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Understanding and Harnessing Biomimetic Molecular Machines for NEMS Actuation Materials

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Abstract—This paper describes the design, assembly, fabrication, and evaluation of artificial molecular machines with the goal of implementing their internal nanoscale movements within nanoelectromechanical systems in an efficient manner. These machines, a unique class of switchable molecular compounds in the shape of bistable [2]rotaxanes, exhibit internal relative mechanical motions of their ring and dumbbell components as a result of optical, chemical, or electrical signals. As such, they hold promise as nanoactuation materials. Although micromechanical devices that utilize the force produced by switchable [3]rotaxane molecules have been demonstrated, the current prototypical devices require a mechanism that minimizes the degradation associated with the molecules in order for bistable rotaxanes to become practical actuators. We propose a modified design in which electricity, instead of chemicals, is employed to stimulate the relative movements of the components in bistable [3]rotaxanes. As an initial step toward the assembly of a wholly electrically powered actuator based on molecular motion, closely packed Langmuir–Blodgett films of an amphiphilic, bistable [2]rotaxane have been characterized and an *in situ* Fourier transform infrared spectroscopic technique has been developed to monitor molecular signatures in device settings.

Note to Practitioners—Biological molecular components, such as myosin and actin in skeletal muscle, organize to perform complex mechanical tasks. These components execute nanometer-scale interactions, but produce macroscopic effects. Inspired by this concept, we are developing a new class of mechanical nanodevices that employ a group of artificial molecular

machines called bistable rotaxanes. In this paper, a series of experiments has been conducted to study the molecular properties of bistable rotaxanes in thin films and on solid-state nanodevices. Our results have shed light on the optimization of future molecular machine-based systems particularly with respect to their implementation and manufacture.

Index Terms—Actuators, infrared spectroscopy, nanotechnology, thin-film devices.

I. INTRODUCTION

Automated robotics systems within modern assembly lines depend on well-coordinated linear and rotary movements. Using artificial molecular machines, we have developed the capability and demonstrated the feasibility of these same principles at the nanoscale level [1], [2]. Molecular machinery [3] has been produced in a variety of chemical research laboratories around the world in the form of rotors [4], elevators [5], and gyroscopes [6], in addition to various classes of linear and rotary molecular mechanical assemblies [7], [8]. Our research has focused, in part, on the basic modes of motion in a class of linear motor molecules illustrated in Fig. 1 known as bistable rotaxanes [9].

Created by a bottom-up approach, based on self-assembly and molecular recognition, these switchable rotaxanes are promising actuation molecular materials for nanoelectromechanical systems (NEMS) [10]. They can be customized and optimized, thus conferring the flexibility necessary for a multitude of engineering applications. For example, bistable rotaxanes can be activated by various mechanisms—chemically, electrochemically and photochemically [2]—while biomolecular motors and most conventional actuation materials are limited to a single switching mechanism. Furthermore, bistable rotaxanes can be derivatized with disulfide tethers [11] or prepared with amphiphilic properties [12] to facilitate the formation of self-assembled monolayers (SAMs) or Langmuir–Blodgett (LB) films, both of which are key bottom-up manufacturing technologies for the simultaneous self-organization of a multitude of molecules. The electrostatic force generated in the molecular switching process undergone by some bistable rotaxanes is estimated to be 100 pN per molecule [13] (i.e., an order of magnitude greater than the force produced by biomotors such as kinesin and myosin). Given a packing density of 10^5 molecules per μm^2 , the cooperative motion within a monolayer of bistable rotaxanes can generate a force of $10 \mu\text{N}/\mu\text{m}^2$, which is sufficient to power a wide range of NEMS/microelectromechanical-system (MEMS) devices. Moreover, the fact that bistable rotaxanes display switching [14] characteristics and require a very low operating voltage [2] and energy input makes them desirable for a wide range of applications, such as in molecular valves [15], light switches [2], and nanomechanical amplifiers. With these advantages in mind, we have become interested in developing bistable rotaxane-based mechanical devices using the mechanical force and movement generated by the molecular switching process as a power source or actuator. These devices could have numerous applications. For example, an optical grating consisting of a row of reflective ribbons in parallel can be actuated by artificial molecular machines. Thus far, most optical gratings are manufactured on the microscale using piezoelectric or parallel plate actuation methods. In both cases, limitations exist due to high-voltage requirements and small actuation distances, difficulties which would not exist in rotaxane-based systems.

