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A Mechanical Actuator Driven Electrochemically by Artificial Molecular Muscles

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Inspired by the inherent promise and opportunities in nanotechnology, the scientific community has been attempting to decrease the characteristic length scales that define mechanical, electronic, and other devices.1–2 A wide range of applications, including robotic, optical, and microfluidic systems, call for microscale and nanoscale actuators.3 Most conventional electrostatic and piezoelectric materials, however, require high driving voltages, and they have to be fabricated using photolithography and other top-down manufacturing techniques that cannot easily achieve4 feature sizes below 100 nm. In contrast, bottom-up approaches5 that employ atoms and molecules as their fundamental building blocks and working units can potentially deliver mechanical operations on much reduced size scales.6–9 Recently, research has been directed10 toward developing an integrated approach that combines the functionality of bottom-up assembly with top-down techniques for the manufacture of hybrid nanoelectromechanical systems (NEMS).

A number of nanomechanical actuators11–23 have been fabricated by hybrid top-down/bottom-up approaches. Electromechanical expansion in sheets of single-walled carbon nanotubes, proposed by Baughman et al.,11 has resulted in microscale actuation with strains higher than those obtained using conventional ferroelectrics. The phenomenon of hydrogel swelling by radiative forces was used by Juodkazis et al.12 to build light-sensitive actuators. Redox-activated electrostatic repulsion in polymer molecules, such as polyaniline15 and polypyrrole,16 has also been employed to power reversible actuation in microcantilevers. Raguse et al.17 have utilized the intercalation of ions in nanoparticle films to achieve electrochemical actuation. These systems rely upon the bulk response of materials, and recently, researchers have started to harness work from molecular-scale mechanical motions. For example, Shu et al.19 demonstrated the controlled, reversible actuation of a microcantilever, using pH-controlled

ABSTRACT A microcantilever, coated with a monolayer of redox-controllable, bistable [3]rotaxane molecules (artificial molecular muscles), undergoes reversible deflections when subjected to alternating oxidizing and reducing electrochemical potentials. The microcantilever devices were prepared by precoating one surface with a gold film and allowing the palindromic [3]rotaxane molecules to adsorb selectively onto one side of the microcantilevers, utilizing thiol-gold chemistry. An electrochemical cell was employed in the experiments, and deflections were monitored both as a function of (i) the scan rate (≤20 mV s−1) and (ii) the time for potential step experiments at oxidizing (> +0.4 V) and reducing (< +0.2 V) potentials. The different directions and magnitudes of the deflections for the microcantilevers, which were coated with artificial molecular muscles, were compared with (i) data from nominally bare microcantilevers precoated with gold and (ii) those coated with two types of control compounds, namely, dumbbell molecules to simulate the redox activity of the palindromic bistable [3]rotaxane molecules and inactive 1-dodecanethiol molecules. The comparisons demonstrate that the artificial molecular muscles are responsible for the deflections, which can be repeated over many cycles. The microcantilevers deflect in one direction following oxidation and in the opposite direction upon reduction. The ∼550 nm deflections were calculated to be commensurate with forces per molecule of ∼650 pN. The thermal relaxation that characterizes the device’s deflection is consistent with the double bistability associated with the palindromic [3]rotaxane and reflects a metastable contracted state. The use of the cooperative forces generated by these self-assembled, nanometer-scale artificial molecular muscles that are electrically wired to an external power supply constitutes a seminal step toward molecular-machine-based nanoelectromechanical systems (NEMS).

KEYWORDS: bistable rotaxanes · electrochemistry · microcantilever · molecular machines · NEMS · supramolecular chemistry

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conformational changes (duplex to i-motif) in self-assembled monolayer (SAM) matrices of DNA. While a monolayer of a photosensitive protein complex (bacteriorhodopsin) has been employed by Thomas et al.\textsuperscript{20} and Ren et al.\textsuperscript{21} to actuate microcantilevers photochemically, other experimentalists\textsuperscript{22} have exercised photochemical control upon the configurational (cis/trans) isomerization of azobenzene molecules to actuate microcantilevers.

