2000 Å representative areas of FNPPB/1ATC9 at (A) positive sample bias and (B) negative sample bias. (C and D) Apparent height distributions of FNPPB-o in 2000 Å × 2000 Å representative areas of FNPPB-o/1ATC9 at (C) positive sample bias and (D) negative sample bias. Data acquisition conditions: (A) total measurement time = 22.3 h, V_{sample} = +1.0 V, I = 2 pA; (B) total measurement time = 18.5 h, V_{sample} = −1.0 V, I = 2 pA; (C) total measurement time = 26.4 h, V_{sample} = +1.0 V, I = 2 pA; (D) total measurement time = 26.4 h, V_{sample} = −1.0 V, I = 2 pA.

The ON/OFF ratios indicate that the ON state is still preferred at positive sample bias, although not as dramatically as for NPPB/1ATC9, where the ON/OFF ratio at positive sample bias is 17.8.[17]

To reverse the dipole moment and align its direction perpendicular to the substrate, an isomer of FNPPB was considered. The FNPPB-o molecule has the −NO₂ group positioned on the central phenylene ring, closer to the outer surface of the film, producing an overall dipole moment of −8.1 D and a dipole component along its molecular axis of −5.2 D. From the apparent height distributions of FNPPB-o/1ATC9 (Figure 2C,D), we find a preference for the OFF state at positive sample bias and a preference for the ON state at negative sample bias, which is opposite to that found for NPPB/1ATC9. This bias dependence is reflected in quantitative terms by the ON/OFF peak area ratios (1.6 and 2.6 for positive and negative sample bias, respectively), although not as strongly as for NPPB/1ATC9.[17] One possibility is that the −NO₂ group is not in close enough proximity for hydrogen bonding to occur with neighboring 1ATC9 matrix molecules, which reduces the strong bias dependence that was observed for NPPB/1ATC9.

The FAPPB molecule is another fluorinated OPE that was designed to have a negative relative dipole moment for bias-dependent switching. The −NH₂ group serves two purposes: (1) it contributes to the dipole moment of FAPPB (−4.4 D overall, and −3.9 D along its molecular axis; Table 1), and (2) it allows for hydrogen bonding since it is in close proximity to the amide groups of the matrix molecules. However, studies of FAPPB inserted into 1ATC9 indicated that there was no significant bias dependence since the resulting height distributions appeared similar at both sample bias polarities and exhibited ON/OFF peak area ratios of 4.7 and 6.1 at positive

and negative sample bias, respectively (data not shown). To enable hydrogen bonding between the amino group of FAPPB and the amide carbonyl of the matrix, it was necessary to change the position of the amide group on 1ATC9. Thus, a different amide−alkanethiol (R1ATC9) was used in which the amide group was inverted relative to its position in 1ATC9. As a demonstration of the bias dependence exhibited by this system, six sequential STM images of the FAPPB/R1ATC9 switch/matrix system were obtained at alternating sample biases of +1 and −1 V (Figure 3). The majority of the FAPPB molecules in the field of view switched conductance states between OFF at +1 V and ON at −1 V sample bias. This is indicated in Figure 3 by the disappearance (OFF state) and reappearance (ON state) of the protrusions in the STM images (FAPPB molecules). The red and green boxes in Figure 3 highlight one FAPPB molecule that exhibited this preference for the OFF state at positive sample bias and the ON state at negative sample bias. The ability to control the conductance states of the FAPPB molecules based on the polarity of the sample bias indicates that the dipole moment of the inserted OPE determines the observed bias polarity dependence.

