

FUNCTIONAL SUPRAMOLECULAR ASSEMBLIES: FIRST GLIMPSES AND UPCOMING CHALLENGES

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ABSTRACT

Functional supramolecular assemblies have emerged as candidates for nanosystems because of their potential for efficient, green, and cost-effective fabrication, as well as the capacity for tunability at molecular and atomic scales. Recent advances in the synthesis and characterization of supramolecular assemblies have already pointed to many opportunities ahead. While the practical integration of supramolecular assemblies into device manufacturing remains out of reach, learning to design the precise interactions between molecules and to control (and to predict) their structures will drive excitement, interest, and advances in bottom-up approaches to new materials and devices. This review discusses several key advances in the preparation of (and applications for) functional supramolecular assemblies, upcoming challenges, and our approaches toward the analysis of and precise control over functional supramolecular assemblies.

INTRODUCTION

A supramolecular assembly is an organized system of two or more molecules, where order originates from the weak, non-covalent binding interactions between the substituent parts [1, 2]. By tailoring molecular geometry and functionality, supramolecules may be designed and developed into functional nanosystems. While the lion's share of attention has been focused

on the synthesis and characterization of various supramolecules, practical applications rely on the functional supramolecular assemblies that operate both independently and in concert [3]. It has been demonstrated that simple supramolecular components, after organization and assembly, can link molecular motions and reactions to complex macroscopic functions – including actuation and optical signal modulation [4–8]. Although the incorporation of functional supramolecular assemblies into modern fabrication methodologies remains a lofty goal, impressive progress has been made toward the development of functional nanomaterials and nanodevices [9]. Here, we highlight these materials and devices with focus on the upcoming challenges and our progress toward the precise control and analysis of functional supramolecular assemblies.

FUNCTIONAL SUPRAMOLECULAR ASSEMBLIES AT WORK

The understanding of how molecules spontaneously organize on surfaces has facilitated the design of functional supramolecular assemblies [10]. Exerting control over molecules at their fundamental scale has had a revolutionary impact on molecular electronics, nanoelectromechanical systems (NEMS), nanophotonics, and nanomedicine [4, 8, 11, 12]. A few examples of such designed assemblies are presented in the subsequent section to illustrate the power of these techniques.

Monolayers of bistable [2]rotaxanes for molecular plasmonics

Artificial molecular machines such as rotaxanes represent one class of supramolecules [1, 8, 13–15]. The rotaxanes may be described simply as a molecular dumbbell with mechanically interlocked rings (Fig. 1a) [4]. The bistable [2]rotaxanes employ the intramolecular recognition between the π -electron-poor tetracationic macrocycle cyclobis (paraquat-*p*-phenylene) (CBPQT⁴⁺) rings and two π -electron-rich stations, namely 1,5-dioxynaphthalene (DNP) and the redox-active tetrathiafulvalene (TTF). The ring may be triggered to move from the TTF station to the DNP by oxidizing the TTF moiety, and subsequent TTF reduction reverses the motion. Before oxidation, the encircling ring is docked at the neutral TTF unit. Oxidation of the TTF unit to either the radical TTF^{•+} or dicationic TTF²⁺ lowers its affinity to the CBPQT⁴⁺ ring, triggering the transit of the ring to the DNP station. Subsequent reduction of the TTF^{•+} or TTF²⁺ allows the ring to return to the neutral TTF station. This molecular motion is reversible, and may be repeated by cycling the TTF oxidation state.

Huang, Jensen, Stoddart, Weiss, and co-workers took advantage of the reversible, controllable mechanical motions in bistable [2]rotaxanes, and demonstrated a molecular-level plasmonic switch in which the localized surface plasmon resonances (LSPRs) of gold nanodisks could be reversibly controlled by mechanical motions in rotaxane molecules assembled on the disk surfaces [4]. Surface-plasmon-based nanophotonics, or “plasmonics”, enables the development of photonic integrated circuits because of the capability for guiding and manipulating light at a scale smaller than its wavelength [16, 17]. Although major

breakthroughs for passive components have been reported, including plasmonic waveguides, couplers, and lenses [18, 19], there have been few efforts to develop active components including switches and modulators [20–23].

