

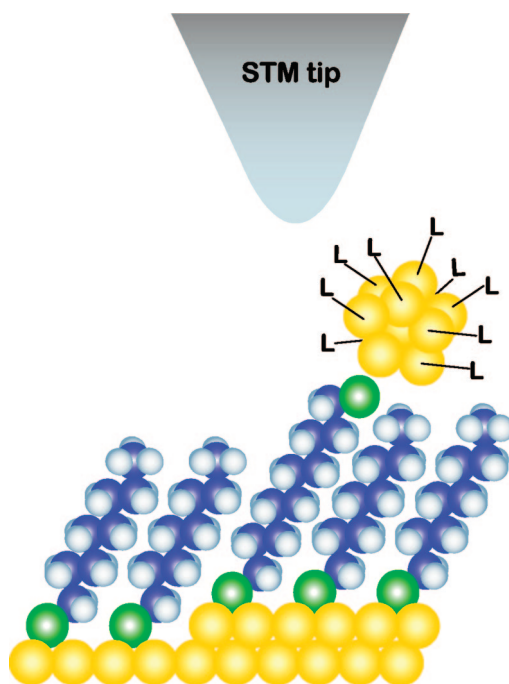
## Functional Molecules and Assemblies in Controlled Environments: Formation and Measurements

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### CON SPECTUS



**T**he local environment of a functional molecule or nanoscale assembly has tremendous impact on it and thus can be used for functional control. In addition, the local environment is critical in the interface to the physical, chemical, and biological worlds beyond the assemblies that are the most common applications targeted. Functional measurements without local structural information lack key insight into both the details and the roles of the environment. This Account focuses on progress toward and challenges in the controlled assembly and measurements of functional nanostructures in well-defined environments.

The study of single precise supramolecular assemblies in well-defined environments offers unique insights into both interactions and function. By designing interactions between molecules and controlling assembly conditions, we can create and place atomically precise nanostructures. The tools to test the structures targeted and to measure the function of these assemblies are just now being developed and becoming available. Advances in this field have depended on gaining access to measurements at this scale. In particular, we recognize but do not yet understand the critical role of the chemical and physical environment of the assemblies. Likewise, we are just now realizing the important role that the substrates to which the assemblies are attached play in these processes. In order to develop a predictive understanding and the ability to design and to optimize functional assemblies, we must elucidate the physical, chemical, and electronic couplings among the molecules in the assemblies and with their substrates. With a suite of atomic- and molecular-resolution analytical tools, we are able both to ascertain whether the targeted structures have been formed and to measure their function. One of the keys to our ability to determine structure and measure function has been the development and application of methods for the automated acquisition, analysis, and associations of thousands or tens of thousands of single-molecule/particle/assembly structural, dynamic, spectroscopic, and functional data points.

## Introduction

This Account focuses on progress toward and challenges in the controlled assembly and measurements of functional nanostructures in well-defined environments. The local environment of a functional molecule or assembly has tremendous impact on it and thus can be used for functional control.<sup>1–12</sup> The local environment is also critical in the interface to the physical, chemical, and biological worlds beyond the assemblies that are the most common applications targeted.<sup>13–17</sup> Functional measurements without local structural information lack key insight into both the details and the roles of the environment. We have developed methods to record and to analyze statistically significant numbers of functional measurements while retaining all the information of the heterogeneity of each molecule or assembly measured.<sup>1,7,10–12,18–21</sup> In addition, the ability to measure down to the single-molecule scale has enabled us to develop and to optimize methods for selectively isolating single molecules, pairs of molecules, one-dimensional lines of molecules, or larger groups of molecules.<sup>1–12,18–33</sup>

Isolating molecules and assemblies in a two-dimensional matrix has several advantages. The molecules can be probed individually, and thus each sample is “monodisperse”.<sup>34</sup> The role of the matrix can be determined by comparing behavior as a function of environment. This requires retaining the heterogeneity of each measurement and associating it with the local environment by data sorting and mining.<sup>1,7,10–12,18–21</sup> Likewise, the matrix can be used as a control element and can be designed to be an interacting part of the assembly (Figure 1).<sup>3,4,11,12</sup>

Additionally, in functionalization reactions of patterned molecules that have been assembled on surfaces, care must be taken that the heats of the reactions used do not reorganize the molecules and thus dissolve the patterns. Molecular-resolution measurements have shown that this is a significant issue for alkanethiol self-assembled monolayers (SAMs) on Au{111}.<sup>35</sup> It is also likely to be problematic on other relatively soft substrates in which substrate atoms are mobile or for other monolayers in which the molecules can move.<sup>36–40</sup> However, insertion of single or a few isolated molecules circumvents this problem because the heat from the (subsequent) reactions is distributed.<sup>15,24–27,34,41</sup> It remains to be seen what the limits are and whether more gentle reactions can be developed for functionalizing large fractions of monolayers or large domains of phase-separated SAMs.