This bias polarity dependence is also shown in the corresponding height distributions for a time-lapse series of images recorded for the FAPPB/R1ATC9 system at positive and negative sample biases (Figure 4A,B). At positive sample bias, the ON/OFF peak area ratio of 0.8 demonstrates a strong preference for the OFF state, which we attribute to a repulsive interaction between the negatively-biased STM tip with the negative dipole moment of FAPPB. We also observed a preference for the ON state at negative sample bias, designated by the ON/OFF peak area ratio of 6.0.
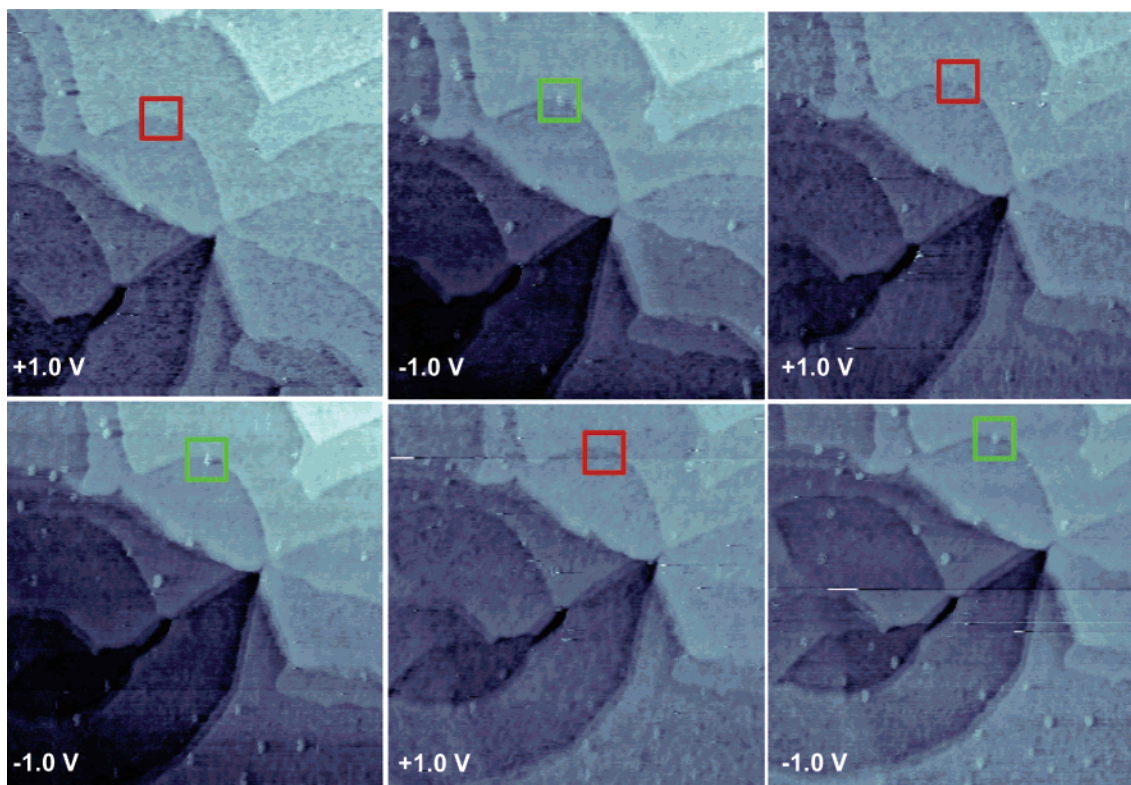
Figure 3. Sequential STM images of FAPPB/R1ATC9 obtained at alternating sample biases of +1.0 and −1.0 V. The majority of the FAPPB molecules (apparent protrusions, displayed as bright spots) switch conductance states between OFF at +1.0 V and ON at −1.0 V sample bias. The red and green boxes follow one FAPPB molecule that exhibits this bias dependence. Imaging conditions: 4000 Å × 4000 Å, $I = 2$ pA.
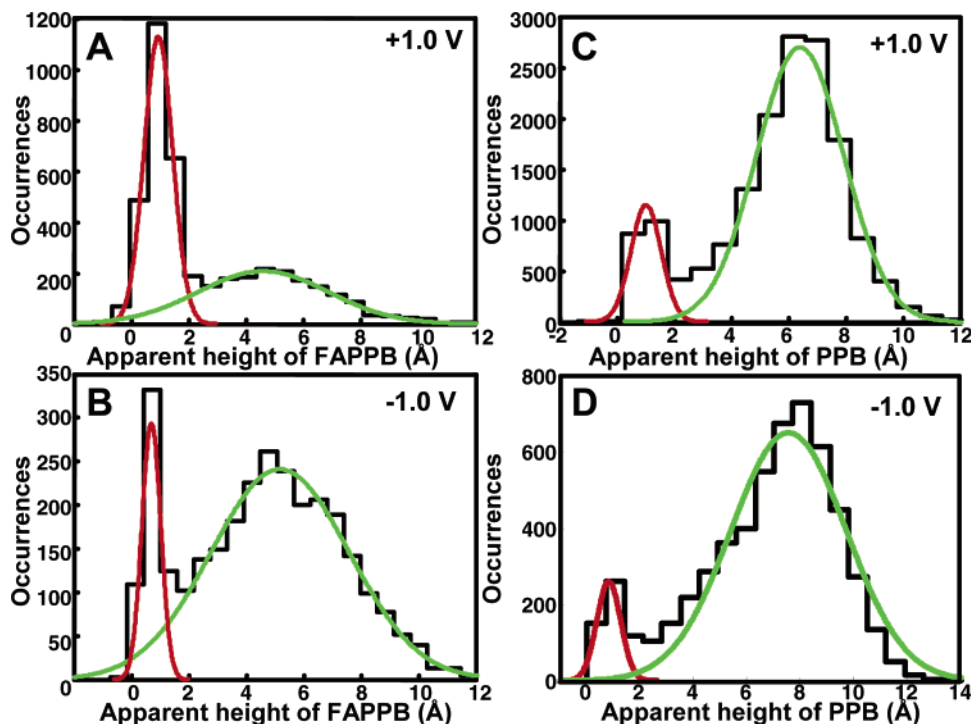