As a substantial step toward the long-term objective of creating rotaxane-based nanomechanical devices, we have shown that bistable rotaxanes maintain their switching properties in highly packed monolayers while the molecules are mounted on solid supports [12]. We have further demonstrated a proof-of-concept nanomechanical device driven by the bistable rotaxanes' switching mechanism [10]. In this

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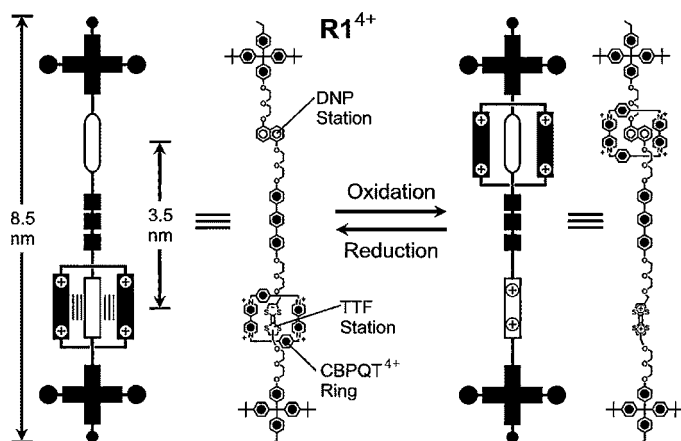


Fig. 1. Graphical representation and chemical structure of bistable rotaxane $R1^{4+}$ and its redox-controlled switching.

present work, experiments have been conducted to explore methods for exploiting these molecular machines' potential as actuation materials and optimizing their design. This paper is divided into three sections describing 1) the synthesis of bistable rotaxane-based molecular machines, along with the accompanying experimental observations used to identify their nanometer linear movements in solution; 2) a revealing observation that indicates the limitation and consequent direction toward optimization of the system; and 3) an outline of our current work and the future objectives that serves as a guide for the design of the next generation of devices to be derived from molecular machines.

II. GENESIS OF MOLECULAR MACHINES IN SOLUTION

A. Synthesis of Bistable Rotaxanes

Bistable rotaxanes represent one of several classes of mechanically interlocked molecules that consist of two or more components held together as a consequence of mechanical linking rather than by covalent bonds [9]. The scientific community's interest was initially piqued by the challenges inherent in their synthesis, as well as by their relatively unconventional architectures—an unusual and fascinating aspect of their structure that marries topology with chemistry. Bistable rotaxanes merely represent the forerunners, however, of a growing family of increasingly intricate molecular assemblies [5], [7], [8]. Fig. 1 shows that they contain a linear dumbbell-shaped component—bearing bulky end-groups or “stoppers”—around which one or more macrocyclic rings are trapped. Template-directed synthesis allows for precise control over the formation of the ring around the dumbbell to produce these mechanically interlocked molecules [16]. This high degree of organization lays the foundation for the assembly and mechanical function of molecular machinery [1], [2]. In particular, with the addition of two or more stations within the dumbbell component, the higher order property of controllable motion emerges [14], [17], [18].

Though seemingly complex in terms of their chemical structure, bistable rotaxanes are conceptually simple compounds whose mechanical switching operates on fundamental electrostatic principles. Fig. 1 illustrates the structure of a bistable rotaxane $R1^{4+}$ as a linear rod containing two different stations—a tetrathiafulvalene (TTF) station and a 1,5-dioxynaphthalene (DNP) station—separated by a rigid spacer and terminated by two bulky tetraarylmethane stoppers. This dumbbell-shaped component is encircled by a positively charged macrocyclic ring known as cyclobis(paraquat-*p*-phenylene) (CBPQT $^{4+}$). The resting state of rotaxane $R1^{4+}$ has the electron-deficient CBPQT $^{4+}$ ring preferentially encircling the electron-rich