## Assembly

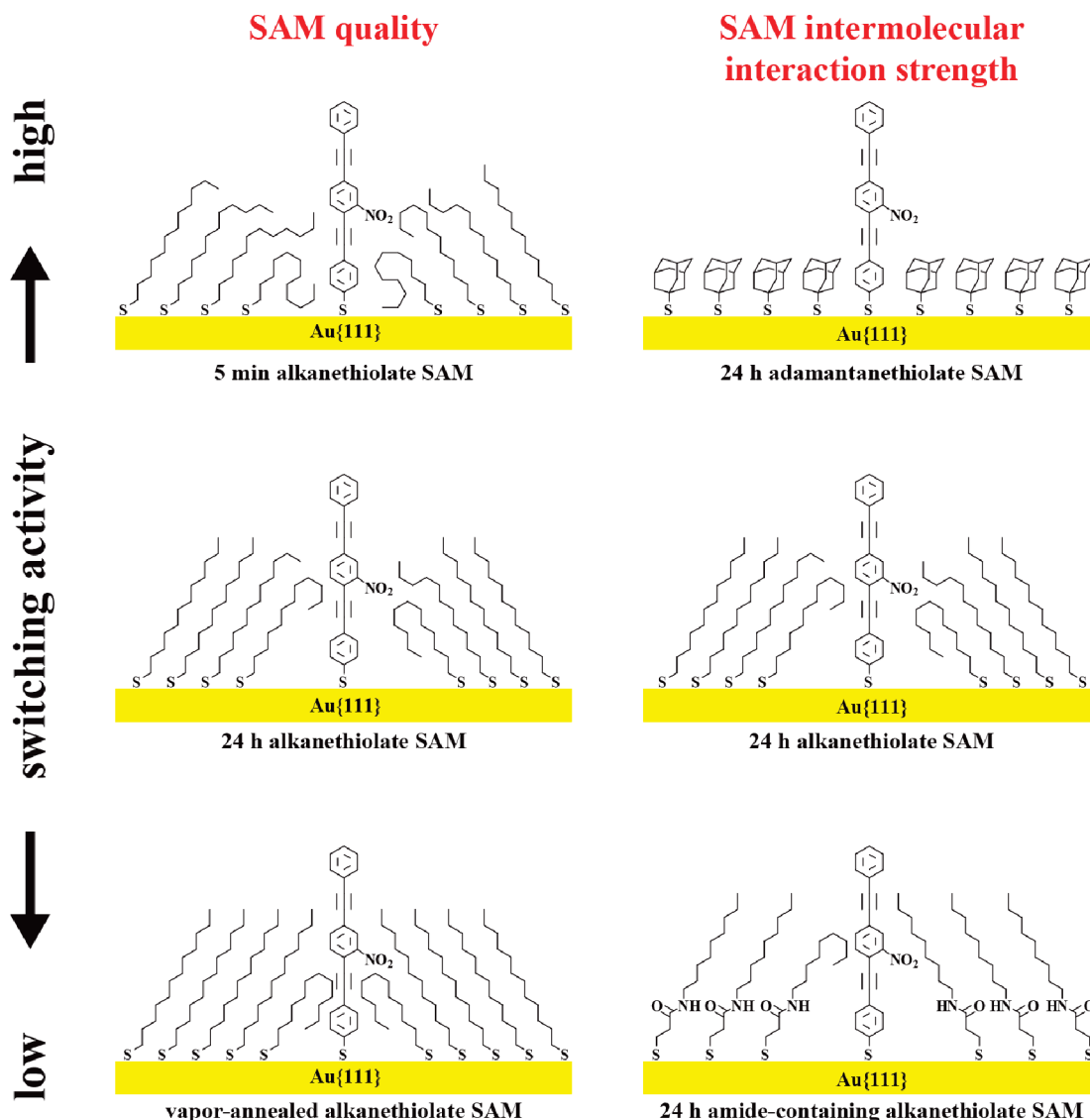
In order to isolate single molecules and assemblies, we exploit the defects in SAMs. These can be tailored so that only single molecules can be inserted, or more molecules can be placed in larger defects.<sup>10–12,15,24–28</sup> These defects can be controlled selectively by processing the film and substrate. Figure 2 shows a molecular-resolution image of an alkanethiol on a Au{111} SAM in which a number of different types of defects are highlighted. At substrate step edges, since the alkyl chains cannot tilt so as to maximize van der Waals overlap between molecules on opposite sides of steps, voids are accumulated, and these are often sites for multiple (or larger) molecules to insert. The same is true for the substrate vacancy islands that are the result of deposition (from solution or vapor). These substrate defects can be minimized by annihilating them through substrate step flow. Low-density regions of the surface (if present) allow both substantial motion and substantial insertion or exchange. These regions can be identified both by observing motion and by spectroscopic means (since the alkyl chains conformationally relax and bend over). The defects that are most useful for the insertion of *single* molecules or assemblies are structural domain boundaries.

