Designing, Measuring, and Controlling Functional Molecules and Precise Assemblies

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Abstract

Bottom-up assembly of functional molecules on solid surfaces provides a promising approach toward ever smaller and more functional devices. Molecule-substrate and intermolecular interactions can be exploited so that when molecules are transferred from solutions to substrates targeted structures can be obtained. Understanding correlations between the interactions and function of molecules is essential to elucidating the rules of working towards the ultimate limits of miniaturization. This paper covers our recent progress towards this goal by measuring single molecules and precise assemblies confined in self-assembled monolayers (SAMs). By isolating molecules in SAMs, we are able to obtain both accurate measurements and precise control of function. The measurements, in combination with theoretical calculations, allow us to apply molecular design to optimize function and to direct the assembly of molecules. We are now applying the assembly strategies that we have developed for flat surfaces to curved and faceted substrates, while developing new tools to measure the environment, interactions, and dynamics of single molecules and precise assemblies.

INTRODUCTION

Self- and directed assembly of functional molecules on surfaces provide promising approaches towards ever smaller devices and systems featuring superior performance, cost-effectiveness, and low energy consumption [1 – 8]. A broad range of functional molecules has been synthesized and studied in solution where molecules are randomly distributed and cannot be addressed individually [9, 10]. However, transferring molecules from solutions to solid surfaces is required for device applications and detailed measurements [6, 7, 11 – 14]. Molecules function differently on surfaces due to molecule-substrate and intermolecular interactions. This difference makes it important to characterize the effects of interactions on structure and function of surface-bound molecules.

By measuring both single molecules and precise assemblies confined in self-assembled monolayers (SAMs), we are able to obtain accurate information on the structures, interactions, and function of molecules simultaneously at these scales [5 – 7, 11, 15, 16]. Importantly, we measure statistically significant data sets while retaining all of the single-molecule/assembly data so as to be able to elucidate the effects of interactions, environments, measurement conditions, etc. [16 – 19]. Here, we present our recent progress in both directed assembly and measurements. We have developed and applied new imaging and spectroscopic tools for functional measurements [5, 15, 20]. We aim to operate the molecules together in precise assemblies, both cooperatively and hierarchically, in analogy to biological muscles [8]. Our initial efforts in this area reveal both interference and cooperativity. The measurements, in combination with theoretical calculations, allow us to apply molecular design to optimize function and to control assembly [5, 21, 22]. Some of the assembly strategies that we have developed for flat surfaces can be applied to curved and faceted substrates, but new tools must be developed to measure the environment, interactions, and dynamics of single molecules and precise assemblies [23, 24].

ASSEMBLY

We exploit defects in SAMs to insert functional molecules and to control the placement and orientation of these molecules [15, 16, 25 – 31]. Alkanethiolate SAMs on Au substrates are the well-characterized systems that have the advantages of high stability, easy fabrication, and precise tenability [30, 32 – 43]. Scanning tunneling microscopy (STM) provides molecularly resolved images of the SAMs on Au surfaces that reveal several types of defects [5]. Some of the common defects include substrate defects (*i.e.*, step edges and vacancy islands) and monolayer defects (*i.e.*, tilt domain boundaries and regions of poorly ordered molecules) [5]. At these defects, the alkyl chains cannot tightly pack into their crystalline tilted configurations that have maximized van der Waals forces [5]. We have addressed these defects by designing and assembling symmetric upright cage molecules to simplify both assembly and defect structures. As noted above, we exploit defects in SAMs to insert single molecules as well as pairs, lines, and clusters of molecules [7, 16, 25, 26].

Controlled defects in SAMs facilitate insertion of functional molecules by limiting substrate access. Defect type and density can be controlled by molecular design and by processing the films [34, 35, 44]. Multiple methods have been developed for insertion, including solution deposition, vapor deposition, and microcontact insertion printing [16, 30, 45, 46]. Alternatively, in order to isolate single molecules within domains of SAMs, we employ co-adsorption of functional molecules and matrix molecules [27 – 29, 45, 47].

