Designing, Measuring, and Controlling Molecular- and Supramolecular-Scale Properties for Molecular Devices

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***Abstract*-We use molecular design, tailored syntheses, intermolecular interactions, and selective chemistry to direct molecules into desired positions to create nanostructures, to connect functional molecules to the outside world, and to serve as test structures for measurements of single or bundled molecules. Interactions within and between molecules can be designed, directed, measured, understood, and exploited at unprecedented scales. We examine how these interactions influence the chemistry, dynamics, structure, electronic function, and other properties. Such interactions can be used to advantage to form precise molecular assemblies, nanostructures, and patterns, and to control and to stabilize function. These nanostructures can be taken all the way down to atomic-scale precision or can be used at larger scales. We select and tailor molecules to choose the intermolecular interaction strengths and the structures formed within the film. We selectively test hypothesized mechanisms for electronic switching and driven motion by varying molecular design, chemical environment, and measurement conditions to enable or to disable functions and control of these molecules using predictive and testable means. Critical to understanding these variations has been developing the means to make tens to hundreds of thousands of independent single-molecule measurements in order to develop sufficiently significant statistical distributions, comparable to those found in ensemble-averaging measurements, while retaining the heterogeneity of the measurements. We quantitatively compare the conductances of molecule-substrate junctions. We find that the contacts and substrate play critical roles in switching. Switching of rigid, conjugated molecules is due to changes in the molecule-substrate bonds, which involves motion of the molecules and of substrate atoms. We are able to measure the coupling of the electrons of the molecules and substrate by measuring the polarizabilities of the connected functional molecules in high and low conductance states. These polarizabilities are compared to those of other families of molecules and to detailed calculations.**

I. Introduction

Single molecules on surfaces can be placed in precise environments using self- and directed assembly, and can be visualized, probed, and even actuated using scanning probe microscopes [1-27]. The development of the scanning tunneling microscope and related scanning probe methods enabled understanding and ultimately control of molecular assemblies at the sub-nanometer scale [1].

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We have applied these tools to understand self- and directed assembly from the sub-nanometer to the sub-micron scales [1-4]. In so doing, we have learned to control the placement of single molecules, pairs of molecules, and larger bundles into controlled environments [1-19,21-23,27]. In the case of functional molecules, interactions between the placed molecules and the surrounding matrix/environment can be designed in order to stabilize or to probe that function, or can be used to space molecules and to control the overall film properties. Both single molecules and larger groups can be addressed with the scanning probe or via external stimuli.

II. New Tools and Methods

One of the keys to success in this area has been the development of our ability to make many thousands of measurements of structures, function, and dynamics [7,12]. Despite the relatively slow recording speeds of scanning probe microscopes, this can be accomplished over many (>10) orders of magnitude of dynamic range [23]. In addition to recording statistically significant data sets, all the heterogeneity of the single-molecule or assembly data is retained in order to enable "data mining" to sort out the critical roles of environment, including proximity to other structures, measurement conditions, etc. [1,4-6,8,12-14,19,22,23].

Requirements thus include highly stabilized microscopes so that the same spot or area can be imaged repeatedly, automated data acquisition, and automated (and flexible) data analysis methods. We have developed and applied each of these both in these areas and many others (such as in the precise quantitative measurement of long-range interaction potentials).

III. Systems Studied

We have probed and driven the conductance changes of molecular switches. We find that single molecules can be switched with the electric field supplied by the probe tip. They can be stabilized by designing interactions between the functional molecules and the surrounding matrix. These interactions can be used to elucidate aspects of the assembly

structure related to molecular function, such as molecular tilt [1,13].

We have also examined families of "molecular motors" in which actuation is driven by light, electric field, ion binding, or electrochemical potential changes. Again, in each case, probing the individual species and their environment has been critical to understanding and to controlling their function.

Assemblies of proximate motors switch less efficiently, as do those (mechanically) impeded by their environment. Both electronic and mechanical aspects likely play important roles in operating such assemblies in concert.

IV. Future Prospects

By learning to place and to operate functional molecules in controlled environments and hierarchically, we hope to enable understanding and operation of efficient synthetic equivalents of muscles [27], sensing organs, and perhaps even neural circuits. While our current state in this regard is primitive, new tools that provide atomic-scale views and measurements are already enabling the precise assembly of structures. These systems are thus amenable to theoretical treatment and simulation, which we expect to guide both optimization of function, and the design of new, increasingly complex assemblies.

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