Molecules can be inserted from solution or vapor or by contact.<sup>1,10–12,23,24,26</sup> By preparing a nearly complete matrix, it is possible to insert and to isolate single molecules preferentially. The scanning tunneling microscope (STM) can be used both to confirm this and to *select* isolated single molecules within the field of view. This isolation of single molecules in well-defined environments is critical in such areas as bioselective capture surfaces.<sup>14,15</sup>

## Measurements

Scanning probe microscopies and related spectroscopies enable simultaneous measurements of structure, dynamics, and indicators related to function.<sup>1–12,20,21,29,34,42–47</sup> We have specifically developed highly stabilized STMs that are able to measure the same area repeatedly for many hours.<sup>1,48,49</sup> Likewise, high sensitivities and thus low tunneling currents enable measurements that minimize the perturbations of the systems measured.<sup>1,50</sup> Other methods give additional information on the assemblies but lack the detailed views of the local environment.<sup>1–3,51–53</sup>

Digital image processing techniques are used to align each image to the others, using a key frame method.<sup>7,20,21</sup> Data on single assemblies are automatically extracted from larger fields of view (Figure 3). These data are specifically associated with their locations in images and can thereby be correlated with the local environment. Either apparent height



**FIGURE 1.** The environment around single-molecule switches determines the rates at which they switch stochastically. This has been tested by making looser matrices prior to insertion of switches, by adding matrix molecules to tighten the environment, by finding matrices that are disordered and thereby loosened, and by employing matrix molecules with relatively strong interactions that stiffened the environment. Figure courtesy Dr. T. J. Mullen.

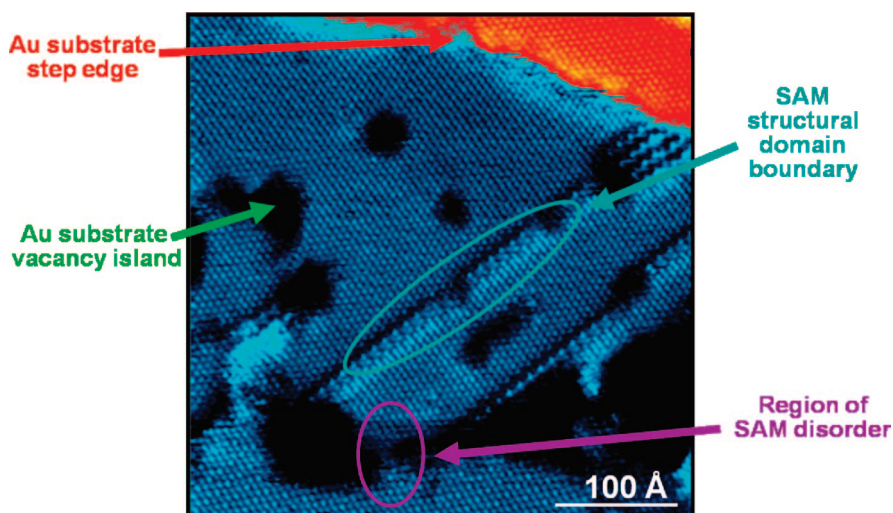
information is recorded relative to a local reference<sup>7,20</sup> or adsorbate positions are determined to assign changes between images in order to follow surface dynamics.<sup>21</sup>