Artificial molecular machinery\textsuperscript{5–8,24–36} has emerged as one of the most attractive alternatives for performing controllable mechanical work that begins at the nanoscale. These molecular machines have proven to be integral to the operation and performance of many nanoscale and microscale systems, including molecular electronics\textsuperscript{9,26,37–47} and biomimetics for drug delivery.\textsuperscript{48–51} Tunable electrochemical devices\textsuperscript{54–58} as well as light-powered devices for transporting liquid over millimeters\textsuperscript{59} and for rotating microscale objects.\textsuperscript{60} The class of artificial molecular switches, based on bistable rotaxanes, is especially promising.\textsuperscript{61,62} These particular nanomachines are mechanically interlocked compounds\textsuperscript{63} composed of a dumbbell-shaped component that is encircled by one or more ring components.\textsuperscript{44,64} Bistable, donor–acceptor rotaxanes have many advantages as actuation materials. Most importantly, bistable rotaxanes can deliver controllable mechanical motions at the molecular level—a characteristic that most existing micro/nanoactuators\textsuperscript{1,10–22} do not possess—and thus can be ideal for applications where ultrasmall nanoactuators are needed. In addition, (1) they can generate tunable strains (e.g., up to 42%), while the strain generated\textsuperscript{6} by traditional piezoelectric actuators is typically less than 1%\textsuperscript{65,66} (2) they can undergo controlled mechanical motion, following the input of a variety of external stimuli (chemical, electrochemical, and optical), while traditional actuators\textsuperscript{3,67} and biomotors\textsuperscript{68} usually rely on a single stimulus; and (3) bistable [2]rotaxanes also offer the synthetically tunable property of hysteretic switching by taking advantage of a metastable state.\textsuperscript{39,54,69,70} In this manner, the molecules can persist in their actuated state long after the stimulus is removed.

We recently extended research beyond simple bistable [2]rotaxanes by designing and synthesizing a disulfide-tethered, palindromic, bistable [3]rotaxane $R^{8+}$ (Scheme 1) that mimics\textsuperscript{65,66} biological skeletal muscle’s contraction and extension. Skeletal muscles convert chemical energy to mechanical energy by the cumulative actions of myosin biomotors.\textsuperscript{71} Coherent and cooperative conformational changes in this biosystem are harnessed in order to obtain macroscopic muscle contraction and expansion.\textsuperscript{72,73} By imitation of the changes in shape that occur in skeletal muscles, the palindromic, bistable [3]rotaxane $R^{8+}$ undergoes controllable mechanical motions in the presence of external stimuli. It has a pair of redox-active tetraethylfulvalene (TTF) units, a pair of naphthalene (NP) stations separated by an (ethylene glycol) spacer, and two movable tetracationic, cyclobis(paraquat-para-phenylene) (CBPQT\textsuperscript{4–1}) rings (Scheme 1). In the ground-state co-conformation, both the CBPQT\textsuperscript{4–1} rings encircle the TTF units, courtesy of electron donor–acceptor interactions.\textsuperscript{56} Oxidation of the TTF units causes the CBPQT\textsuperscript{4–1} rings to move toward the NP stations because of the electrostatic repulsion between the rings and the positively charged TTF\textsuperscript{2+} units. Reducing the TTF\textsuperscript{2+} dications back to their neutral state causes the rings to shuttle back onto the TTF units. The incorporation of a disulfide tether onto each CBPQT\textsuperscript{4–1} ring component provides a point of attachment to gold surfaces. More critically, this connection provides the means to transfer the energy of contraction within the artificial muscle molecules to an underlying substrate.