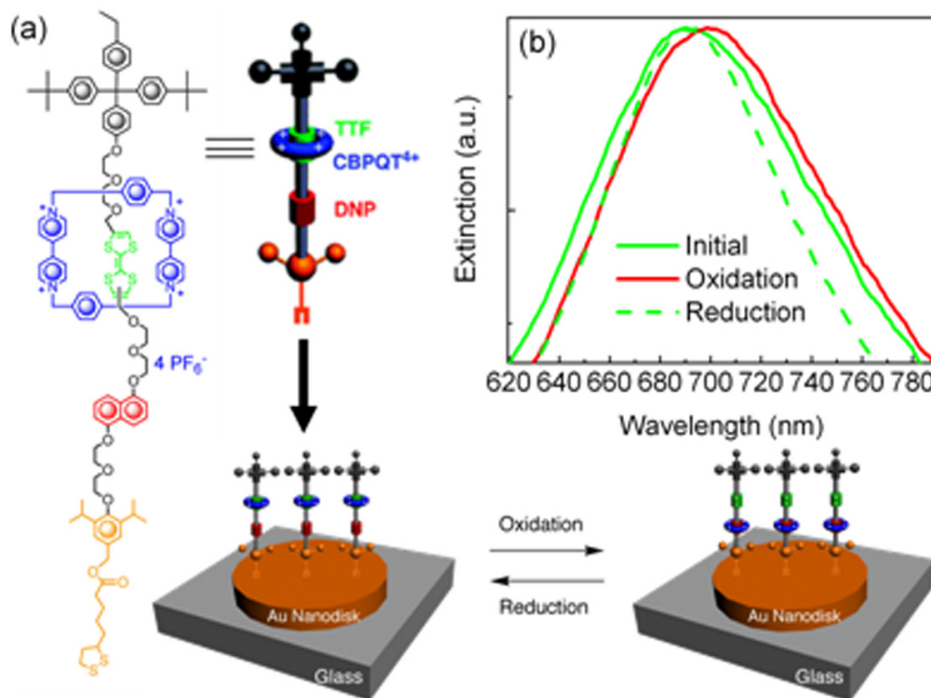


Figure 1. Plasmonic switches with rotaxanes as functional elements. **(a)** Functionalizing the rotaxane with the disulfide functional group allows it to be immobilized on the Au nanodisk surface. **(b)** Extinction spectra recorded from the rotaxane-derivatized gold nanodisks during the redox process provide a spectroscopic handle for monitoring the shuttling of the ring system. Reproduced with permission from reference [4]. Copyright 2009 American Chemical Society.

In their prototypical molecular plasmonic switches, Huang and co-workers have used the bistable [2]rotaxanes as the active component. Assembly on gold nanodisks via disulfide attachment to only one end of the rotaxane gives a non-centrosymmetric, upright orientation for the rotaxane molecules, and provides a strong chemical bond to the surface. A simple spectroscopic signature was used to track the ring position in this configuration. There is a strong visible absorption band centred at 820 nm while the ring is at the TTF station, a result of charge-transfer (CT) excitation between the highest occupied molecular orbital (HOMO) at the TTF and the lowest unoccupied molecular orbital (LUMO) of the CBPQT⁴⁺ ring. As before, oxidation causes the ring to shuttle from the TTF to the DNP station, which results in the disappearance of the absorption band centred at 820 nm. This change in the absorption

band is associated with the change in the wavelength-dependent polarizability of rotaxane molecules, and thus the LSPRs of gold nanodisks. The extinction spectra for the rotaxane-derivatized gold nanodisks show that the oxidation causes the LSPRs peak to shift from 690.4 ± 0.2 to 699.9 ± 0.2 nm, while reduction caused the peak to blue shift back to its initial position (Fig. 1b). The reversible peak shift is reproducible for many redox cycles.

Monolayers of bistable [3]rotaxanes for nanoelectromechanical systems

As actuation materials, the rotaxanes have several advantages over biological molecular motors: high force density, wide range of pH stability (active at pH between 4 and 10), insensitivity to ambient temperature (operating between -30 to 100°C), and may be triggered by multiple external stimuli [5]. These molecules have been engineered to generate precise, cooperative mechanical motion at the molecular scale, and represent the first step toward the engineering of systems that operate with the same elegance, efficiency, and complexity as the biological motors that drive the functions of the human body [24].