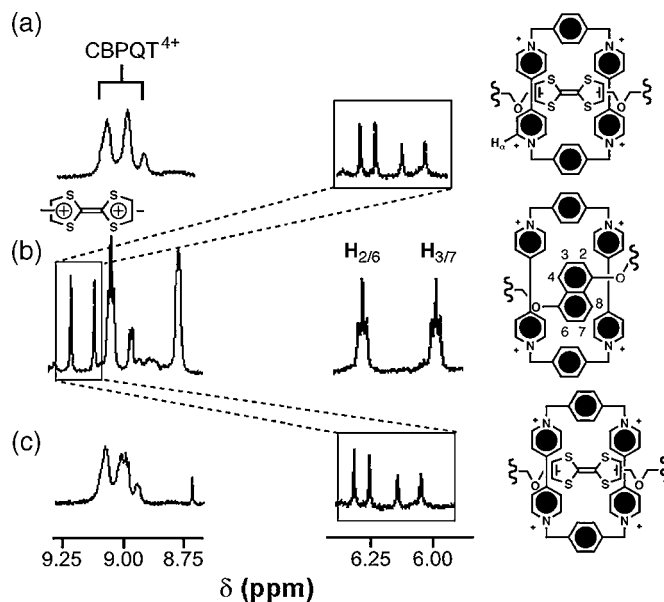


Fig. 2. ^1H NMR spectra of rotaxane $R1^{4+}$ showing (a) the TTF station encircled by the CBPQT $^{4+}$ ring in the resting state, (b) movement of the ring to the DNP station upon oxidation in the switched state, and (c) return of the ring to the TTF station following reduction.

TTF unit [14]. Upon oxidation, the TTF unit loses two electrons to become the positively charged TTF $^{2+}$ dication, causing it to repel the CBPQT $^{4+}$ ring electrostatically. The ring is preferentially attracted toward the modestly electron-rich DNP station. Conversely, the reduction of the positive TTF $^{2+}$ dication back to a neutral TTF unit causes the CBPQT $^{4+}$ ring to return to its starting position around the dramatically more electron-rich TTF station. This rotaxane-based “molecular shuttle” is bistable [18], meaning that it remains entirely (>9:1) in one switching state until electrochemically triggered to change to the other state [16].

B. Verification of Oxidation and Movement in Solution

In order to verify beyond any doubt the linear mechanical function of bistable rotaxanes, two processes—discrete *oxidation* of the TTF units and *movement* of the CBPQT $^{4+}$ rings—need to be unambiguously identified. ^1H NMR spectroscopy is a definitive tool for the determination of structural and electronic information in solution-phase chemical systems. By way of example, the ^1H NMR spectrum of the bistable rotaxane $R1^{4+}$ shown in Fig. 2, displays four characteristic singlets in the range of $\delta = 6.02$ – 6.28 ppm, an observation which indicates that the CBPQT $^{4+}$ ring resides predominantly around the electron-rich TTF unit [14]. Fig. 2 also shows the spectroscopic changes that were observed when an oxidant—tris(*p*-bromophenyl)ammonium hexachloroantimonate—is added to the solution. The TTF protons shift dramatically to $\delta = 9.25$ and 9.15 ppm, indicating that the TTF unit is fully oxidized to its dicationic form. Furthermore, the appearance of a new set of resonances at $\delta = 6.28$, 5.99, and 2.33 ppm (not shown), assigned to the three pairs of protons on the DNP station, suggests that the CBPQT $^{4+}$ ring has moved from the TTF station to the DNP station upon oxidation of the rotaxane. The addition of zinc powder to the solution, followed by vigorous shaking, leads to the reduction of the TTF $^{2+}$ dication back to its neutral state, accompanied by shuttling of the CBPQT $^{4+}$ ring back to the TTF station, thus restoring the original ^1H NMR spectrum. With solution-phase switching well established, we next confirmed the ability for these linear movements to operate in LB films [12] and in SAMs [11].

III. NANO-CHEMOMECHANICAL ACTUATOR BASED ON ARTIFICIAL MOLECULAR MACHINES

In order to realize the amplification of these linear movements, we have developed [10] a cantilever-based, redox-controllable nanomechanical device that uses the contraction and extension of a custom-designed “molecular muscle” rotaxane incorporating two bistable entities [13]. Upon oxidation of the TTF units, the rotaxane’s surface-anchored rings contract with respect to each other and generate compressive stress on a cantilever beam, resulting in its upward deflection. Reduction of the oxidized molecule releases the stress and the cantilever retracts to its original position [10]. Subsequently, we observed that the magnitude of the beam bending decreases as the oxidation-reduction cycle is repeated [19]. The magnitude of the beam deflection decreases exponentially from 35 nm in Cycle 1 to 3 nm in Cycle 23. Since the cantilever’s actuation is caused by the movements of molecular machines, this loss in performance must be related to the properties of the rotaxane molecules themselves, or to the nature of their anchorage to the underlying gold substrate. Interestingly, our data also showed that this decrease qualitatively matches a separately observed trend in which a UV/visible band of a closely related rotaxane degrades similarly in solution [19]. The solution phase decay was estimated from the percent restoration of the original UV/visible absorption band intensity of the rotaxane after one oxidation-reduction cycle. This correlation suggests that a chemical process is primarily responsible for the gradual decrease in the magnitude of the beams’ bending. In order to develop a more efficient and practical molecular machine-based nanomechanical actuator, it would be best to carry out future experiments in an environment in which air and solutions are absent. This requirement suggests a modification of the switching stimulus to electricity or light in lieu of chemicals, thereby potentially increasing the system’s lifetime.