The collective motions induced by oxidation and reduction of $R^{8+}$ usually rely on a single stimulus and biomotors\textsuperscript{68} can be harnessed to perform mechanical work on a microcantilever.\textsuperscript{65,66} Reversible flexing of a microcantilever coated with $R^{8+}$ during the cyclic injection of oxidizing and reducing solutions was correlated to the collective contraction and extension—relaxation of the surface-bound muscle molecules. This work constituted a starting point in molecular-muscle-based NEMS. However, the introduction of different chemicals into the system
RESULTS AND DISCUSSION

In order to detect the mechanical work exerted by the surface-bound, palindromic, bistable [3]rotaxane $R^{8+}$ on microcantilevers during electrochemical activation, we combined (Figure 1) an optical deflection technique based on atomic force microscopy (AFM) with an in situ electrochemical method. A microcantilever coated on one side with gold was used as a working electrode, a silver wire as a quasi-reference electrode, and a platinum wire as a counter electrode. These three electrodes were placed in a Teflon cell filled with aqueous electrolyte (0.1 M NaClO$_4$). The silver wire pseudo-reference electrode was subsequently calibrated against a Ag/AgCl 3 M KCl reference. The data illustrated in Figures 2–4 represent the calibrated redox potentials. The gold surface of the microcantilever was coated with a monolayer film of $R^{8+}$ molecules, and the redox state was changed by applying a desired potential using a potentiostat (CHInstruments, Inc.). A laser beam reflected by the silicon side of the microcantilever was collected by a split photodiode. The deflections in the microcantilever during electrochemical activation of the muscle molecules were measured from the variations in the reflected laser beam position on the photodiode.

Previously, redox-activated mechanical switching of $R^{8+}$ molecules in solution was characterized extensively using cyclic voltammetry and UV–visible spectrophotometry. When $R^{8+}$ molecules are attached onto surfaces, our expectation is that, upon the application of a sufficiently oxidizing potential, the TTF units in $R^{8+}$ will become positively charged, causing the surface-bound rings to move toward the NP units. Consequently, this action will increase the bending moment of the supporting microcantilever. A reducing potential will regenerate the neutral TTF units, causing the rings to move back to these TTF units. The deflection in the microcantilever would then decrease. Therefore, by applying an electrochemical potential, it will be possible to harness the collective mechanical motions from surface-bound molecular muscles and to control the deflection of the microcantilever.

To describe the direction of the microcantilever deflection, we use the terms “down” for deflection of the microcantilever toward the gold side (negative deflection) and “up” for deflection away from the gold side (positive deflection). To determine the mechanical work exerted by molecular muscles on the microcantilevers, all competing forces acting against the mechanical work performed by molecular muscles should be low in magnitude or, ideally, nonexistent. Such competing forces, however, do exist in microcantilevers during electrochemical activation. They include electrostatic repulsion forces at solid–liquid interfaces and surface stress induced by specific adsorption and desorption of ionic species in the electrolyte. To assess the influence of these competing forces, we subjected a nominally bare gold-precoated microcantilever without a molecular muscle monolayer film to a sweep of triangular potential. Figure 2a shows the performance of a bare microcantilever subjected to anodic and cathodic sweeps of electrochemical potential at a slow scan rate of 2 mV/s. The bare microcantilever was deflected upward during the anodic sweep and deflected back
down again to the neutral position during the cathodic one. On the basis of the magnitudes of surface stress reported in earlier work,75–78 we attribute this deflection signature to the specific adsorption of perchlorate (ClO$_4^-$) counterions onto the gold-coated side of the microcantilever.

We expected that, upon the oxidation of the TTF units and the consequent contraction of the distance between the rings, the collective moments of deflection caused by the many muscle molecules would flex the microcantilever (Figure 1) in the negative direction, that is, opposing the competing effect (Figure 2a) of specific adsorption by perchlorate counterions. Both effects were observed (Figure 2b) in triangular sweep experiments performed on a microcantilever coated with a monolayer film of the [3]rotaxane R$^{8+}$ (green line) on one side of the microcantilever (20 mV s$^{-1}$). The directions of the arrows indicate the corresponding y-axis of the parameter plotted.