Huang, Stoddart, Weiss, and co-workers have demonstrated a mechanical actuator based on [3]rotaxane assemblies [6, 8]. Here, doubly bistable palindromic [3]rotaxane molecules self-assembled on a gold substrate have been used as an artificial molecular muscle (Fig. 2a). Before oxidation, the two TTF stations are nominally 8 nm apart. Oxidation causes the rings to move toward the centre of the molecule, with a spacing of approximately 4 nm. By attaching thiol functionality to each moving ring, rotaxanes could then be attached to cantilevers coated on only one side with gold (Fig. 2b). Oxidation triggers billions of these molecules simultaneously; the nanoscale motions collectively apply stress to one side of the cantilever. This stress is measured by the macroscopic deflection of the cantilevers. Figure 2c shows the time-dependent deflections of the rotaxane-modified microcantilever. This electrochemical method shows that the simultaneous 4-nm motions of individual molecules may be transduced into 300-nm deflections of a microcantilever ($500\text{ }\mu\text{m} \times 100\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$), illustrating the power of concerted nanoscale motions (Fig. 2b). The experimental observations, combined with elementary beam theory and analysis, indicate that the cumulative molecular-level movements within rotaxane assemblies bound on surfaces can be harnessed to perform macroscale mechanical work.

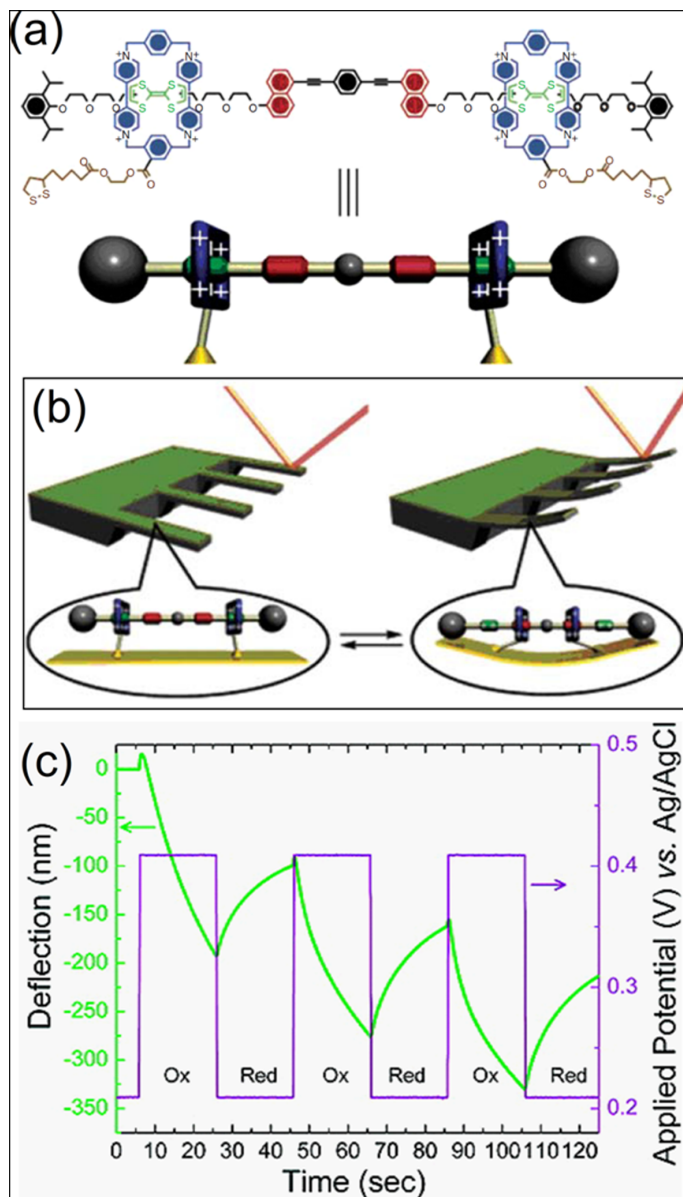


Figure 2. (a) Chemical structure and graphical representation of a disulfide-tethered bistable [3]rotaxane; (b) Schematic diagram of the deflections of cantilever by the cumulative molecular-level movements in [3]rotaxane assemblies bounded on the surface. Reproduced with permission from reference [6]. Copyright 2004 American Institute of Physics; (c) The deflection versus time (green line) of a cantilever coated on one side with the [3]rotaxanes on gold when subjected to a series of oxidation and reduction processes (purple line). Reproduced with permission from reference [8]. Copyright 2009 American Chemical Society.