New types of molecules with greater symmetry such as adamantanethiols, carboranethiols, and cubanethiols are being designed and assembled on Au and other substrates to gain new insight into self-assembly and to control defects [44, 48]. The limited degrees of freedom of cage molecules have significant advantages in terms of defect types and densities as compared to linear molecules. These defects will also be exploited for insertion and control of functional molecules.

PHOTOISOMERIZATION

One key challenge has been coupling external energy to molecules on surfaces in order to perform useful work at the nanoscale. When adsorbed directly on metal surfaces, photo-excited molecules are quenched by the underlying substrate and steric hindrance from the proximate molecules. By isolating tethered azobenzene molecules within the domains of a tightly packed SAMs where the functional azobenzene moiety protrudes above the SAMs to reduce both coupling with substrates and interaction with surroundings, we demonstrated reversible *trans-cis* isomerization (Fig. 1) [27].
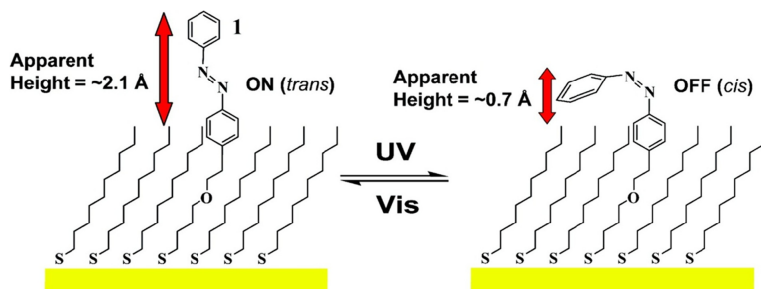

Figure 1. Schematic showing single azobenzene-functionalized molecules (1) isolated in a decanethiolate SAM on Au{111}. Azobenzene undergoes reversible photoisomerization observed as a change in apparent height in STM images. We define trans and cis as ON and OFF states with apparent heights of 2.1 ± 0.3 and 0.7 ± 0.2 Å with respect to the surrounding matrix, respectively. Reproduced with permission from reference 27. Copyright 2008 American Chemical Society.

Scanning tunneling microscopy was employed to image azobenzene molecules and to track their photoisomerization. As shown in Figure 2A, azobenzene molecules were initially in their thermodynamically stable *trans* state and appeared as 2.1 ± 0.3 Å protrusions over the 1-decanethiolate matrix in topographic STM images (also see figure 1). Upon exposure to

UV light (~365 nm; ~12 mW/cm^2), the molecules isomerized to their *cis* state associated with a reduction of the apparent height of ~1.4 Å (figures 2B – 2E). Measurements with STM indicate that with UV illumination for 160 min, over 90% of the azobenzene molecules isomerized from *trans* to *cis*. Subsequent illumination with visible light (~450 nm; ~6 mW/cm^2) for 30 min switched ~50% of the molecules back to *trans* conformation (Fig. 2F). The number of molecules switched as a function of UV exposure time is fitted into an exponential curve with a decay constant τ of 54 ± 15 min (Fig. 2G) [27].

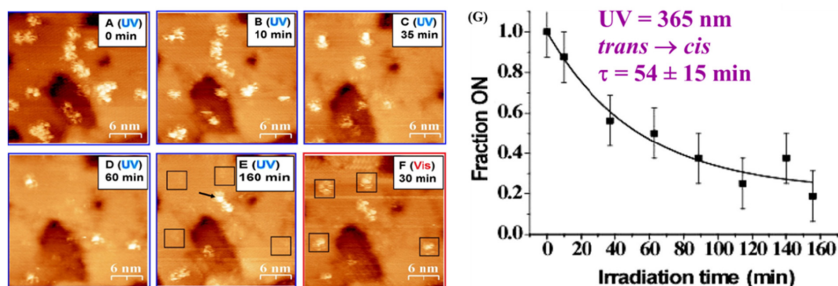Figure 2. (A-F) Measurements with STM show reversible trans-cis photoisomerization of tethered azobenzene molecules upon irradiation with UV (~365 nm) and visible (~450 nm) light. (G) The switching of azobenzene molecules from the more stable trans form as a function of UV illumination time is fitted into exponential function with a decay constant (τ) of 54 ± 15 min. Imaging conditions: $V_{sample} = 1$ V; $I_{tunneling} = 2$ pA. Reproduced with permission from reference 27. Copyright 2008 American Chemical Society.