Figure 2. Deflection signature (colored lines) in response to a triangular sweep (purple lines) of the electrochemical potential for (a) bare microcantilever (orange line, 5 mV s$^{-1}$) and (b) microcantilever modified with a monolayer film of the palindromic bistable [3]rotaxane R$^{8+}$ (green line) on one side of the microcantilever (20 mV s$^{-1}$). The directions of the arrows indicate the corresponding y-axis of the parameter plotted.

The initial deflection (when the driving potential is below $+0.24$ V) of the microcantilever started to deflect downward for various scan rates of the electrochemical potential (see Supporting Information, Figure S1a). The observed downward deflection was attributed to the collective motions of surface-bound muscle molecules that generate tensile stress on the microcantilever. Subsequent application of a cathodic sweep caused the microcantilever to return to its original position. This restoration was believed to occur on account of the fact that reduction of the TTF$^{2+/+}$ units will lead to shuttling of the rings back to their original positions. When the potential went below $+0.12$ V, the microcantilever deflected downward, an observation that we attribute to the desorption of perchlorate counterions from the microcantilever occurring in the background. The initial deflection (when the driving potential is below $+0.24$ V) of the R$^{8+}$-coated cantilevers, attributed to the specific ion adsorption, was higher than what was observed in bare cantilevers. This phenomenon is assigned to the presence of positive charges on R$^{8+}$ that make the cantilever surface highly charged and more prone to specific adsorption than bare cantilevers. Another cantilever coated with R$^{8+}$ molecules also showed similar deflection signatures for the same potential window and scan rate (see Supporting Information, Figure S1b), indicating good reproducibility of our experiments. It should also be noted that the magnitude of deflection observed here is much larger than the ones observed in our previous studies,65,66 which utilized chemical stimuli and were likely limited by the diffusion and partial activation of the molecules.

To determine other effects that could contribute to the deflection of the cantilever, such as electron injection into the cantilever, we conducted control experiments with monolayer films composed of two different compounds. The first control compound (Scheme 1b) was a disulfide-tethered dumbbell compound D. This compound contains a pair of TTF and NP units with the same relative geometry as that present in R$^{8+}$ and retains the redox activity of the [3]rotaxane. However, D lacks mechanically mobile CBPQT$^{4+}$ rings, while the disulfide tethers are attached at the two stoppers of the dumbbell. The second control compound (Scheme 1c) was 1-dodecanethiol (C$_{12}$H$_{26}$SH) C12, which lacks both moving elements and redox-active units, but which is known to form well-ordered SAMs that would thus block adsorption of other species.79–84 Neither control compound was expected to perform mechanical work on the microcantilever, but it is expected that oxidation of D changes the electronic structure of the gold metal and creates tensile stresses on the cantilever. To test these hypotheses, monolayer films of the control molecules, assembled on microcantilevers, were subjected to triangular sweeps (Figure 3) at slow scan rates of 20 mV s$^{-1}$. The deflection for both control compounds was opposite to that observed in the case of R$^{8+}$. This opposite movement indicates that the mechanically active, disulfide-tethered CBPQT$^{4+}$ rings in R$^{8+}$ are essential for the redox-controlled bending of the cantilever beams. The small upward deflections of the microcantilevers coated with control compounds were attributed to the adsorption of perchlorate counterions on the gold side of the microcantilever. The potential-induced
deflections, observed for microcantilevers coated with any of the monolayers (R^8+, D, or C12), were smaller in magnitude than those observed for bare microcantilevers. In these cases, the monolayers served as protective blocking layers that decreased adsorption. The adsorption for the ordered SAMs of the C12-coated microcantilevers was somewhat less pronounced than that observed for microcantilevers coated with D, as well as for those coated with R^8+ prior to the onset of downward deflection. We attribute this to the ordered, dense surface packing of the C12 SAM providing the best protection (of the films studied) from ion adsorption. The upward deflection, in the case of D-coated microcantilevers, suggests that the effects from specific ion adsorption dominate over the tensile stresses induced by the injection of electrons into the cantilever.