Figure 4. (A and B) Apparent height distribution of FAPPB in representative areas of FAPPB/R1ATC9 at (A) positive sample bias and (B) negative sample bias. (C and D) Apparent height distribution of PPB in 2000 Å × 2000 Å representative areas of PPB/1ATC9 at (C) positive sample bias and (D) negative sample bias. The occurrences at ON and OFF peak heights indicate that there is no bias dependence for PPB/1ATC9. Data acquisition conditions: (A) total measurement time = 29.8 h, 3000 Å × 3000 Å, $V_{sample} = +1.0$ V, $I = 2$ pA; (B) total measurement time = 11.5 h, 2000 Å × 2000 Å, $V_{sample} = -1.0$ V, $I = 2$ pA; (C) total measurement time = 22.5 h, $V_{sample} = +1.0$ V, $I = 2$ pA; (D) total measurement time = 19.3 h, $V_{sample} = -1.0$ V, $I = 2$ pA.

We have performed a series of control studies to determine the influence of the hydrogen-bonding groups in the amide−alkanethiolate matrix. For studies of NPPB molecules inserted into an alkanethiolate matrix, no bias dependence was observed, indicating that hydrogen bonding with the matrix influences switch stability.[15]

Table 2. Summary of the Data Discussed in This Paper[a]

	sample bias (V)	OFF peak height (Å)	ON peak height (Å)	hydrogen bonding	dipole moment	ON/OFF ratio
NPPB/	+1.0	0.8 ± 0.3	6.7 ± 1.1	yes	+	17.8
1ATC9[17]	−1.0	1.0 ± 0.6	6.7 ± 1.3	yes	+	1.1
FNPPB/	+1.0	0.9 ± 0.3	5.8 ± 1.8	yes	+	6.9
1ATC9	−1.0	0.9 ± 0.4	3.8 ± 1.2	yes	+	1.6
FNPPB-o/	+1.0	1.0 ± 0.4	6.3 ± 2.0	yes	−	1.6
1ATC9	−1.0	1.0 ± 0.6	4.2 ± 1.0	yes	−	2.6
FAPPB/	+1.0	1.0 ± 0.5	4.6 ± 2.3	yes	−	0.8
R1ATC9	−1.0	0.7 ± 0.3	5.2 ± 2.4	yes	−	6.0
PPB/	+1.0	1.0 ± 0.5	6.4 ± 1.5	no	+	6.8
1ATC9	−1.0	0.8 ± 0.5	7.6 ± 2.2	no	+	12.0

[a] Data previously found for NPPB/1ATC9 are included for comparison.[17] The relative directions of the dipole moments are shown, indicated as plus (minus) if the positive (negative) end of the molecular switch is at the outer surface of the film. The possibility of hydrogen-bond formation between the OPE and adjacent SAM molecules is also indicated.