As an instrument for local surface analysis, STM scans only a small area with few, dilute, single azobenzene molecules isolated in SAM matrices. In order to have statistically significant numbers of measurements of function or dynamics, thousands of STM images must be recorded. This makes it extremely time-consuming to track the time-dependent photophysics or photochemistry that require series of images after every light exposure of the sample. To enable more efficient measurements, we have developed a surface-enhanced Raman spectroscopy (SERS) method to track azobenzene isomerization in the far field [20]. Surface-enhanced Raman spectroscopy, which is based on enhanced interactions of light with molecular vibrations, has played an important role in the study of molecular structure and conformation due to its non-invasiveness, single-molecule sensitivity, and vibrational signatures of chemical identity and bonding changes [41 – 47]. We employed focused ion beam lithography to fabricate cylindrical nanoholes in square arrays on the Au substrates for the enhancement (Fig. 3a). The areas of the substrates surrounding the nanoholes are also accessible to STM and confirm the isolation of single azobenzene molecules in SAMs. Figure 3b shows the Raman spectra of azobenzene recorded at areas with and without nanoholes, respectively. While no obvious Raman signal appears in the spectra recorded from the areas without nanoholes, a strong signal with five peaks was obtained for the azobenzene in the area of nanoholes due to the plasmonic enhancement from the patterned substrate. We assign the five peaks as the P1-P5 modes. Closely coupled theore-

tical calculations identify the modes and help select which can be used as indicators of switching and which others can used as controls because they are insensitive to isomerization state [20 – 22]. We obtain the switching kinetics (*i.e.*, decay constant τ as defined in figure 2G) of azobenzene by tracking the Raman mode changes as a function of light exposure time. Employment of SERS has accelerated our measurements and thus the optimization of function through molecular design.
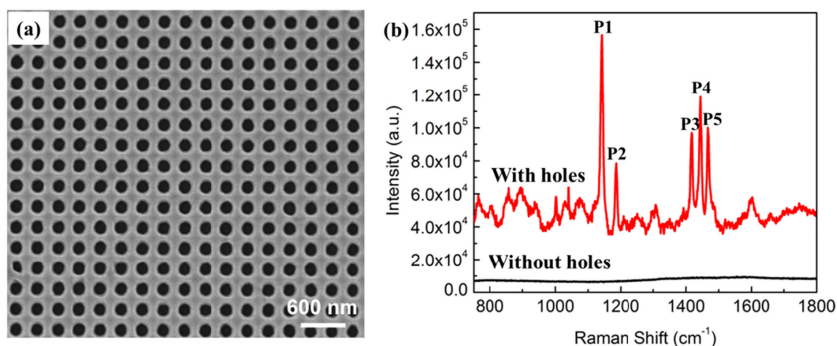

Figure 3. (a) Scanning electron micrograph of a nanohole array on Au{111} on mica fabricated by focused ion beam lithography. **(b)** Raman spectra were recorded from the substrate areas with nanoholes (red) while there were no discernible spectral features from the areas without nanoholes (black). Five vibrational modes are identified as P1-P5. Reproduced with permission from reference 20. Copyright 2011 American Chemical Society.