We have also performed dynamic studies in which the potential steps were alternated on a microcantilever coated with molecular muscles (Figure 4a) in order to initiate oxidation and reduction, and the deflections were measured as a function of time. On the basis of the observed deflection curves (Figure 3), the voltages of +0.4 and +0.2 V were selected in order to effect the TTF unit’s oxidation and reduction, respectively. It was observed that at +0.4 V, the microcantilever deflects downward, and at a lower potential, +0.2 V, where TTF is reduced to its neutral state, the microcantilever is deflected upward. The alternate bending down and up of the microcantilever corresponds to the alternate oxidation and reduction of the surface-coated muscle molecules, respectively.

We applied similar alternating potential steps to other microcantilevers, coated with either the control compounds D or C12. The cantilevers bent upward during the application of a higher potential step and bent downward during the application of a lower potential step (Figure 4b,c). Both deflections were in the opposite directions to those observed (Figure 4a) for the R^8+-coated microcantilevers.

When we repeated the redox chemistry, we observed (Figure 4a) a gradual downward deflection of the cantilever. This overlying strain effect, or creep,85 has been observed in other electrochemical actuator systems.86–90 The creep in these systems is purportedly caused by the disentanglement of the adsorbed molecular components.87,90 We believe that a similar creep mechanism may apply here but, in our case, arising from a reorganization of the muscle molecules within the monolayer film that plays an important role during the electrochemical perturbation. Similar behavior—the gradual deflection toward the coated side of the cantilever—was also observed in the microcantilevers coated with D (Figure 4b) and C12 (Figure 4c). However, such behavior was not observed in experiments (data not shown) conducted on bare microcantilevers. These observations are consistent with our hypothesis on the creep mech-

![Figure 3](image-url)  
Figure 3. Deflection versus applied potential with respect to the working electrode for a bare microcantilever (orange line, 5 mV s^-1) as well as for microcantilevers coated with monolayer films of the bistable [3]rotaxane R^8+ (green line, 20 mV s^-1), the dumbbell D (black line, 20 mV s^-1), and 1-dodecanethiol C12 (dark gray line, 20 mV s^-1).

![Figure 4](image-url)  
Figure 4. Time-dependent operation of microcantilevers coated with (a) the palindromic bistable [3]rotaxane R^8+ (green line), (b) the dumbbell D (black line), and (c) 1-dodecanethiol C12 (dark gray line), when subjected to a series of oxidation and reduction potential steps (purple lines).
anism. The creep of microcantilevers coated with \textbf{C12} was substantially less pronounced than that for \textbf{D} or \textbf{R}*-coated microcantilevers. One would expect molecules such as \textbf{C12}, which form more organized monolayer films, to experience far less reorganization. We further note that recent investigations have indicated the importance of the substrate atoms in thiolate motion on gold, so that we may also expect substrate atoms to move when substantial molecular forces are applied.\(^{91-93}\)

The deflections of the cantilever caused by the two competing effects (anion adsorption and electron transfer into the cantilever) can be estimated from the response of the \textbf{D}-coated cantilevers. The dumbbell molecule \textbf{D} is similar to \textbf{R}*-, except for lacking the moving rings. Figure 3 indicates that the expected deflections from the two competing effects reach maximum deflections of \(\sim 250\) nm in the upward direction. Therefore, experimentally, the total deflection produced by the muscle contraction alone can be estimated to be \(\sim 550\) nm (Figure S1, Supporting Information).