For very active molecules or assemblies, the STM probe tip can be positioned such that only the data from one molecule/assembly are recorded (Figure 4).<sup>8,54,55</sup> In this way, the dynamics can be tracked on the millisecond time scale. These molecules or assemblies are still associated with their environments through images recorded before and after the dynamical data. By not recording apparent height and instead just measuring tunneling current fluctuations, one can achieve dynamics up to the high-frequency limit of the tunneling current amplifier (typically  $\sim 1$  MHz). Spectroscopic measurements

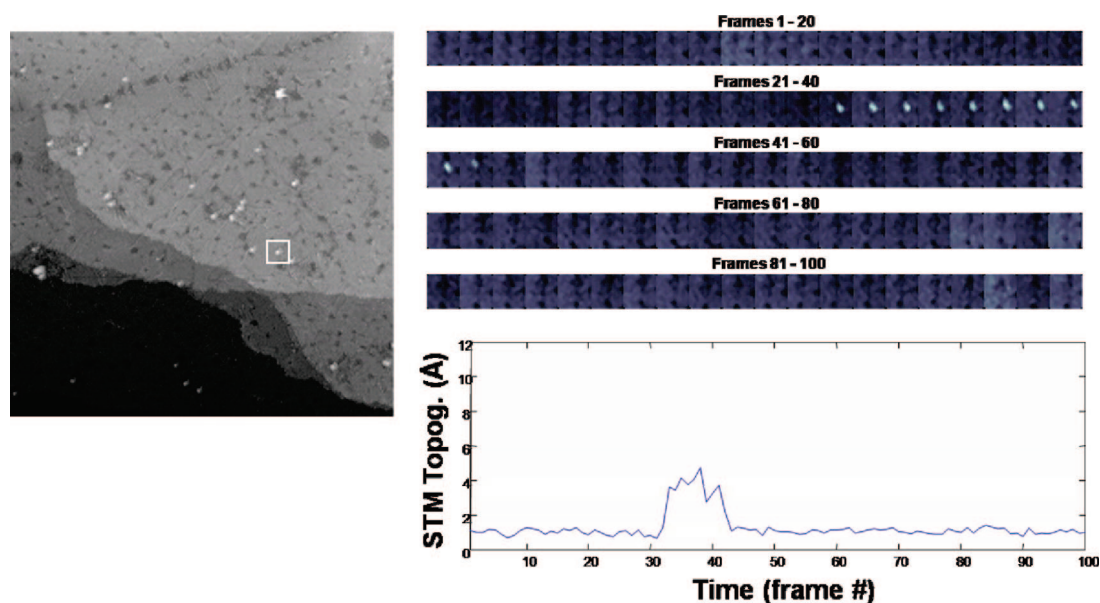
can be used to track dynamics into the gigahertz range and beyond.<sup>48,56–60</sup>

## Single-Molecule Switches

Initial observations of single-molecule oligo(phenylene ethynylene) (OPE) switches indicated that the tightness of the environment around the molecules determined their stochastic switching rates and thus some form of molecular motion was a critical part of switching.<sup>1,2,10–12</sup> In order to test this observation, looser matrices were made by depositing SAMs from alkanethiol solution for short times; indeed, the stochastic switching rates increased. Conversely, when more alkanethiol matrix molecules were added around switches (from vapor),<sup>61</sup>



**FIGURE 2.** Molecularly resolved STM image of a decanethiol self-assembled monolayer on Au(111) indicating defect types. Courtesy of Dr. T. J. Mullen.



**FIGURE 3.** In order to record many thousands of functional measurements, automated acquisition tools were applied to specially stabilized custom scanning tunneling microscopes that can record over the same area for many hours. Then, automated analysis tools extracted the data for each functional molecule. The small images (right) illustrate the extraction of the time history of a single nitro-functionalized OPE switch molecule in a matrix of dodecanethiolate on Au(111) from a sequence of larger STM images (one shown on left). Such data were then accumulated to get statistically significant values for the difference in apparent height of the ON vs. OFF states (see text and Figure 4). Imaging conditions:  $V_{\text{sample}} = 1.4 \text{ V}$ ;  $I = 0.2 \text{ pA}$ ; 3 min/frame. Data courtesy of Dr. Zach Donhauser.

