Thiophene-based conducting polymer molecular actuators

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ABSTRACT

Traditional conducting polymer actuators such as polypyrrole offer tremendous active stress at low actuation voltages but with moderate strain, strain-rate and efficiency. We report the synthesis of novel thiophene based conducting polymer molecular actuators, exhibiting electrically triggered molecular conformational transitions. In this new class of materials, actuation is the result of conformational rearrangement of the polymer backbone at the molecular level and is not simply due to ion intercalation in the bulk polymer chain upon electrochemical activation. Molecular actuation mechanisms results from π - π stacking of thiophene oligomers upon oxidation, producing a reversible molecular displacement which is expected to lead to surprising material properties such as electrically controllable porosity and large strains. The hypothesis of active molecular conformational changes is supported by *in situ* electrochemical data. Single molecule techniques are considered for molecular actuator characterization. Mechanical properties of these new materials are currently being assessed.

Keywords: Molecular actuator, conducting polymer, thiophene, large strain, molecular design, single molecule, high-throughput synthesis, optical tweezers, AFM.

1. INTRODUCTION

Human skeletal muscle exhibits properties in combined terms of active strain, active stress, active strain rate, variable stiffness, power to mass ratio and bandwidth which classical actuator technologies do not match [1]. On the other hand, conducting polymer materials offer properties enabling the creation of biomimetic artificial muscles. Polypyrrole-based actuators, for example, generate forces per cross-sectional area that are up to two orders of magnitude greater than human muscle (40 MPa) with equal power to mass ratios (39 W/kg). In addition, these actuators require low drive voltages and offer typically limited active strain (2%) and limited active strain rate (1%/s) [2].

Actuation in conducting polymers such as polypyrrole or polyanilines is based on electrochemical oxidation and a resulting diffusion and intercalation of ionic species into the polymer bulk film [3]. This ionic intercalation process arises to maintain electro-neutrality during the oxidation process, leading to significant volume changes. In addition, accommodation of these ions and their associated solvated species is favored by the weak polymer interchain interactions compared to the modulus along the polymer molecular backbone [4]. As a result strains on the order of 2% are produced upon electroactivation. It is conceivable that ultimately the maximum strain achievable in these "classical" conducting polymer actuators is going to be limited by the inability of the polymer molecular backbone to significantly change length to accommodate further ions.

Nature being our source of inspiration [5] [6] [7], a more powerful approach is to design conducting polymer backbones with chemically driven shape changes that translate into large alterations of their length in response to electrically induced changes in oxidation state. Advances in synthetic organic chemistry enable the creation and manipulation of such molecules that mimic natural mechanisms. They are built upon novel molecular design elements for creating volume changes. Diversity in material properties and characteristics is introduced through a combination of design

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elements. These include molecules that distort from bent to planar structures upon electrochemical activation, materials that undergo volume changes due to stacking of redox units and molecular scaffolds that behave as "accordion-like" structures capable of being switched between an extended and a tightly folded molecular structure.

Molecular actuators, i.e. biological or synthetic molecular systems performing work upon consumption of energy have triggered great interest in various fields such as biology, chemistry, chemical engineering and mechanical engineering [8], [9], [10], [11]. Various biological machines such as the ATP synthase, or kinesins have been studied extensively; Synthetic non-conducting polymer molecules embedding metal complexes that exhibit electron-induced (redox) chirality have been created [12]; Molecular (robotic) grippers made from resorcin[4]arene have been demonstrated [13], to cite just a few. A possible mechanism of molecular actuation using cyclooctatetrathiophene conducting polymers has also been recently investigated by Marsella and colleagues [14].

Within the framework of molecular actuation, we present herein two thiophene-based candidate conducting polymer molecules which have been synthesized in our laboratory from monomers designed for particular actuation purposes. One compound under study features an accordion like polymer formed by calix[4]arene hinges separated by conducting quaterthiophene rods. The second compound considered is quaterthiophene alone. In both compounds, actuation is believed to result from π -stacking of thiophene oligomers upon oxidation, producing a reversible molecular displacement. Polymer synthesis, mechanical and electrical properties as well as principle of molecular actuation of these novel compounds are discussed.

2. MOLECULAR MUSCLE CANDIDATES

The first thiophene-based molecular actuator candidate, polymer **1**, shown in Figure 1, employs hinge molecules (calix[4]arene) interconnected by rigid rods (quaterthiophene). The rods attract one another in the oxidized state, contracting the material. This actuation characteristic results from π - π stacking of thiophene oligomers upon oxidation, producing a reversible molecular displacement [15]. The second candidate, polymer **2** is poly(quaterthiophene) (poly(QT)), a system used to study the π -stacking effect of the oxidized thiophene oligomers upon oxidation. In other words, this latter candidate is a non-hinged version of the poly(calix[4]arene-bithiophene) molecule.



Figure 1: Structure of calix[4]arenebithiophene.

Rigid 3-dimensional structures with significant amounts of free internal volume are ideal prospects for the formation of novel materials capable of unprecedented volume changes. Calix[4]arene is a particularly attractive building block to incorporate into an actuator polymer. It is well known that calixarenes have the property of producing well-defined binding sites and have a large versatility for functionalization [16]. Furthermore, the calix[4]arene scaffold has the ability to exist in a number of different conformations which are often in thermal equilibrium labeled as the cone, 1,2-alternate, 1,3-alternate, and partial cone (Figure 2). The calix[4]arene scaffold is a hinge structure introducing many possibilities for the formation of materials with novel architectures and shape changing ability.