We attempted to quantify the magnitude of the deflection observed analytically in the microcantilever coated with \textbf{R}* using cantilever mechanics. The deflection, \(\Delta z\), caused by the collective contractions and extensions of molecular chains can be quantified using a special case of Euler–Bernoulli’s beam equation, which includes a moment at the free end of the beam, and is given by

\[
\Delta z = \frac{M_{\text{beam}} \cdot L^2}{2E I}
\]

where \(M_{\text{beam}}\) is the collective deflection moment on the beam; \(L\) is the total length of the beam (450 \(\mu\)m, considering the effect of laser spot diameter); \(E\) is the biaxial Young’s modulus of the microcantilever (additional stiffness due to Au and \textbf{R}* monolayer is neglected) and is given by \(E/(1 - \nu)\), where \(E\) is Young’s Modulus (187.5 GPa) and \(\nu\) is the Poisson’s ratio \((0.182);^{94}\) and \(I\) is the area moment of inertia of the beam’s cross section. The spacer, di(ethylene glycol), between the two DNP sites provides a semirigid character to the molecule. In an idealized model for quantitative analysis, we assume that the molecular muscles are rigid and the interactions between neighboring molecules are negligible. With these assumptions, the collective deflection moment of the beam is given by

\[
M_{\text{beam}} = N \cdot 2 \cdot P \cdot \left(t / 2\right) \cdot f_1 \cdot f_2 \cdot f_3
\]

where \(N\) is the total number of molecules adsorbed along the width of the microcantilever; \(P\) is the Coulombic repulsion force causing the ring to move away from the TTF unit; \(t\) is the beam thickness (1 \(\mu\)m); \(f_1\) is the surface coverage factor; and \(f_2\) and \(f_3\) are the constants corresponding to the idealized geometry and the molecule’s orientation, respectively (assumed to be random). Since only the molecular segment between the two rings generated a moment that contributed to the deflection, \(f_2 = L_1/L_2\), where \(L_1\) is the length between two rings at their starting positions and \(L_2\) is the total length of the molecule. For a molecule in its extended inter-ring co-conformation, \(L_1\) was 4.2 nm and \(L_2\) was 7.4 nm.\(^{95}\) With the molecules and deposition protocol employed, we do not expect all the molecules to be fully extended; thus \(L_1\), and \(L_2\) would vary and they could each be smaller than indicated above. Since the molecules were randomly aligned and only the force exerted along the longitudinal axis of the beam will contribute to deflection, \(f_3 = 2/\pi\). The number of molecules along the width was approximated as \(w/b\), where \(b\) was the breadth of each rotaxane (1 nm) and \(w\) was the width of the cantilever (100 \(\mu\)m). The success of the model to quantify the deflection observed in the experiments lies in the ability to predict the repulsion force between CBPQT4 ring and the TTF2 ring accurately. Assuming the TTF unit is oxidized to TTF2+ and neglecting the effects of (1) electrolyte, (2) presence of counteranions, and (3) orientation of the molecules, we can use the actuation energetics of a similar molecule reported by Brough \textit{et al.} \(^{95}\) By augmenting the force spectroscopy data with molecule dynamics simulations and considering the effects of thermal fluctuations as a function of the probe’s loading rate, they were able to predict the actuation energy, \(W\), between TTF2+ and CBPQT4+. A value of 65 kcal/mol was determined to be the actuation energy, a value that also matches with \textit{ab initio} calculations. To convert actuation energy, \(W\), to average actuation force, \(P\), we divide \(W\) by the distance between TTF2+ and DNP, \(d = 1.4\) nm, giving a value of 320 pN. Using this magnitude for the force and assuming a surface coverage of 100\%, the theoretical displacement was predicted to be 620 nm. This value is slightly larger than the magnitude of deflection (\(\sim 550\) nm) observed in the experiments, but well within the accuracy of various assumptions made in the model.