Carbon nanotube yarns as multifunctional materials

Carbon nanotubes have attracted considerable interest due to their high tensile strength, as well as high electrical and thermal conductivities [25]. While individual carbon nanotubes have been successfully incorporated into electronic transistors, NEMS devices, and sensors [26–28], micro- and macroscale applications such as artificial muscles, conducting textiles, and fibre battery assemblies require trillions of long, oriented nanotubes [25, 29, 30]. Break-throughs in the preparation of nanotube-based ropes have produced high-quality assemblies of both single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs) [29]. Baughman and co-workers spun and twisted forests of MWNTs into multi-ply, torque-stabilized yarns (Fig. 3) [25]. Due to the high surface-to-volume ratio of the MWNT and the high interfibre contact area per yarn volume, these yarns exhibit high twist retention and can be further knitted and knotted for a wider range of applications. The excellent material properties of individual nanotubes lead to yarns of superior mechanical properties with high strength, toughness, thermal stability, and abrasion resistance. The intertube mechanical coupling introduced by twisting also allows yarns to retain electronic connectivity between all component nanotubes, even during infiltration of poly(vinyl alcohol) (PVA).

With these enhanced mechanical and electrical properties, carbon nanotube yarns can serve as multifunctional materials and find important applications across many fields. Nanotube yarns could replace metal wires in electronic textiles with new functionalities, such as the ability to actuate as an artificial muscle and to store energy as a fibre supercapacitor or battery [25]. Furthermore, their conductivity can be exploited in soft, radio- and microwave-absorbing fabrics, personal protective equipment to protect against electrostatic discharge, and heat-resistant textiles [25].

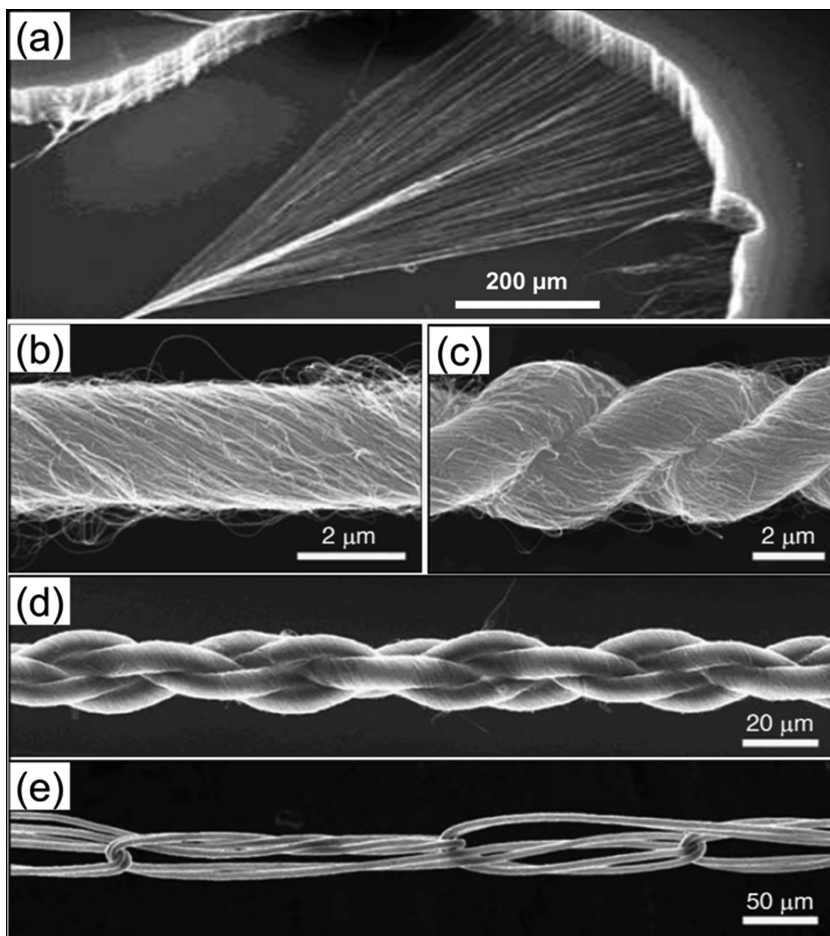


Figure 3. (a) A scanning electron microscopy (SEM) image showing a carbon nanotube yarn fabricated by simultaneous drawing and twisting from a vertically aligned multiwall nanotube (MWNT) forest; SEM images of (b) single, (c) two-ply, and (d) four-ply MWNT, as well as (e) knitted yarns. Reproduced with permission from reference [25]. Copyright 2004 American Association for the Advancement of Science.