IV. NEW DESIGN: A MOLECULAR MECHANICAL DEVICE STIMULATED BY ELECTRICITY

Artificial molecular machines can be switched, not only chemically as demonstrated in the previous device [10], but also electrically [2], [11], [20]. An electrical stimulus has greater potential for engineering applications. Thus, efforts focused on electrically powered molecular machine-based nanomechanical devices in which motor molecules are sandwiched between two electrodes and switched by voltage changes are desirable. However, at least two challenges exist. First, the integration of molecular motors into such designs involves the vapor deposition of an electrode on top of a molecular monolayer [20]. In order to prevent an electrical short caused by penetration of the top electrode during the deposition process, closely packed films are essential. However, SAMs of molecules have yet to be optimized to produce sufficiently close packed films to prevent an electrical short in micron-scale domains. Second, once the molecules are sandwiched between the top and bottom electrodes, barely any information about the newly cloaked molecules’ structure or properties can be obtained. For molecular electronics devices [21], however, kinetic and thermodynamic measurements on the switching speeds obtained from bistable [2]rotaxanes in devices, in SAMs [11], in polymer matrices [22], and in the solution phase [23] show that the molecular structure is the primary factor that influences the device’s switching speeds. In such cases, the structure-dependent properties of the molecules are revealed; however, the details of their structures within the devices remain hidden from view.

As an initial step toward a rational approach for developing wholly electrically powered nanoactuators using the force generated by artificial molecular machines, we have characterized [24] closely-packed LB films of rotaxanes and developed an *in situ* Fourier-transform infrared (FTIR) spectroscopic technique [25] that has the capability

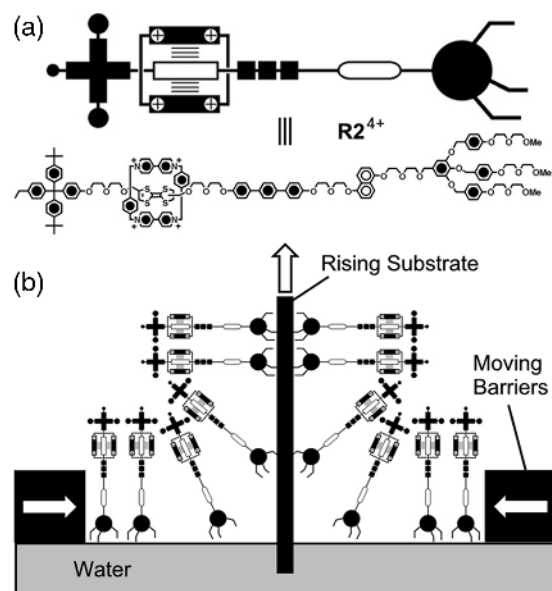


Fig. 3. Diagram of (a) the graphical representation and chemical structure of rotaxane $R2^{4+}$, and (b) the process for transferring a Langmuir monolayer from the air–water interface onto a solid substrate as a Langmuir–Blodgett film.

of simultaneously monitoring molecular properties and structures in a single-molecule-thick nanomechanical device. Our studies have the potential to aid in 1) establishing empirical molecular-structure/device-function relationships, in order to 2) provide an explanation of a device’s operating mechanism, that will help with 3) the rational design of new compounds for optimal device performance, hence, 4) providing researchers in the field of molecular machinery and electronics with a general tool for understanding molecular properties in device settings.

A. Characterization of Closely Packed Rotaxane Langmuir–Blodgett Films

The LB technique is an efficient means of transferring organized single-molecule-thick monolayers from an air–water interface onto a solid substrate [26]. Using this manufacturing approach, we can guide the self-organizing orientation of amphiphilic-bistable rotaxanes, such as $R2^{4+}$, illustrated in Fig. 3. These rotaxanes in LB films can be considered to be in a “liquid crystalline-like” environment and, therefore, are likely to maintain their mechanical switching properties, even when covered by top electrodes [12], [20]. The combination of the controlled orientation of the condensed phase superstructure with the retention of mechanical switching properties found in the solution phase makes the LB technique an ideal method for establishing a functional interface between amphiphilic-bistable rotaxanes and solid supports.