The first cycle of oxidation and reduction caused a larger deflection than did subsequent cycles. The extent of the deflection stabilized (Figure 5) after the first cycle. We attribute the sudden changes in the downward and upward deflection at the end of the first cycle to the incomplete recovery of the ground-state co-conformation from the metastable state coconformation,\(^{39,54,69,70}\) which leaves only a portion of the muscle molecules active for subsequent cycles. This observation suggested that a microcantilever, if left in a reducing environment after a series of oxidation and reduction cycles, should have most of the surface-bound rotaxane molecules recover to their ground-state co-conformation. With a new set of actuation cycles, the first cycle would once again exhibit large changes in downward and upward deflection.
To test this hypothesis, we applied three stages of potential variations (Figure 6) while the cantilever deflection was recorded. Stage I included seven steps of alternating oxidation and reduction potentials with 20 s intervals at each potential for each step. During these steps, the microcantilever bent alternately downward and upward, as expected for these artificial molecular muscles. Large changes in the downward and upward deflections were observed in the first cycle of actuation, followed by constant upward and downward deflections in the following actuation cycles. Sudden changes or “spikes” in the deflection of the microcantilever were observed at the end of each oxidation and reduction stage. These spikes most likely resulted from desorption and adsorption of the perchlorate counterions. In Stage II, the microcantilever was left electrochemically unperturbed at an open circuit potential—that is, no potential applied—for ~175 s. During this stage, the cantilever deflected upward with a first-order decay ($k = 0.012 \text{s}^{-1}$). The recovery of the cantilever position appeared to be incomplete, possibly as a result of the irreversible creep observed in Stage I. A time interval of 175 s was chosen for Stage II in order to ensure saturation of the recovery process. In Stage III, we again applied alternating redox potentials with the same durations as those applied in Stage I. We observed deflection signatures similar to those in Stage I. Large changes in the downward and upward deflections were again observed in the first cycle of operation. These changes were followed by constant upward and downward deflections in later cycles within the error of our measurements.

The observation of an exponential decay for the relaxation of the R8+-coated microcantilever’s deflection curve is consistent with the behavior of bistable [2]rotaxanes in solution,70,74 embedded in polymer matrices,54 and self-assembled onto gold surfaces.69 In these previous cases, the relaxations of the molecules were observed directly using electrochemistry, and it was found that the rates of motion slowed down59,70 as the rotaxanes were transferred into more highly condensed phases. Their kinetic behavior was found to correlate with the thermal relaxation of the electrical signature from a device that has rotaxanes incorporated within them as Langmuir–Blodgett monolayers.59,70 We posit, therefore, that the first-order decay in the deflection of the microcantilever arises from the thermally activated motion of the mobile rings from the NP stations back to the neutral TTF stations. The rate constant correlates with an activation barrier of $\Delta G = 20 \text{kcal mol}^{-1}$. On the basis of solution-phase studies66 on the molecular muscle prototype to R8+, the corresponding barrier was estimated to be less than 14 kcal mol$^{-1}$. Consequently, there is an increase of 6 kcal mol$^{-1}$ on going from solution to surface-bound devices. This increase is greater than the ~2 kcal mol$^{-1}$ expected on the basis of the bistable rotaxane studied, first in solution, and then self-assembled onto gold electrodes. Slower than usual thermal relaxation has been observed for the cis-to-trans isomerization96 in single polymer strands incorporating multiple azobenzene units when these strands are placed under loads by utilizing microcantilevers in force spectroscopy experiments. We concur with the rationalization presented in this previous report that the load-induced motion is no longer able to proceed along the lowest pathway possible. The exponential decay arises either when configurationally active molecules (azobenzene) or when active rotaxanes with two mobile rings (R8+) relax in confluence with an applied restoring force. The data suggest that the active units are not interacting with each other. Nevertheless, the observation of a relaxation process is a crucial molecular
signature that confirms the dominant role that the surface-bound rotaxanes serve in bending the microcantilevers.