We have established the role of tether conductivity on the photoisomerization of azobenzene-functionalized molecules on Au surfaces [21]. Molecules were designed so as to tune the conductivity of the tethers that separate the functional azobenzene moiety from the underlying Au substrate (azobenzene with a saturated, non-conductive tether is indicated as **1** in figure 1; azobenzene with conductive tether is indicated as **2** in figure 4).
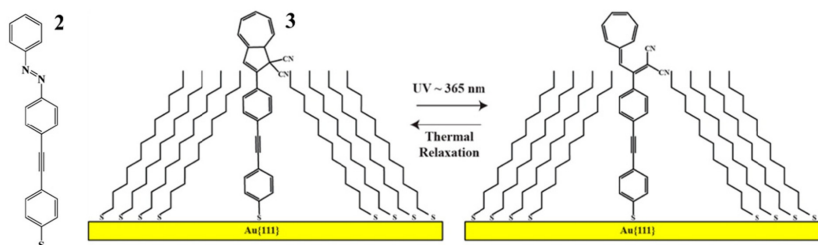

Figure 4. Left: Schematic of azobenzene with a conductive, phenylene ethynylene tether (**2**). Right: Schematic of single dihydroazulene-functionalized molecules (DHA, **3**) in alkanethiol SAMs. The DHA molecules isomerize to vinylheptafulvene (VHF) upon UV irradiation and undergoes back reaction via thermal relaxation. Reproduced with permission from reference 21. Copyright 2012 American Chemical Society. Reproduced with permission from reference 22. Copyright 2013 American Chemical Society.

The decay constants from the SERS analyses reveal that photoisomerization on the Au surface is reduced when the conductivity of the tether is increased (Table 1), consistent with the importance of quenching of the excitation by electronic coupling to the substrate [21].

New molecular switches have been explored to enhance photoswitching efficiency on surfaces. One example is dihydroazulene (DHA, **3** in figure 4). DHA is a photochromic molecule that reversibly switches between two states [22]. We employed SERS to measure the photoreaction kinetics of isolated single dihydroazulene-functionalized molecules in SAMs on Au substrates. The measurements showed that the molecules underwent a ring-opening reaction upon illumination with UV light and switched back to the initial isomer via thermal relaxation. Photokinetic analyses reveal the higher efficiency of the DHA photo-reaction on solid substrates than that of azobenzene isomerization (Table 1) [22].

Table 1. Comparison of SERS-measured decay time constant and photoswitching cross section for isolated single photoswitchable molecules in SAM matrices: azobenzene with non-conductive tether **1**, azobenzene with conductive tether **2**, and dihydroazulene **3**. The smaller time constant and larger cross section indicate higher switching efficiency of DHA as compared to the two tethered azobenzene molecules studied [21, 22].

Photoswitches	τ (min)	σ (cm^2)
Azobenzene 1	38	4.1×10^{-19}
Azobenzene 2	61	2.6×10^{-19}
Dihydroazulene 3	10	1.5×10^{-18}

COORDINATED ACTION

While measuring matrix-isolated single molecules in SAMs provides insight into molecule-substrate interactions and their effects on function, two and more molecules neighboring each other are common in practical applications. To elucidate the interactions and function of the neighboring molecules requires new test beds with precise assemblies of molecules in well-defined environments. While biological systems regularly exploit cooperative action, interference is more commonly observed in synthetic systems studied to date.

By developing new assembly strategies, we have fabricated one-dimensional (1D) chains of tethered azobenzene in SAMs that serve as test beds for measuring and understanding intermolecular interactions and function [49, 50]. Interestingly, photoswitching of the chains exhibits coordinated actions where the molecules within individual chains isomerize coop-eratively (albeit with lower efficiency) compared to the random switching of the isolated single molecules (Fig. 2). The coordinated action of molecules in assemblies is an important step along the way toward linking molecular-scale motion to macroscale function as ex-emplified by biomolecules working hierarchically in nature in order to produce complex

functions. For tethered azobenzene chains, we infer that the cooperative action arises partly from electronic coupling along the chain [50]. We found that the thicknesses of the 1D chains play a key role in the efficiency of photoisomerization. Complete reversibility in the isomerization of one-row chains was observed, but the two-row chains had partial switching. Once the molecules were assembled into 2D clusters, the switching efficiency was further reduced. Moreover, the electronic coupling along the chains inspired us to trigger the switching of the chains locally with electrons from the STM tip positioned atop one of the molecules in the chains [49].