UPCOMING CHALLENGES AND OPPORTUNITIES

Functional, oriented nanotube materials and robust supramolecular motors demonstrate the collective, macroscale effects of individual molecules acting in concert. [4, 8, 25, 29]. Despite research successes and growing momentum of the field over the last decade, there remain great opportunities for further advances. Controlling and measuring the physical, chemical, and electronic couplings between assembled molecules and between the assemblies and their substrates is a rich area for developments leading to a predictive under-

standing and the underlying design principles of optimized functional assemblies [11, 31 – 41]. Could arbitrary deflections of the cantilevers be achieved by controlling molecular orientations and interactions in the rotaxane assemblies? Can the response speed of the plasmonic switches be enhanced by engineering the rotaxane assemblies on the Au nanodisk surfaces? Is there a systematic approach toward optimization of the twist of MWCN yarns to have both maximized strength and conductivity? The study of single and precise supramolecular assemblies in well-defined environments offers insight into both couplings and functions. By isolating molecules and assemblies in a two-dimensional matrix, we can probe individual molecules, determine the role of the matrix, and design the matrix as an interacting part of the assembly [42 – 45]. In the following section, we report our progress in these directions, highlighting the capabilities of precise control and measurements we have and expect to have.

Using defects in self-assembled monolayers for precisely controlled molecular assemblies

Self-assembled monolayers (SAMs) are ultrathin films that spontaneously self-organize into one-molecule-thick structures on surfaces (Fig. 4a). The model system for SAMs has long been the *n*-alkanethiolate monolayers on gold; strong thiol-gold bonds and mobile complexes allow the alkyl chains to pack and to organize themselves rapidly into ordered structures [46 – 49]. Figure 4b shows a molecularly resolved scanning tunnelling microscopy (STM) image of a 1-dodecanethiolate SAM on Au{111}. A number of different types of defects exist in SAMs, and may be controlled by processing the film and substrate [50 – 52]. Defects are separated into two classes, substrate defects and monolayer defects, and are highlighted as indicated by arrows in Figure 4b. Gold substrate vacancy islands and gold terrace step edges are among the most prominent defects in the image. Step edges are a single-atom-high transition from one atomically flat terrace to another. Vacancy islands result from the removal of gold atoms during the self-assembly reaction, and manifest as one-atom-deep depressions in an otherwise atomically flat terrace. These two substrate defects can be treated identically, but are distinct features. The mismatch in substrate height prevents alkyl chains from maximizing tilt and thus van-der-Waals interactions. This loss of registry at the step edges results in voids that become active sites for molecular exchange and for the insertion of multiple (or larger) molecules. The mobility of gold atoms allows substrate vacancy islands to drift collectively relative to step edges; they will eventually merge with a terrace, a process that is greatly accelerated by elevating the deposition temperature and increasing deposition time.