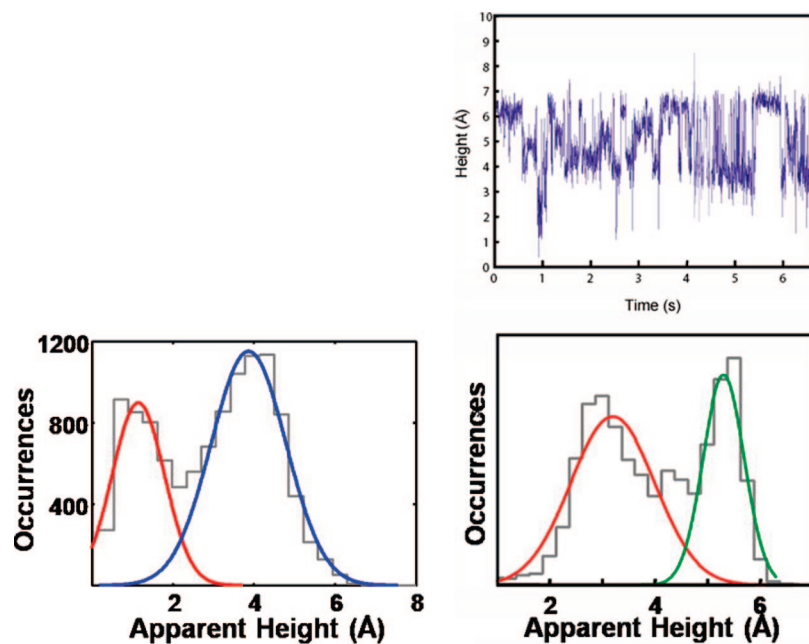
the stochastic switching rate decreased.<sup>1,2</sup> This is shown schematically in Figure 1 for the most studied (nitro-functionalized) OPE switch molecule.

This ultimately led us to infer that switching was due to a change in hybridization at the molecule–surface bond that was concomitant with a change in tilt of the OPE molecule. This and other mechanisms were tested by designing molecules that could and could not exhibit all the different proposed mechanisms of switching.<sup>5,11,12</sup> Only this tilt mechanism was consistent with all data, although we could

not exclude the possibility that the molecule changed its (ground) oxidation state when it tilted (reduction and oxidation were ruled out as the primary effect by showing that the molecules could be switched by an electric field without supplying electrons, by a STM tip kept out of tunneling range, but there is nevertheless a ready supply of electrons from the substrate).

Next, more strongly interacting matrices were designed and assembled.<sup>3,4,30,31</sup> Hydrogen bonds between the buried amide functionality doubled the interaction strength between chains





**FIGURE 4.** For very active switches (right), statistically significant data can be recorded for one molecule in real time that is comparable in signal-to-noise for accumulated data from STM images from tens of molecules and many hours of measurements (left). In this case, only the apparent height of the molecule is recorded as a function of time. Careful analyses of these data revealed additional dynamics, which have been attributed to substrate atom motions. Data courtesy of Dr. Zach Donhauser and Dr. Amanda Moore.

(as compared with alkanethiolates) and thus stiffened the matrix. The matrix could also be designed to enable hydrogen bonding between the functionality on the center ring of the switch molecules and the buried amide functionality in the matrix (Figure 1, bottom right) when the appropriate combinations of molecules are used.<sup>3–5,11,12</sup> According to the OPE functionality (e.g., nitro vs. amine), the amide in the matrix molecules needs to be properly placed and oriented to enable such interactions.<sup>4</sup> This, in turn, enabled a crude estimate of the tilt angles of the ON and OFF molecular states, ca.  $0^\circ$  and  $30^\circ$ , respectively.