The switching of an unsubstituted OPE (PPB) was examined in the 1ATC9 SAM to investigate the influence of hydrogen bonding between the OPE and the 1ATC9 matrix since PPB lacks substituents that can hydrogen bond with the adjacent amide groups in the matrix. A series of time-lapse images was recorded for ~22.5 h at positive sample bias and ~19.3 h at negative sample bias over 2000 Å × 2000 Å areas of PPB/1ATC9. Figure 4C,D shows the resulting height distributions for all PPB molecules in the field of view at both sample biases. Gaussian peaks fit to the height distributions at positive sample bias indicate that the OFF and ON peaks occur at approximately the same apparent topographic heights (1.0 ± 0.5 and 6.4 ± 1.5 Å, respectively; $\Delta h = 5.4 \pm 1.2$ Å) as at negative sample bias (0.8 ± 0.5 and 7.6 ± 2.2 Å, respectively; $\Delta h = 6.8 \pm 2.3$ Å). These results are also consistent with the apparent topographic heights for the OFF and ON peaks of NPPB inserted into 1ATC9 SAMs.[17]

The ON/OFF peak area ratios for positive and negative sample bias for PPB/1ATC9 were 6.8 and 12.0, respectively, indicating that the ON state was preferred at both positive and negative sample bias and can be attributed to reduced switching caused by the hydrogen-bonded matrix. The fact that the ON/OFF peak area ratios were similar at positive and negative sample bias demonstrates that there was no bias dependence for PPB/1ATC9. This suggests that interaction between the hydrogen-bonding matrix and the inserted OPE is a necessary factor in stabilizing the bias-dependent switching.

Table 2 summarizes the data for each of the OPE/SAM matrix systems. The relative direction of the dipole moment is shown

(indicated as plus (minus) if the positive (negative) end is at the outer surface of the film) as well as the possibility of hydrogen-bond formation between the OPE and adjacent SAM molecules. For OPE/SAM systems in which hydrogen bonding was possible and the dipole moment was designated as positive, the bias dependence that was observed showed a preference for the ON state at positive sample bias and the OFF state at negative sample bias (NPPB/1ATC9,[17] FNPPB/1ATC9). In contrast, the OPE molecules showed a preference for the OFF state at positive sample bias and the ON state at negative sample bias for hydrogen-bonding OPE/SAM systems in which the dipole moment was designated as negative (FNPPB-o/1ATC9, FAPPB/R1ATC9). For OPE/SAM systems that did not have hydrogen bonding capability (PPB/1ATC9), no bias dependence was observed, indicated by similar ON/OFF peak area ratios at both positive and negative sample biases. These results are consistent with our proposed mechanism in which the STM probe tip interacts either attractively or repulsively with the OPE molecule, depending on the sample bias polarity and the dipole direction of the OPE. The ON/OFF peak area ratios for each of the OPE/SAM systems indicate that the direction of the dipole as well as hydrogen bonding ability are important in determining both the existence and the polarity dependence of the observed bias-dependent switching.

Conclusions

We have tailored the behavior of molecular switches by designing these molecules to have dipole directions and magnitudes sufficient to interact with the electric field applied by a STM tip. The polarity of the bias dependence can be controlled by changing the direction of the dipole moment. In addition, hydrogen bonding engineered between matrix molecules and substituents of the OPE molecules contribute to switch stability. Thus, by systematically modifying the functional groups on the OPE molecules and the matrix molecules, it is possible to mediate stochastic switching of the OPE molecules. On the basis of this and previous studies, we conclude that designing the local chemical and structural environment of molecular electronic components is crucial to optimizing their function.