

Molecular Actuators—Designing Actuating Materials at the Molecular Level

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Abstract—Nature evolved an elegant actuating system, muscle, which can be controlled by a relatively small molecule, myosin. We briefly introduce herein an artificial approach based on applying molecular actuating building blocks to mimic the function of muscle. A particular focus of this review is the design of a molecular hinge. Designed molecular mechanisms have great potential to produce quick responses and large deformations.

Index Terms—Actuators, artificial muscles, molecular mechanical responses.

I. INTRODUCTION

FROM the transport of intracellular cargoes to the flight of the wandering albatross, movement is one of life's central attributes. Movement with efficiency exceeding natural systems remains as one of humankind's unaccomplished dreams. At the root of all actuation lies movement at the molecular level [1]–[3]. Inspired by biomechanical systems, there is an intense effort to use “bottom-up” molecular and materials principles to build actuating systems. These principles are reviewed herein with an emphasis on understanding actuating material at the molecular level.

II. MOLECULAR APPROACH: NATURAL AND ARTIFICIAL

In higher eukaryotes, muscle contraction is powered by adenosine 5' triphosphate (ATP) consumption and actuation begins with the sliding of interdigitized myosin and actin filaments as shown in Fig. 1(a), [2]. This filament motion is controlled by a protein-based molecular motor, myosin, which is linked to the end of thick filaments. The motion of myosin in muscle contraction begins with the rotation of the myosin head on top of the thin filament. In this power stroke, a portion of myosin tilts by $\sim 45^\circ$ and thereby moves the thick filament $\sim 100 \text{ \AA}$ for every ATP hydrolyzed.

With nature as our inspiration, we are pursuing new approaches to achieve muscle-like characteristics by designing molecules or polymers in which a large fraction of the energy input leads to specific molecular or structural changes as shown in Fig. 1(b). Similar to muscle, the motion originates with a defined molecular mechanism, and we illustrate one example,

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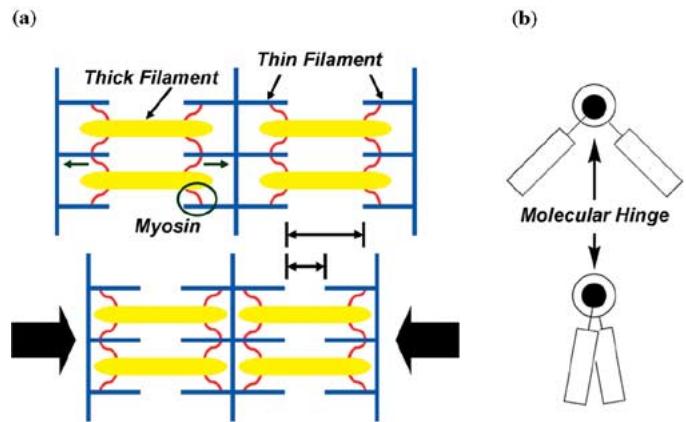


Fig. 1. (a) Schematic representation of a natural sliding filament molecular assembly. (b) General representation of a molecular hinge to molecular actuation.

the “molecular hinge.” Given the complexity of a rotary motion, linear motion is desired for initial artificial systems in order to simplify the molecular design. Motion is designed to be triggered by either an electrochemical or ionic stimulus, thereby mimicking natural systems.

III. MOLECULAR HINGES—CALIX[4]ARENES

Among the candidate structures for molecular motions, we are most interested in molecular hinges. This is due to their potential for large deformations and rigid structures. One particular candidate family of molecular hinge compounds are the calix[4]arenes.

Calix[4]arenes are cyclic tetramers synthesized from phenol and aldehyde units whose chemical structure is shown in Fig. 2 [4]. Although each phenol unit can rotate to move the oxygen through the annulus of the macrocycle, they often favor a cone conformation due to stabilization by intramolecular hydrogen bonding interactions among-OH groups. However, upon covalent linkage of different substituents to the phenolic oxygens or benzene rings, calix[4]arenes often exhibit more complex conformational behavior due to the absence of such intramolecular hydrogen-bonding interactions. Thus, four possible conformational isomers must be taken into account in functional systems [5].