Recent measurements have provided clues that the substrate also plays an active role in the switching process.<sup>8,60</sup> Fluctuations of  $0.5 \text{ \AA}$  in the apparent height of isolated switch molecules appear in the real-time tunneling data. This correlates with the X-ray data of Woodruff and co-workers.<sup>8,62</sup>

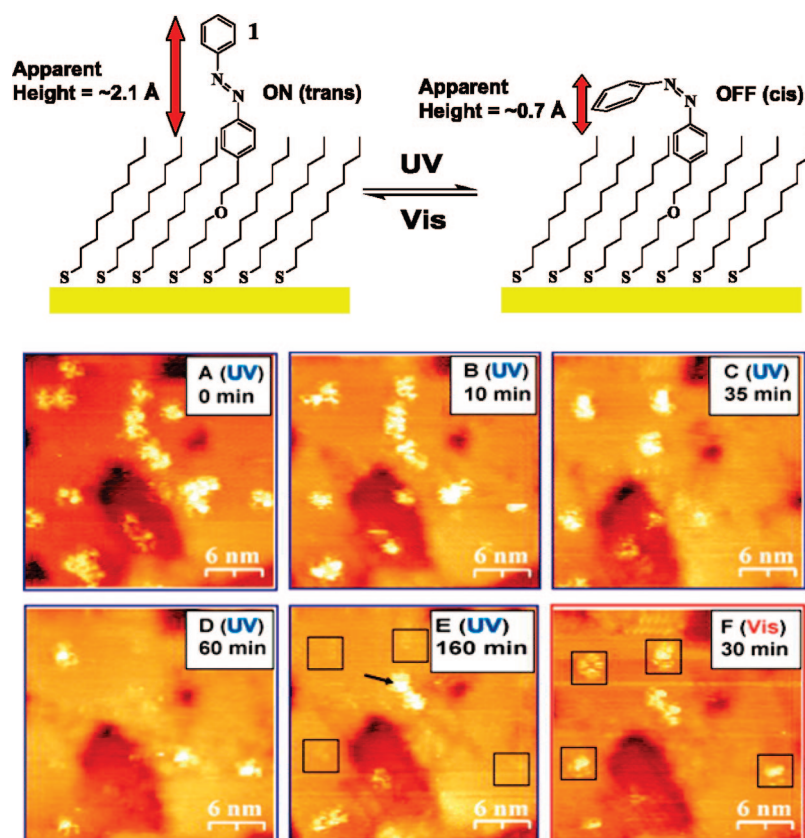
In fact, one would *expect* substrate atoms to reconfigure as the switch molecules change their tilt angles or hybridization. The substrate is “soft”, and even the alkanethiol (or other molecule) matrix deposition removes the reconstruction of the Au surface and redistributes the top layer of atoms.<sup>63,64</sup> Significant substrate atom mass transport is observed on deposition of these and other monolayers, such as alkaneselenols, and in other dynamics involving the adsorbed molecules.<sup>37,65–67</sup> The roles of the substrate atoms in the conductance changes have not yet been addressed. It is *known* that shifting a line of atoms from their equilibrium positions

changes the conductance of the chain.<sup>68</sup> Measurements have not yet determined this contribution to the changes of the functional assembly.

## Photoisomerization

One challenge in such assemblies has been coupling external excitation efficiently to surface-bound molecules.<sup>9</sup> This is related both to the *deexcitation* of the molecules due to coupling to one another and to the substrate and to the difficulty in the measurements. By specifically decoupling the functional parts of the molecules from the substrates via the chemical tether used, and by fixing this ether tether within a crystalline alkanethiolate matrix, we have been able to observe the *cis–trans* isomerization of a tethered azobenzene (Figure 5).<sup>9</sup> Crommie, Fréchet, and their co-workers used tetra-*tert*-butyl-functionalized azobenzene, and these side groups also sufficiently decoupled the azobenzene such that reversible switching could be observed on alternating ultraviolet and visible excitation.<sup>69</sup> Nevertheless, the switching efficiency of the adsorbed molecules was substantially reduced from that of the molecules in solution.

In our experiments, as tethered azobenzene molecules were placed in proximity, the efficiency of photoisomerization dropped. This could be due to steric hindrance, to excitation coupling, or both. By lengthening the matrix around the tethered azobenzene so that the molecules collide with the matrix when they isomerize, we have shown that steric hin-



**FIGURE 5.** Isolated azobenzene-functionalized molecules are embedded within 1-decanethiolate monolayer domains so as to eliminate motion about the S–Au bond. Then, ultraviolet (~365 nm) and visible (~450 nm) light photoisomerize the molecules from *trans* to *cis* and back, respectively. The isomerization is observed as an apparent height change in STM images. Imaging conditions:  $V_{\text{sample}} = 1$  V;  $I_{\text{tunnel}} = 2$  pA. Reproduced with permission from ref 9. Copyright 2008 American Chemical Society.

drance reduces efficiency. In order to determine the role of intermolecular excitation coupling, it will be important to vary the (precise) spacings between the active molecules. This can be done through hierarchical assembly of specially designed molecules. As in previous experiments, the separations and environments of the molecules can be measured precisely and associated with function.