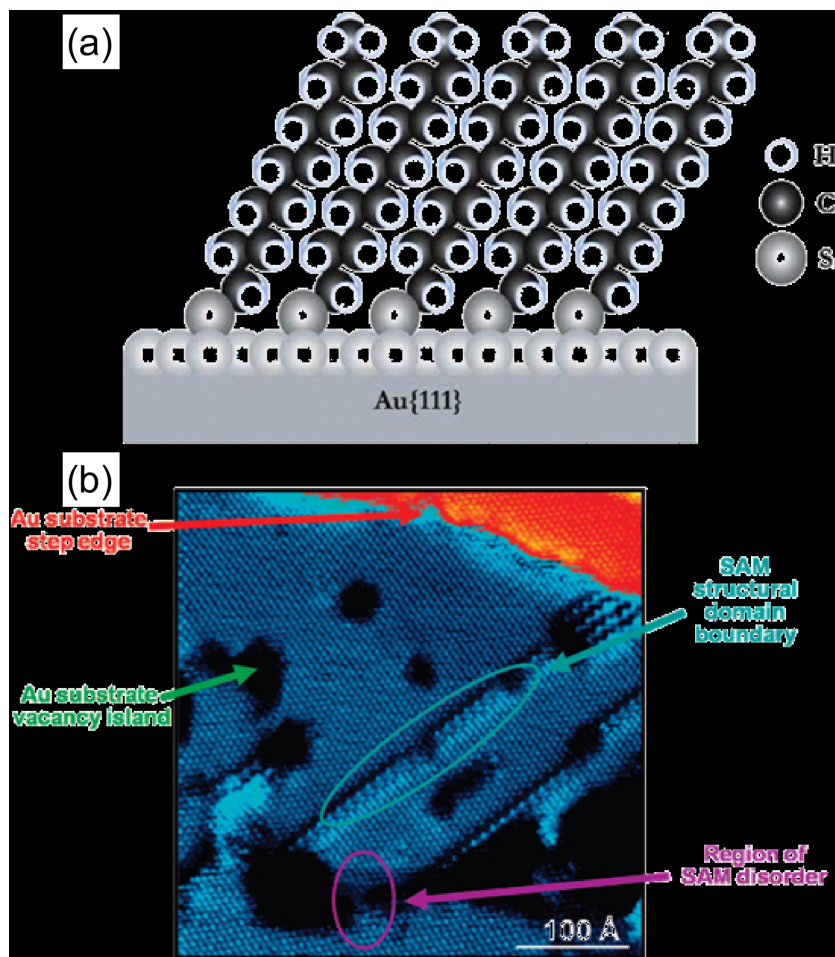


Figure 4. (a) Schematic of a SAM of 1-dodecanethiolate on an atomically flat gold substrate. Reproduced with permission from reference [51]. Copyright 2004 Elsevier Ltd; (b) A molecularly resolved STM image of a decanethiol SAM on Au{111}, indicating different types of defects. Reproduced with permission from reference [3]. Copyright 2008 American Chemical Society.

Monolayer defects include low-density, disordered regions and SAM structural domain boundaries. There are two types of domain boundaries: tilt domain boundaries and translational domain boundaries. Tilt domains result from a loss of registry due to different collective molecular tilts in ordered domains, while translational boundaries arise from mismatched positions of Au-S bonds between two domains. Structural domain boundaries are available sites for molecular exchange or for the insertion of *single* molecules or assemblies. Molecules can be inserted from the solution or vapour phases, or by contact via techniques such as micro-contact insertion printing [40, 53]. Isolating single molecules in

well-defined environments is a powerful technique to control the orientation, isolation, and reactivity of individual molecules, and provides the basis for efficient bioselective capture surfaces (Fig. 5) [12, 54].

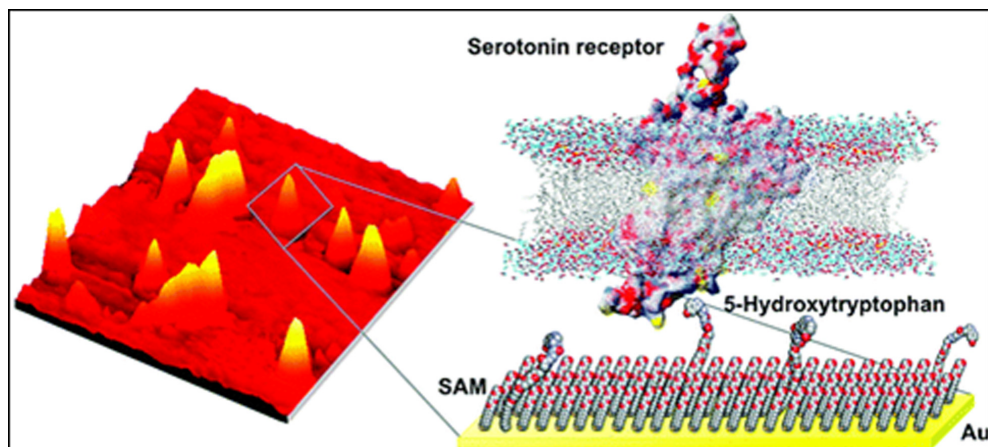


Figure 5. Capturing receptor proteins via surface-tethered small probes. A substrate is functionally modified with serotonin attached to oligo(ethylene glycol)-terminated alkanethiols self-assembled on Au{111}, and anti-5-hydroxytryptophan antibodies recognize the substrate, demonstrating bioavailability. Reproduced with permission from reference [12]. Copyright 2010 American Chemical Society.

Controlling azobenzene assemblies at surfaces

Photoisomerization about an azo functionality represents a fundamental molecular motor [21, 45, 55]. The coupling of external photoexcitation for the efficient control of surface-bound molecular assemblies remains a challenge [45]. This coupling is hampered by both the *quenching* of the excited states of the molecules by energy transfer to adjacent molecules and to the substrate, and to the inherent difficulty in measuring fast, transient events at a single-molecule scale. The molecule and its environment must be carefully designed to allow the tracking of single-molecule photoisomerization. First, molecules are isolated by insertion into the defects of SAMs, limiting their geometric degrees of freedom. The local environment has been prepared such that molecules tend to remain isolated, preventing energy transfer to neighbouring azobenzene units. The azobenzene moiety was attached to an ethoxy-butane-1-thiol tether. This serves to sever the functional part of the molecules from the substrate (**1** in Fig. 6). By controlling both the structure of the molecule and its local environment, we have been able to observe and to control the *trans-cis* reversible isomerization of individual azobenzene units using STM [45].