Characterization of rotaxane-based LB films provides information on the thin film’s uniformity and quality [27]. Atomic force microscopy (AFM) has been used to investigate an LB film of the rotaxane $R2^{4+}$ on an atomically flat mica surface. The surfaces were scanned in tapping mode at $1 \mu\text{m/s}$ with a 256 line per image resolution over a $1 \mu\text{m}$ by $1 \mu\text{m}$ area. Silicon cantilevers (Veeco Instruments, Inc., $120 \mu\text{m}$, tip radius 5–10 nm) and a $10\text{-}\mu\text{m}$ E scanner were used in a series of imaging experiments. Fig. 4 shows the molecular topography resulting from different packing densities. The domains formed at the water–air interface were transferred to the solid substrates and, at higher transfer pressures, the domain spacing decreased with a more highly packed molecular monolayer. AFM studies, in association with ellipsometry measurements, have revealed that the films are densely packed with a predictable thickness and regular topography when the

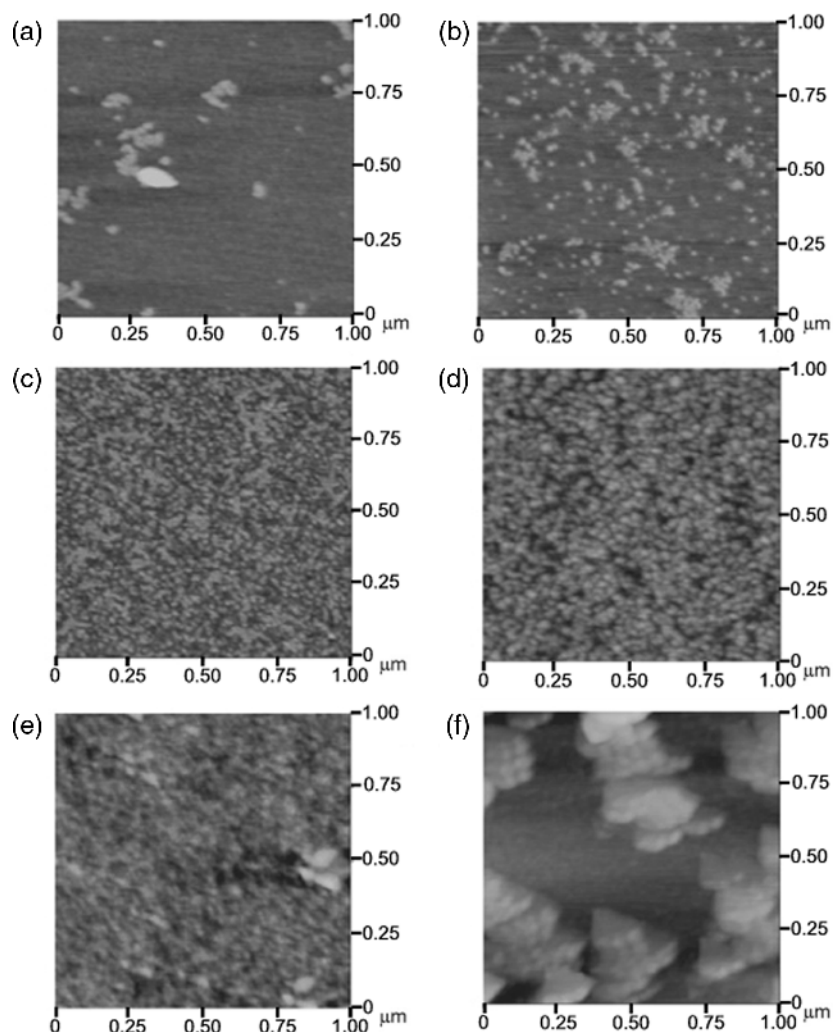


Fig. 4. AFM images of LB films of rotaxane $\mathbf{R2}^{4+}$ on a mica surface transferred at different surface pressures: (a) 5 mN/m, (b) 15 mN/m, (c) 25 mN/m, (d) 35 mN/m, (e) 40 mN/m, and (f) 43 mN/m.

surface pressure approaches 25 mN/m. However, when the surface pressure exceeds 35 mN/m, the monolayers start to fold and partially collapse [Figs. 4(d)–(f)]. Noncontiguous molecular monolayers with folding and partial collapse will not be able to prevent penetration of the top electrode during the deposition process and, therefore, are not desirable for our application. AFM studies confirm that the optimal deposition pressure based on topographical uniformity is around 25 mN/m.