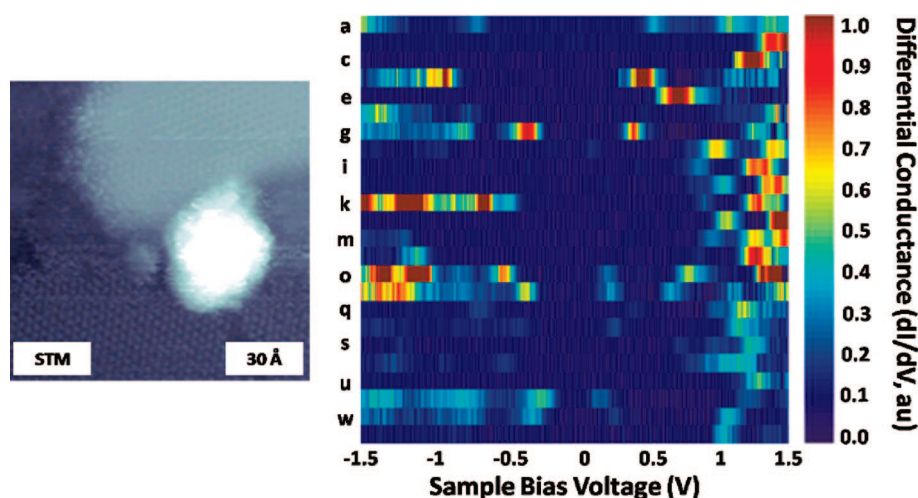
### Precise Assemblies

Because single functional molecules can be selectively inserted into controlled matrices, these can be used to bind precise clusters to make precise assemblies.<sup>34</sup> Measurements of individual assemblies in an ultrastable, low-temperature, extreme-high-vacuum STM<sup>70</sup> were expected to yield definitive electronic structures that could stand as tests of theoretical approaches. Surprisingly, the electronic spectra were found to be unstable under these conditions (Figure 6) for precise ligand-stabilized Au<sub>11</sub> clusters (for both triphenylphosphine and octanethiolate ligands) tethered with single inserted decanedithiol molecules in an octanethiolate SAM matrix on Au{111}. Averaging many of

these spectra and also those for isolated, tethered, nearly monodisperse Au<sub>101</sub> clusters gave “consensus” spectra that qualitatively matched those expected for these different size clusters based on prior work on measurements of many clusters with narrow dispersities. Experiments and theory to establish the origins of the spectral diffusion remain to be done. Working hypotheses for the spectral diffusion include partial charging of the cluster and conformational changes of some part of the assembly even at these low temperatures (4 K). Some of these effects will be isolated and tested by using rigid, conjugated tethers. Thus, despite these exquisitely well-defined assemblies, mysteries remain to be explained in their electronic structures.

### Coordinated Action

One exciting prospect is that the coordinated actions of molecules and assemblies working together can be used to convert from nanoscale function to micro- or nanoscale actuation in much the same way that biomolecules work together and hierarchically to form our muscles and carry out other processes. Nature has come up with great efficiency in informa-



**FIGURE 6.** The electronic spectra of precise assemblies measured under ultrastable conditions at low temperature are surprisingly unstable. STM image (left) and 24 consecutive tunneling spectra (right) of a triphenylphosphine-stabilized  $\text{Au}_{11}$  cluster tethered by a decanedithiolate molecule inserted in an octanethiolate SAM matrix. Imaging conditions:  $V_{\text{sample}} = 1.5 \text{ V}$ ;  $I_{\text{tunnel}} = 14 \text{ pA}$ ;  $T = 4 \text{ K}$ . Reproduced with permission from ref 34. Copyright 2006 American Chemical Society.

tion storage, mechanical action, and other functions that serve as proofs of principle in guiding and inspiring our work.