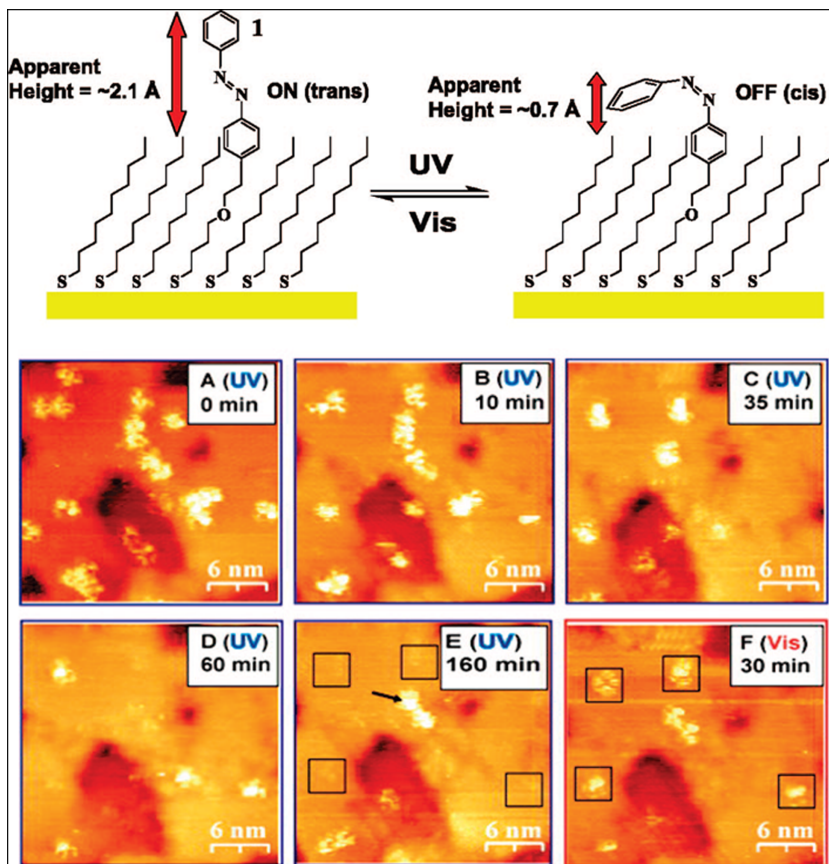


Figure 6. Isolated azobenzene molecules are embedded within 1-decanethiolate monolayer domains so as to eliminate motion about the S-Au bond. Reversible *trans-cis* photo-isomerization of the molecules by irradiating the surface with ultra-violet (~ 365 nm) and visible (~ 450 nm) light can be observed in sequence of images A-F. 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 reference [45]. Copyright 2008 American Chemical Society.

As shown in Figure 6, without illumination, the azobenzenes were initially found to be in their thermodynamically stable *trans* state and appeared as 2.1 ± 0.3 Å protrusions over the 1-decanethiolate matrix in topographic STM images under the conditions shown. The surface was then exposed to UV light (~ 365 nm) and was simultaneously imaged by STM. Azobenzene molecules were found to isomerize to their *cis* state, characterized by an apparent height reduction of ~ 1.4 Å (Fig. 6B – 6E). After 160 min of UV illumination at ~ 12 mW/cm², greater than 90% of the azobenzene molecules had isomerized from *trans* to *cis*. Subsequent illumination with visible light (~ 450 nm) for 30 min at ~ 6 mW/cm² switched nearly 50% of the molecules back to their initial *trans* conformation (Figure 6F) [45].

When the azobenzenes were assembled into a chain, rather than isolated individually, in domain boundaries, a dramatic drop in photoisomerization efficiency was observed. Large steric hindrance and intermolecular electronic coupling could both be contributing to this effect. By increasing the chain length of the host matrix around the tethered azobenzenes we have shown that steric hindrance reduces the efficiency of photoisomerization. In order to determine the role of intermolecular excitation coupling, it is important to vary the intermolecular spacing between the active molecules precisely. This can be done through hierarchical assembly of specially designed molecules in order to elucidate the effects: the functionalization of active parts of the molecules when coupled to substrates, the intermolecular interactions in such assemblies, and the external environment. This will ultimately guide optimization of the assemblies in order to increase the switching efficiency and to have the molecules operate in concert for practical purposes.