BEYOND FLATLAND

Most single-molecule measurements of function have been limited to molecules assembled on atomically flat surfaces that are accessible to surface characterization tools [5]. However, most surfaces in practical applications deviate from ideal atomic flatness [51, 52]. In particular, nanoparticles are emerging as one of the most important functional nanomaterials for such applications as nanoscale catalysts, drug delivery, and theranostics [31]. Nanoparticles have facets, edges, vertices, and curvatures that influence their interactions with molecules and function. Better understanding of the morphological effects of curvature, faceting, and the local chemical environment will enable control of nanoparticle functionalization in ligand exchange in targeted delivery of therapeutics and theranostics and in catalysis [53, 54]. This effort requires development of new assembly strategies and analytical tools that are compatible to the curved surfaces.
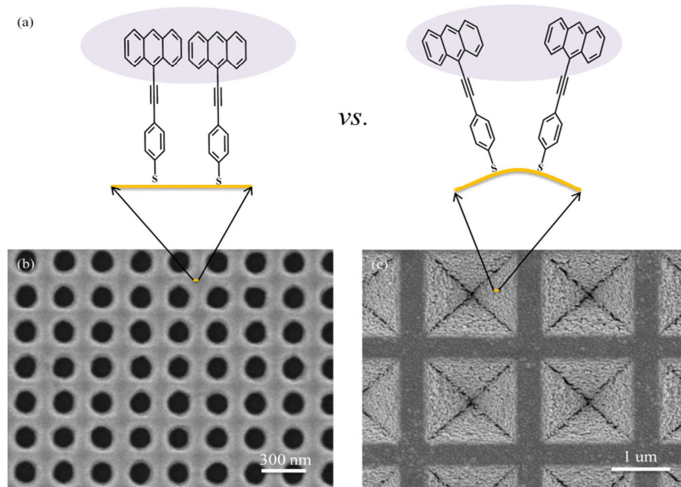

Figure 5. (a) Schematic of UV-exposed 9-(4-mercapto-phenylethynyl)anthracene pairs on atomically flat (left) and curved surfaces (right). Scanning electron micrographs of the two types of surfaces integrated with SERS substrates: **(a)** epitaxial Au on mica patterned with arrays of nanoholes and **(b)** Au nanoparticles on patterned silicon. Reproduced with permission from reference 23. Copyright 2012 American Chemical Society.

In initial efforts along these lines, we assembled pairs of thiolate-linked anthracene pheny-lethynyl molecules on both flat and curved Au surfaces (Fig. 5). By employing SERS, we identified the UV-induced photoreaction paths of the molecules (Fig. 6) and revealed the effects of nanoscale morphology of substrates on the photoreactions [23]. We found that surface constraint drove the unfavorable [4+4] photoreaction of anthracene rather than [4+2] reaction that is favored in solution where there are no conformational constraints. The SAMs on curved surfaces exhibited dramatically lower regioselective photoreaction kinetics and efficiencies than those on atomically flat surfaces. We infer that the slower reaction kinetics and lower efficiency of the reactions on the curved surfaces arise from the larger intermo-lecular distances and variable orientations in the SAMs. Moreover, we propose that the surface-dependent properties of such molecules (molecular pairs) can be used to probe the local chemical environment on curved surfaces [31, 55, 56]. New molecular probes with higher sensitivity to curvature and local environment are now being designed and applied.
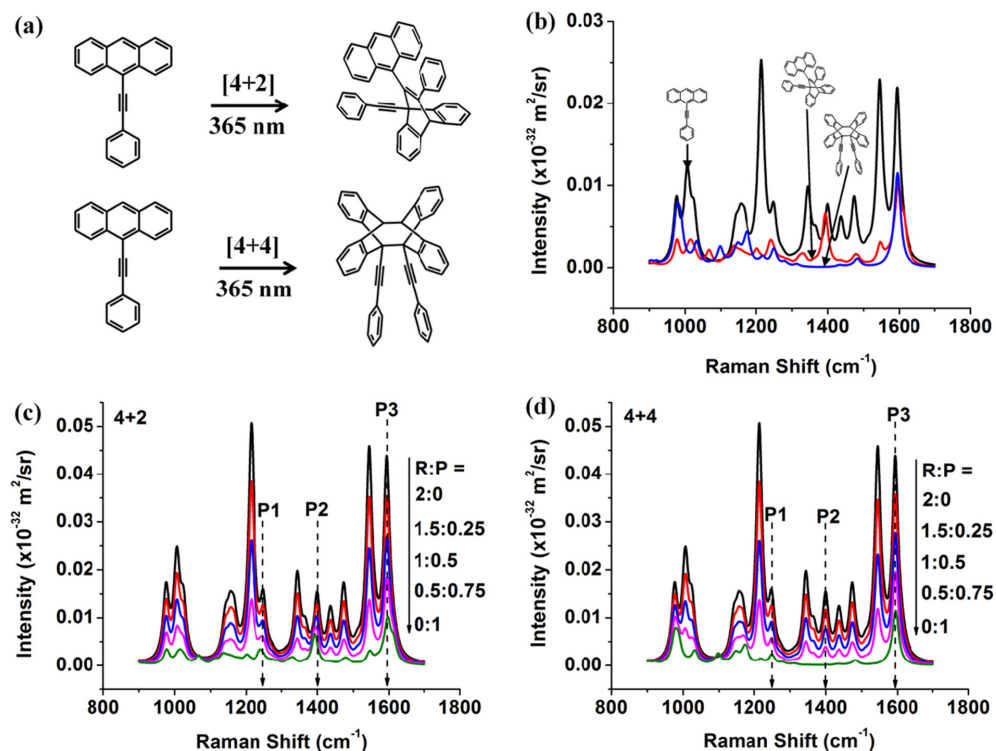