Among the four calix[4]arene isomers, the cone conformation displays the hinge structure capable of the largest dimensional change. It consists of a “pinched-cone to pinched-cone” movement as shown in Fig. 3. In this motion, two opposite benzene rings adapt a close cofacial arrangement while the distance between the other rings increases. Theoretical studies showed that the pinched-cone is the most stable conformation and this

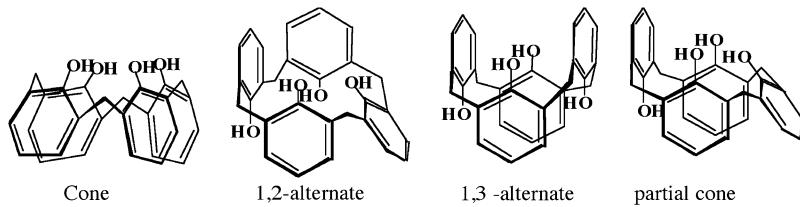


Fig. 2. Four stable conformations of calix[4]arenes.

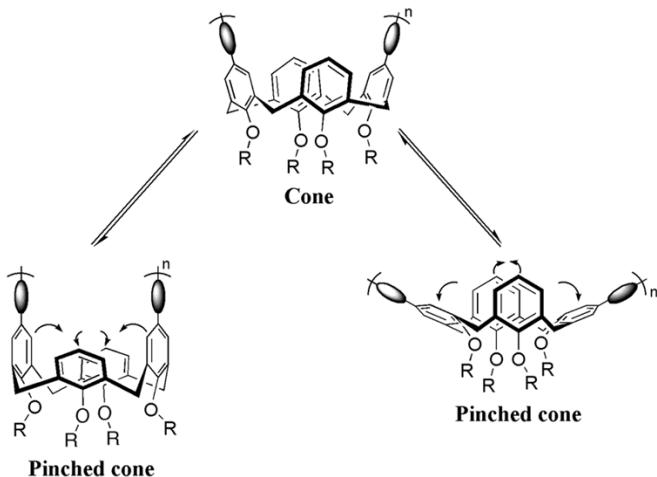


Fig. 3. Interconversion of tetraalkoxycalix[4]arene in the cone conformation.

conformation was also identified in crystal structures of several calix[4]arene derivatives [6], [7].

It is noteworthy to point out that calix[4]arenes are very well-documented compounds [8]–[10]. Their unique cavity has provided a multitude of examples in host–guest chemistry, molecular recognition and sensing. There have been many direct and indirect observations wherein the distance between the opposite rings changes as a result of donor/acceptor interactions, guest incorporation, hydrogen bonding, and $\pi - \pi$ interactions [11], [12].

IV. CONDUCTING POLYMER THIN FILMS FROM HINGE MONOMERS

In order to assemble electrochemically responsive materials based upon calix[4]arenes, the conducting calix[4]arene polymer was designed as shown in Fig. 4 [13]. These materials belong to a class of electroactive materials synthesized from thiophenes that have long been discussed as “conducting plastics” [14]. The incorporation of thiophene units not only provides electrochemical responsive segments but also introduces the possibility of π -dimer/ π -aggregate formation to supply intersegmental attractive elements to drive the molecular hinge contraction.

Polymer films derived from oxidative coupling of calix[4]arene-bis(bithiophene) monomers (Fig. 4) and their electrochemical behavior, structural identity, and conductivity as a function of oxidation states have been investigated [13]. The cyclic voltammograms of these polymers exhibit two redox waves at $E_1^{1/2} \approx 0.22$ V and $E_2^{1/2} \approx 0.45$ V (versus Fc/Fc^+). They are also stable for more than 1000 cycles in ambient atmosphere if the potential sweep is kept below E_2 .