The LB thin-film deposition technique has several useful advantages over SAMs. LB films allow for more user control and, therefore, enable the production of more closely packed and organized films than SAMs. Another advantage lies in the fact that LB multilayers can be produced, resulting in rotaxane films with controllable and well-defined thicknesses for a wide range of engineering applications, such as optical switches. We have used UV-visible-NIR transmission spectroscopy to characterize $\mathbf{R2}^{4+}$ films of 8, 16, 24, and 32 layers mounted on quartz substrates. The UV-visible-NIR spectra of these LB multilayers [Fig. 5(a)] display an intense UV band at 300 nm associated with that observed in solution [14] and a very weak band at 930 nm assigned to the charge-transfer (CT) transition between the TTF station to the CBPQT $^{4+}$ ring. Fig. 5(b) shows that the 300-nm UV absorption band increases linearly with the number of LB layers, an observation that indicates that the multilayers maintain their organization and orientation even as the number of layers increases. Assuming that the UV transition dipole is isotropic, the extinction coefficient measured in solution ($\epsilon_{300} = 74\,000\text{ M}^{-1}\text{ cm}^{-1}$) is still applicable to the thin

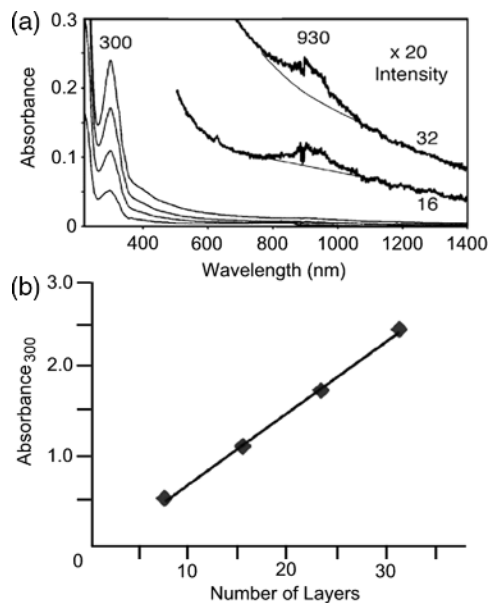


Fig. 5. (a) UV-visible-NIR spectra of rotaxane LB multilayers (8, 16, 24, 32). (b) The 300-nm band displays a linear increase with the number of LB layers.

films. Consequently, the surface coverage of $\mathbf{R2}^{4+}$ is calculated to be 1.6 nm^2 per molecule based on the UV-visible-NIR data. Considering

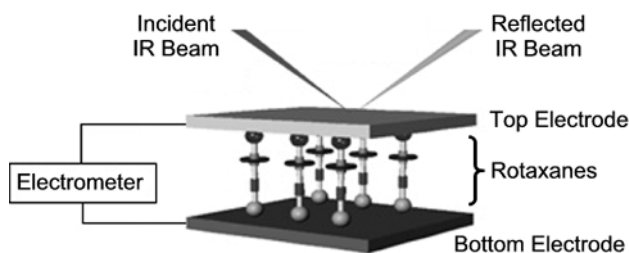


Fig. 6. Schematic diagram of the experimental setup for *in situ* IR spectroscopic investigation of a rotaxane-based crossbar device.

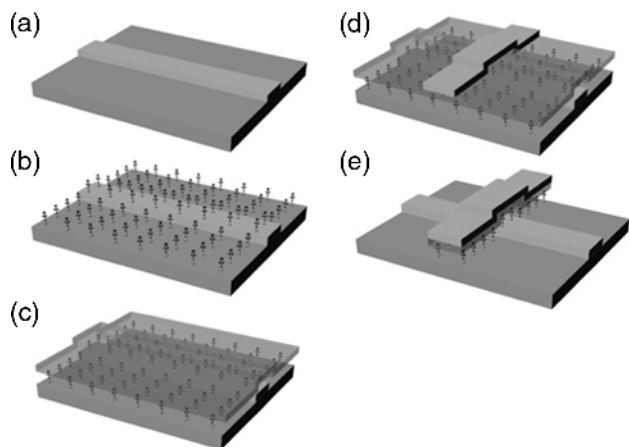


Fig. 7. Fabrication process flow for a rotaxane-based crossbar device outlining (a) evaporation of 100-nm-thick aluminum onto silicon nitride substrates through a contact shadow mask, (b) transfer of rotaxane monolayers onto the substrate, (c) evaporation of a semitransparent protective titanium layer, (d) evaporation of a semitransparent aluminum top electrode, and (e) etching the protective titanium layer.