In the case of photoisomerization, we have found that the efficiencies of assemblies in which the functional molecules are adjacent drop dramatically.<sup>9</sup> As noted above, this will need to be understood and circumvented before the molecules can be made to operate together.

In the case of rotaxanes bound on surfaces, we have been able to follow the motion of single rotaxane molecules with a stabilized STM under electrochemical control. Then, by assembling palindromic birotaxanes onto cantilevers coated with Au on one side, attached through thiolate tethers on the rings, stress could be applied to deflect the cantilevers by moving the rings under electrochemical control between stations nominally 4 and 8 nm apart.<sup>71</sup> These 4 nm motions of individual molecules were transduced into 300 nm deflections of a cantilever. The order of magnitude increase over earlier work<sup>72</sup> is attributable to better assembly and more complete electrochemistry. Superimposed on the deflection, however, were many competing effects, including counterion binding and desorption, a steady drift that could be reversed by cycling electrochemical potential, and others. Some of these effects could be sorted out by examining the potential at which they occurred or applying blocking monolayers; others remain to be explained. Once again, the added complexity of trying to make molecules work together in concert in assemblies adds new problems that we will need to learn how to address. The environment of each molecule no doubt plays

important roles that must be understood and controlled in order for functional properties to be optimized.

## Prospects, Challenges, and Opportunities

Many challenges remain in the control of single molecules and their environments to create precise assemblies. The rewards of success are great; in principle, the increasingly important and dominant statistical variations of small nanostructures (such as dopant atom numbers in small volumes of semiconductor) can be circumvented. If this level of control can be attained, then the next step will be to learn to make such assemblies operate both independently and in concert, in analogy to the hierarchical and coordinated action of biomolecular motors in our muscles.<sup>71–75</sup>

One approach for assembly is to design interactions between components in analogy to the assembly of biomolecular complexes.<sup>76–79</sup> Interactions can be designed at a number of levels.<sup>80–86</sup> This includes using adsorbates to perturb substrate electrons, which is both directional and long-range (several nanometers).<sup>80–83</sup> Parts of one molecule can be used to align, to space, and to orient one another.<sup>85</sup> Much remains to be done in this area; one of the hopes is that as such electronic interactions/perturbations can be “read” with the STM,<sup>80–83</sup> these will be sufficiently understood to turn into a predictive understanding that will lead to supramolecular design tools and precise, robust assemblies.

Even in simple, well-defined single assemblies measured with exquisitely stable tools, we find dynamic fluctuations that are not yet understood.<sup>31</sup> The strengths and origins of cou-



plings between proximal molecules and assemblies must also be understood in detail, if we are ever to learn to use them. Careful experiments and coupled theory, modeling, and simulation will be required to pick apart the origins of these couplings. Then, we will find ways to optimize couplings or to isolate nearby structures, as the situation requires. Likewise, coupling molecules and assemblies to microstructures will enable new functions and control that will cross the boundaries of scale but will retain the advantages precise functional assemblies.

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#### BIOGRAPHICAL INFORMATION

**Paul S. Weiss** is a Distinguished Professor of Chemistry and Physics at The Pennsylvania State University. He received his S.B. and S.M. degrees in Chemistry from MIT in 1980 and his Ph.D. from the UC Berkeley in 1986. He was a Postdoctoral Member of Technical Staff at Bell Laboratories from 1986 to 1988 and a Visiting Scientist at IBM Almaden from 1988 to 1989. His interdisciplinary research group includes chemists, physicists, biologists, materials scientists, electrical and mechanical engineers, and computer scientists. Their work focuses on the atomic-scale chemical, physical, optical, mechanical, and electronic properties of surfaces and supramolecular assemblies. He and his students have developed new techniques to expand the applicability and chemical specificity of scanning probe microscopies. They have applied these and other tools to the study of catalysis, self- and directed assembly, physical models of biological systems, and molecular and nanoscale electronics. They work to advance nanofabrication down to ever smaller scales and greater chemical specificity in order to connect, to operate, and to test molecular devices. He is a Fellow of the AAAS, APS, and AVS and has

been awarded a NSF Presidential Young Investigator Award, the B. F. Goodrich Collegiate Inventors Award, a Guggenheim Fellowship, a Sloan Foundation Fellowship, and the ACS Nobel Laureate Signature Award. He was recently named the founding Editor-in-Chief of *ACS Nano*.

#### FOOTNOTES

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