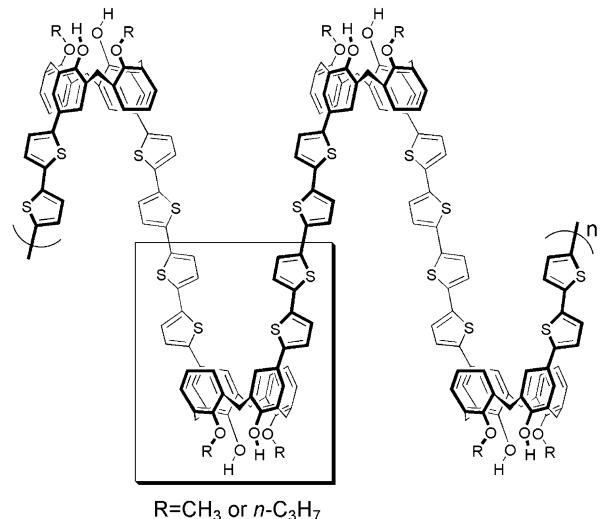
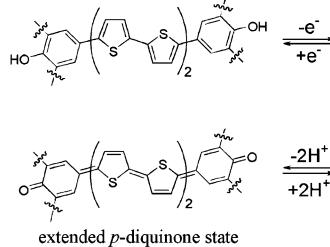


Fig. 4. Schematic presentation of desired polymers.

Insulating

extended *p*-dihydroquinone state



extended *p*-diquinone state

Conducting

extended *p*-diquinone radical cation

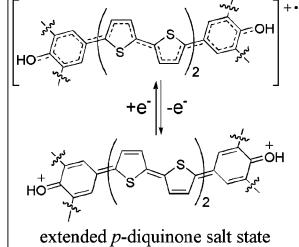


Fig. 5. Different oxidation states of the conductive conjugated system in calix[4]arene-based conducting polymers.

Nuclear magnetic resonance studies and bulk electropolymerization tests confirmed that the calix[4]arene moiety was stable in the desired cone structure. In spite of the fact that the charge is localized by the segmented polymer backbone, a high maximum conductivity of 6.6 S/cm was determined by *in situ* conductivity measurements. In addition, it is also found that the polymer’s conductivity is sensitive to the acidity or basicity of the solvent. Our composite studies have established that the individual electroactive segments and their oxidation states are as shown in Fig. 5.

The expected macromolecular motion is shown in Fig. 6. As we illustrated earlier, analysis of the monomer suggests that the calix[4]arene hinges remain in their cone conformations in the neutral state. The semiempirical simulation (AM1) calculated that the distance between the two centered positions of the thiophene units is 16.3 Å in the expanded state. Upon oxidation,

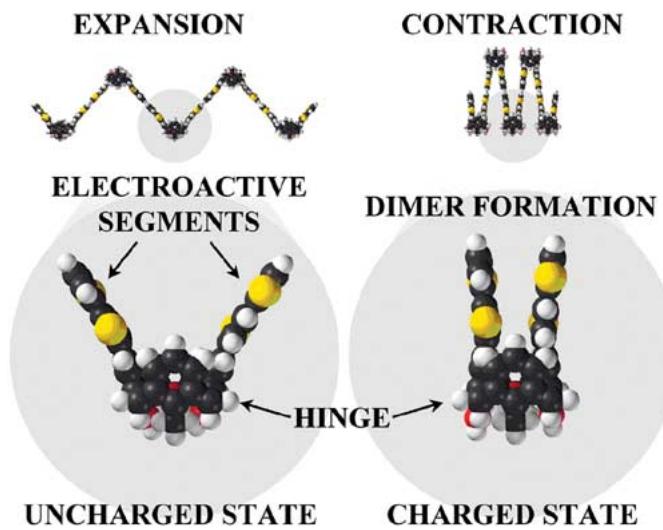


Fig. 6. Schematic illustration of calix[4]arene-based hinge actuators.