the fact that the size of $R2^{4+}$ is ca. $1 \text{ nm} \times 1 \text{ nm} \times 8 \text{ nm}$, the LB multilayers are very highly packed and oriented.

B. In Situ Spectroscopic Technique to Record Molecular Signatures in Device Settings

We have developed an *in situ* FTIR spectroscopic technique that has the capability of monitoring molecular properties in single-molecule-thick nanomechanical devices. The experimental setup (Fig. 6) consists of an electrometer, an FTIR spectrometer, and an IR microscope that can be coupled to a time-resolved step-scan IR detection system used to monitor a monolayer of rotaxane molecules in a crossbar device. This thin layer, solid-state setting simulates the operating conditions under which rotaxanes would function in an electrically driven nanomechanical device. The experiment is designed such that the I/V characteristics of each crossbar device are measured to verify the absence of an electrical short circuit prior to the conducting of any IR spectroscopic experiments. The IR spectra of the rotaxane mono/multilayers are then recorded simultaneously on a Bruker EQUINOX 55 FTIR spectrometer equipped with a Hyperion 1000 IR microscope, while the electrometer is used to apply voltages across the device. The IR microscope is used to focus the incident IR beam onto the crossbar junction device. The experiment is designed not only to record molecular properties within an operating device, but also to quantify the response time for the rotaxanes' switching from one state to another. The time constant determines the operation speeds and, thus, the practical value and future impact of rotaxane-based NEMS devices.

Fig. 7 shows a schematic drawing of the fabrication process for a rotaxane-based crossbar device. Bias voltages are applied to the aluminum bottom electrode while the titanium/aluminum top electrode

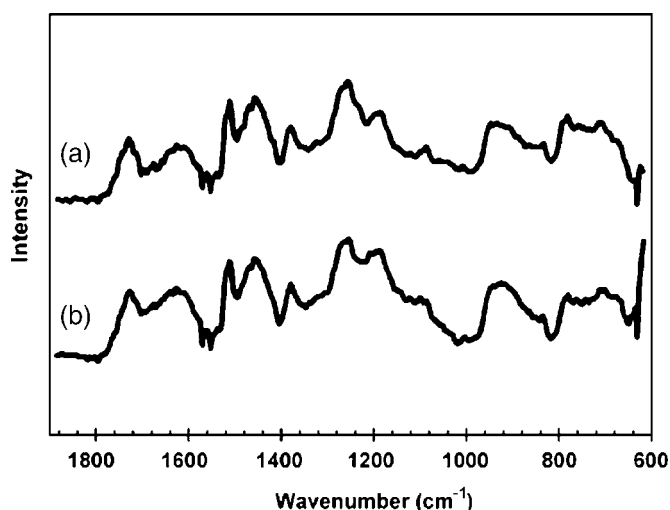


Fig. 8. Grazing angle reflection-absorption IR spectra of a rotaxane as (a) an LB monolayer on an aluminum electrode and (b) an LB monolayer sandwiched between two electrodes.

was connected to ground through a current amplifier. The semitransparent titanium/aluminum top electrode permits most of the incident and reflected IR beam to pass through to the rotaxane LB films, allowing the molecular signatures to be recorded.