CONCLUSIONS AND OUTLOOK
We have demonstrated that surface-bound artificial muscle molecules, when electrochemically activated, cause a microcantilever to bend. Conversely, microcantilever beams that are coated with redox-active but mechanically inert control compounds—the dumbbell of the [3]rotaxane or 1-dodecanethiol—do not display the same bending characteristics. Moreover, using beam theory and analysis, it has been shown that these observations are consistent with the hypothesis that the cumulative nanoscale movements of the surface-bound “molecular muscles” can be activated electrochemically and harnessed to perform much larger-scale mechanical work. The observed “creep” phenomenon in the dynamic studies most likely results from the reorganization of the molecules in the films. Compared with their chemically driven counterparts, the electrochemically driven molecular-muscle-based actuators can be operated much faster, more conveniently, and with larger responses. We also recognize that due to the significant complexity in the dynamic molecular switching behavior on solid substrates, many fundamental questions remain to be answered. We believe that (i) by improving the assembly conditions, (ii) by increasing the rigidity of the muscle molecules, and (iii) by incorporating a blocking layer in a matrix around the active components, the artificial molecular-muscle-based NEMS can be understood and optimized further. Nevertheless, the results constitute significant advances over prior efforts and a key step toward functional NEMS based on artificial molecular muscles.

MATERIALS AND METHODS
Preparation of Microcantilever Samples. Commercial rectangular silicon microcantilevers (NanoAndMore Inc., Lady’s Island, SC) of length 500 μm, width 100 μm, and thickness 1 μm were used in all the experiments. One side of the microcantilevers was coated with a 20 nm thick gold layer by the manufacturer. Before a monolayer film was deposited, each microcantilever was cleaned for 5 min with UV/ozone and then washed with DI water.

Synthesis of Molecular Muscles and Control Compounds and Preparation of Monolayer Films. The palindromic bistable [3]rotaxane R1− and the control dumbbell compound D were synthesized using a method reported earlier.49,50 1-Dodecanethiol, C12 (Sigma-Aldrich), was used without further purification. Microcantilevers were cleaned and then placed for 48 h in solutions containing the target molecule in order to form monolayer films on the gold layers.

Electrochemical Atomic Force Microscope Cell. A scanning probe microscope, combined with an electrochemical cell supply (Pico SPM 2500, Molecular Imaging), was used in all of the experiments. Before each experiment, the electrolyte (0.1 M NaClO4) employed in the electrochemistry setup was purged with nitrogen gas. Both counter and reference electrodes were cleaned by ultrasonication in water and acetone before each experiment. At the end of each experiment, the potential of the reference electrode (Ag) was adjusted with respect to that of a AgCl solution. The sensitivity of each microcantilever was calibrated by fitting the slopes of force curves in order to measure the cantilever deflection (nm) by means of the photodiode signal (V). The sensitivity of each cantilever beam that is coated with redox-active but mechanically inert control compounds—the dumbbell of the [3]rotaxane or 1-dodecanethiol—do not display the same bending characteristics. Moreover, using beam theory and analysis, it has been shown that these observations are consistent with the hypothesis that the cumulative nanoscale movements of the surface-bound “molecular muscles” can be activated electrochemically and harnessed to perform much larger-scale mechanical work. The observed “creep” phenomenon in the dynamic studies most likely results from the reorganization of the molecules in the films. Compared with their chemically driven counterparts, the electrochemically driven molecular-muscle-based actuators can be operated much faster, more conveniently, and with larger responses. We also recognize that due to the significant complexity in the dynamic molecular switching behavior on solid substrates, many fundamental questions remain to be answered. We believe that (i) by improving the assembly conditions, (ii) by increasing the rigidity of the muscle molecules, and (iii) by incorporating a blocking layer in a matrix around the active components, the artificial molecular-muscle-based NEMS can be understood and optimized further. Nevertheless, the results constitute significant advances over prior efforts and a key step toward functional NEMS based on artificial molecular muscles.

REFERENCES AND NOTES