Tracking individual rotaxane molecules on surfaces

Precise and simultaneous measurements of structure, dynamics, and indicators related to function are important for understanding molecular couplings in assemblies, and are powerful advantages of the STM [56, 57]. Weiss and co-workers and others have developed ultrastable and highly sensitive STMs that are able to image continuously a single region with minimized perturbations for several days [11, 58–63]. With advanced digital image processing techniques, data on single assemblies are automatically extracted from larger fields of view (b – e in Fig. 7), and are correlated with the local environment. Apparent height information is recorded relative to a local reference (Fig. 6) or adsorbate positions are determined to assign changes between images in order to follow surface dynamics (Fig. 7).

In the example of surface-bound rotaxanes, Weiss, Stoddart, and co-workers have been able to follow the motion of single rotaxane molecules with a stabilized STM under electrochemical control [64]. These observations were achieved by employing molecular designs that significantly reduced the mobility and enhanced the assembly of molecules in orientations conducive to direct measurement using STM. The results reveal molecular-level details of the station changes of surface-bound bistable rotaxane molecules, correlated with their different redox states (Fig. 7). The trajectories of the rings reveal that, once a bistable rotaxane molecule is adsorbed on a surface, the motion of the CBPQT⁴⁺ ring relative to the dumbbell is affected by its local environment and the flexibility of the molecule. This study suggests that optimizing the design of rotaxane molecules with *rigid* dumbbells could further enhance the performance of rotaxane-based actuators (Fig. 2) [6, 8, 64].

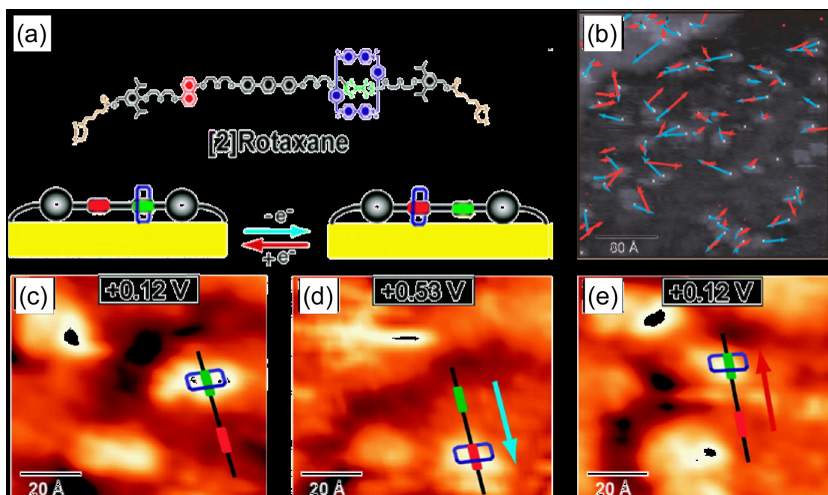


Figure 7. (a) Structure and motion of a bistable rotaxane molecule on Au{111}; (b) A STM image of rotaxanes adsorbed on Au{111} under 0.1 M HClO₄ solution. The three images with potentials +0.12, +0.53, and +0.12 V are superimposed and the protrusions (assigned as CBPQT⁴⁺ rings) have been marked. The trajectories of a large number of motions of the rings after potential steps from +0.12 to +0.53 V and back to +0.12 V are marked with blue and red lines, respectively; high-resolution image of an individual molecule (c) in its reduced state at +0.12 V with the ring at the TTF station; (d) upon oxidation (+0.12 to +0.53 V) the ring shuttling to the DNP station (blue arrow); (e) upon reduction (+0.53 to +0.12 V) with the ring returning to the TTF station (red arrow). Image conditions: $V_{\text{bias}} = 0.3$ V; $I_{\text{tunnelling}} = 2$ pA, Reproduced with permission from reference [64]. Copyright 2010 American Chemical Society.

CONCLUSIONS AND PROSPECTS

Although still in its nascent stage, research in the area of functional supramolecular assemblies has gained momentum over the past decade. A variety of supramolecules with precisely tailored structures and functions have been synthesized and characterized. Prototypical applications based on the collective effects in the functional supramolecular assemblies have emerged. However, many challenges remain in understanding and controlling a variety of molecular interactions in the assemblies, and in realizing coordinated action of functional molecules within such assemblies for practical devices. One effective way to address these challenges is to control assembly precisely and to measure the functional assemblies in well-controlled matrices. To this end, we have successfully developed procedures and tools for probing photoisomerization of azobenzene molecules and assemblies, and for tracking the motions of single rotaxane molecules. With new insights into building the assemblies gained through these studies, we will be able to design and to optimize the assemblies for greater function at the nanoscale.

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