Figure 6. (a) Two photoreaction paths of 9 phenylethynylanthracene in solution: [4+2] and [4+4]. (b) Calculated Raman spectra of reactant (R), [4+2] product, and [4+4] product exhibit different vibrational modes. (c) A series of simulated Raman spectra with various mole fractions of reactant (R) and [4+2] product (P) (indicated by R:P). (d) A series of simulated Raman spectra with various convoluted mole fractions of reactant (R) and [4+4] product (P) (indicated by R:P). Modes P1, P2, and P3 were used in our analyses of the photoreaction paths and kinetics. Reproduced with permis-sion from reference 23. Copyright 2012 American Chemical Society.

Summary and Perspective

In summary, measuring isolated single molecules and precise assemblies confined in well-defined SAMs provides insight into molecule-substrate and intermolecular interactions as well as their effects on function of molecules. These measurements are essential to molecular design in order to optimize interactions and function and to control assembly.

We have achieved reversible photoisomerization of tethered azobenzene as single molecules and 1D chains in SAMs on Au surfaces. Molecules constituting the 1D chains photoisomerized cooperatively but more slowly than did isolated single molecules. Isomerization efficiency is further reduced in 2D assemblies. These first results will guide us in designing new functional molecular assemblies with higher efficiencies [57 – 62].

We apply assembly strategies developed for flat surfaces to curved surfaces. Thiolate-linked anthracene phenylethynyl molecules were assembled on curved Au surfaces. Surface-enhanced Raman spectroscopy measurements revealed that the surface constraint drove unfavorable [4+4] photoreaction of anthracene rather than [4+2] reaction that is favored in solution on both flat and curved surfaces. Molecules on curved surfaces exhibit dramatically slower regioselective photoreaction kinetics and efficiencies than those on atomically flat surfaces due to larger intermolecular distances and variable orientations in the SAMs. The surface-dependent properties of such molecules can be used to probe the local chemical environment on curved surfaces.

Continuous efforts in the three-pronged approach involving assembly, measurements, and molecular design will enable the increasingly complex, precise, and multifunctional assemblies. These complex assemblies can serve as new test beds for gaining deeper insight into interactions and function of molecules. One of our long-term goals for this study are to design and to apply new functional materials controlled at the single-molecule level. By measuring single molecules and precise assemblies as test structures, we aim to elucidate the rules of working at the ultimate limits of miniaturization and to develop cooperative action inspired by biological systems.

Acknowledgments

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