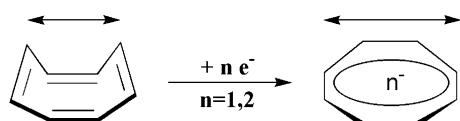


Fig. 7. The conformational change of cyclooctatetraene (COT).

it is envisioned that the electroactive thiophene segments will prefer π -dimer/ π -stacked structures. For a highly stacked structure, the distance may be reduced to 3.5 Å, thereby producing a large deformation. However, it is important to keep in mind that these are one-dimensional deformations. Only the anisotropic alignment of individual polymer chains can maximize the strain of the thin film. Therefore, mechanical measurements of bulk materials from randomly aligned polymers will not generally reflect the real actuation at the molecular level.

V. OTHER MOLECULAR ACTUATING SYSTEMS

In addition to the molecular hinge approach with calix[4]arene-based molecules, there were other valuable building blocks with considerable potential as molecular actuators. Marsella and coworkers suggested utilizing cyclooctatetraene (COT) moiety, which exhibits a boat conformation in the neutral state and becomes planar with injection of electrons [15]. Comparing the boat and planar forms, it is clear that the distance between the two ends of COT increases as shown in Fig. 7.

In order to introduce conducting charge stabilizing groups into these materials, Marsella synthesized monomers based on cyclotetrathiophene [15]. The thiophene units can then undergo electropolymerization to form polymer thin films that had the structures as shown in Fig. 8. Instead of contraction, these polymers theoretically expand with injected charges.

Another approach was reported by Sauvage and coworkers who used a linear rotaxane dimer system as shown in Fig. 9. This system more closely emulates the sliding filament mechanism shown in Fig. 1, [16]. Instead of responding to an electrochemical stimulus, this system operates with a specific metal ion stimulus.

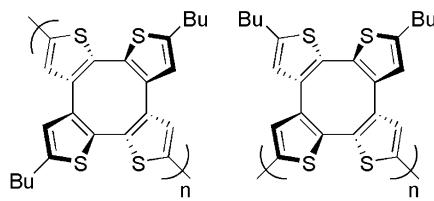


Fig. 8. Polymers reported based on COT molecular actuator.

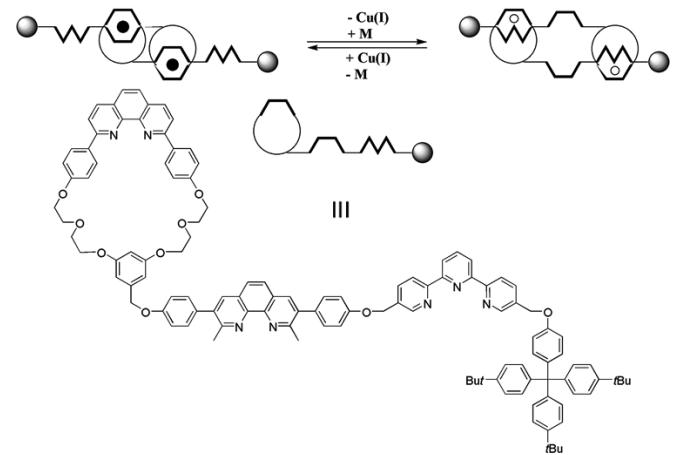


Fig. 9. Schematic representation of the actuation principle of linear rotaxane dimer synthesized by Sauvage and coworkers.

VI. FINAL COMMENTS

This is just a brief summary of recent efforts toward molecular actuating structures. Molecular mechanical concepts offer exciting new prospects for active materials with fast responses and large deformations. Considering that the proposed mechanisms are based on intrinsic molecular properties, the response rate should be faster than the slow ion-diffusion process of traditional conducting polymer actuators. The anticipated large deformations can accelerate the development of new actuating devices. An additional advantage of the “bottom-up” philosophy is that it allows us to apply similar molecular concepts for nanomaterials and nanodevices. It is important to understand that there are other candidates that can provide molecular actuation mechanisms. Advances in this field will not only help us to appreciate nature’s design but also provide engineers with pathways to try to match the magnificent movement of nature.

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