The devices illustrated in Fig. 7 were fabricated and their IR spectra were recorded. Fig. 8 shows the IR spectra of a ground-state rotaxane-based LB monolayer while: a) on top of an aluminum electrode and b) sandwiched between two electrodes. It has been observed that when the thicknesses of the titanium and aluminum electrodes approached 2 and 6 nm, respectively, the IR spectra obtained remained the same as those without the top electrode. These results demonstrate that the top electrode had not damaged the monolayer and that this technique was capable of detecting the molecular signature faithfully within operating devices. The electrical performance of related devices [20] are robust and repeatable while there is minimal loss of performance over 30 cycles. The IR spectra (Fig. 9) of the rotaxane $R2^{4+}$ and its constituent components were recorded as KBr pellet preparations. All of the spectra of the rotaxane molecular subsystems have been analyzed and assigned in terms of their individual constituent parts. The results obtained from this analysis bear directly on the probing of molecular properties in the proposed nanomechanical devices. The spectra are constituted by many overlapping vibrational bands, which have been assigned to almost every component, thus leading to complex data that are challenging to deconvolute. This situation is simplified by taking two observations into consideration. They are: 1) in most cases, the approximate IR band positions and intensities are essentially a simple linear combination of the component parts, and 2) among the key structural components from which the bistable rotaxanes derive their mechanical motion, the signature for the TTF station is too weak for even the most intense marker bands to be identified. The signature for the DNP station is marked by the presence of bands at 1505 and 1268 cm^{-1} , and the ring component, a strong IR absorber, displays characteristic marker bands at 1633, 1555, and 639 cm^{-1} . Thus, IR spectroscopy can be an effective tool in probing the structure and properties of bistable rotaxanes in a crossbar device setting.

V. CONCLUSION

A group of artificial molecular machines, known as bistable rotaxanes, is a promising NEMS actuation material. Here, we described the conceptual background to the synthesis of bistable rotaxanes, along with the accompanying experimental observations used to identify

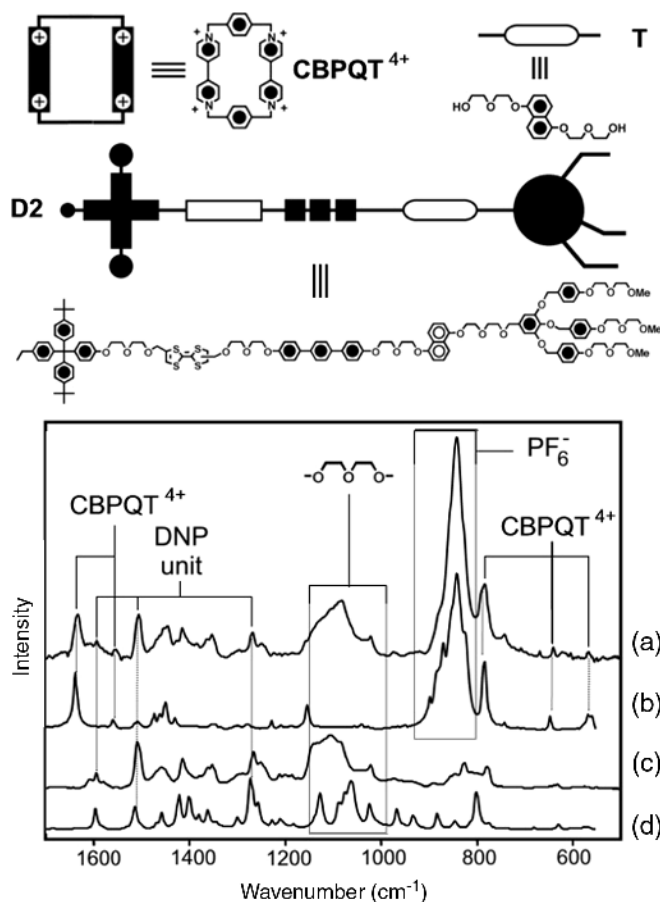


Fig. 9. Top: graphical representation and chemical structure of the ring component $CBPQT^{4+}$, dioxynaphthalene (DNP) component T , and "dumbbell" thread component $D2$. Bottom: assignments of the FTIR spectra of (a) rotaxane $R2^{4+}$, based on the band positions of (b) the ring and (c) the dumbbell $D2$, and (d) the DNP-thread T components.

their nanometer mechanical movements in the solution. Inspired by our observation of the current rotaxane-based NEMS device's limitations, a consequent direction toward the optimization of the system was proposed. A wholly electrically powered, bistable rotaxane-based actuator promises to be the next-generation device, featuring improved performance associated with an increased molecular lifetime. As initial steps toward the realization of this design, we characterized amphiphilic-bistable rotaxane LB monolayers with different packing densities and developed an FTIR spectroscopic technique to monitor *in situ* molecular signatures within bistable rotaxane-based nanomechanical devices. Our experiments have the potential not only to enhance our understanding of bistable rotaxanes for NEMS actuation materials, but also to provide researchers in the field of molecular mechanics and electronics with a general tool for understanding molecular properties in device settings.

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