Various conformations of the calix[4]arene scaffold can be synthesized by alkylation of the phenolic groups. In particular the addition of n-propyl groups is effective at restricting the calix[4]arene core from equilibrating between different conformations, producing primarily the cone conformation [17]. This scaffold is then chemically combined with bithiophene groups to form a C-shaped molecule. Synthesis of polymer **1** has been reported elsewhere [18]. Oxidation under either electrochemical or chemical conditions leads to polymer **1** which has a pinched cone conformation based upon the conformational preferences of the monomer (as determined by NMR spectroscopy). The cone conformation of the calix[4]arene scaffold allows generation of an accordion-like molecule upon polymerization.

Polymer **1** is a promising actuating material. Key features of this material include the deformable calix[4]arene scaffold and the redox active quaterthiophene units. The proposed actuation mechanism and a 3-dimensional space-filling model showing the collapse of a monomer are represented conceptually in Figure 3. The initial polymer displays an equilibrium conformation that has the quaterthiophene groups in a non-aggregated state. Upon oxidation the quaterthiophene groups have a strong tendency to aggregate into a π -stacked structure [15]. Inspection of the spacefilling model in Figure 3 suggests that one dimensional changes of as large as a factor of 5 are possible for Polymer **1**.



Figure 2: Calix[4]arene and its molecular conformations.

Polymer 2 is a non-hinged version of polymer 1, where molecular contracting elements are freely dispersed in the polymer film. The structure of polymer 2 is shown in Figure 4. Similarly as for polymer 1 the quaterthiophene groups have a strong tendency to attract each other and form a π -stacked structure upon oxidation.



Figure 3: Schematic actuation mechanism of polymer 1.

To develop artificial muscle technology for applications in life-like robotics, active prostheses or medical devices it is necessary to obtain the contractile material in bulk form. However, early films of the novel thiophene based monomers

that were grown have been brittle and difficult to handle. Polymer composites of the active polymer with a sulfated polymeric anion were therefore created to increase the mechanical robustness of the films, following the example of Wallace et al. in polypyrrole [19]. This additional polyelectrolyte is Sulfated Poly- β -Hydroxy Ether (S-PHE). It is designed to form a supporting elastic matrix for the new contractile compounds. Notice that the S-PHE polymer is a large molecule, its molecular weight exceeding 30,000 g/mol. The polyelectrolyte is added to the deposition solution during electrochemical polymerization and hence replaces typical salts used, such as tetraethylammonium hexafluorophosphate for example. The structure of the S-PHE is shown in Figure 5. The Molar Ratio (MR) of sulfate groups (n) to hydroxyl groups (m) is also referred as the sulfation ratio and is computed as follows: MR = n/(n+m).



Figure 4: Structure of poly(quaterthiophene), (poly(QT)).

Two different polymers incorporated within the same material will typically phase separate. The sulfate group in the S-PHE, however, enhances the coulombic interaction between each phase of the composite resulting in the minimization of the phase separation between conducting and insulating polymer. Incorporation of the polyanion into the polymer film has the following consequences: first, it provides an elastic mechanical support to the polymer

molecules, reducing film brittleness. Second, the lack of polyanion mobility has the effect that charge compensation during oxidation or reduction is mainly achieved by diffusion of cationic species into the polymer composite. In traditional single phase conducting polymer actuators such as polypyrrole, both ionic species diffuse into and out of the polymer during oxidation and reduction with rates that are size and geometry dependent. The larger the ion, the more likely it is to be immobilized via entanglement. Polyanions such as S-PHE are large enough that they are effectively locked in place.



Figure 5: Structure of the S-PHE polyelectrolyte.

3. EXPERIMENTATIONAL

3.1. Reagents

Calix[4]arene-bithiophene and quaterthiophene (QT) monomers were designed and synthesized in our laboratory according to synthesis techniques presented elsewhere [18] and their structure verified by NMR. Tetraethylammonium hexafluorophosphate (TEAP), Tetrabutylammonium hexafluorophosphate (TBAP), dichloromethane and acetonitrile were obtained from Aldrich¹. Several Sulfated Poly(β -HydroxyEther) (S-PHE) polyanions candidates with different MR sulfation ratio were synthesized according to the method of Wernet [20]. Ag/Ag+ reference electrodes (BAS Bioanalytical Systems²) were constructed from 0.1 M TEAP and 0.01 M AgNO₃ in acetonitrile and referenced versus the Fc/Fc+ redox couple (Aldrich¹).

3.2. Preparation of polymers

Synthesis was performed by electrodeposition under galvanostatic or swept potential conditions onto a conducting substrate. The working electrode materials were glassy carbon or 200 nm gold coated PET films (Alfa Aesar³) and the

¹ www.aldrich.com

² www.bioanalytical.com

³ www.alfa.com

counter electrode was a copper sheet (Aldrich¹). Conducting polymer films were grown from a solution of 5 mM calix[4]arene-bithiophene or quaterthiophene (QT) monomer, 0.1 M tetraethylammonium hexafluorophosphate and diverse S-PHE concentrations (0.02; 0.2; 0.5; 1; 2 % weight) as well as MR values (1; 0.09; 0.06) in acetonitrile. Galvanostatic depositions were conducted at current densities of 1.25 A/m² for 5 hours resulting in film thickness between 120 and 150 μ m. Deposition took place at room temperature (25 °C). The resulting films of poly(QT)/S-PHE were then peeled off the working electrode substrate, rinsed in acetonitrile and allowed to dry for 24 hours. Poly(QT)/S-PHE films had conductivities of 10⁻¹ S·m⁻¹, densities of between 550 and 750 kg·m⁻³ dry, tensile strengths of 20 MPa in their dry form and of 1.3 MPa when soaked in acetonitrile. Polymerization was also performed using swept potential methods (0.0 V to +1.0 V vs. Fc/Fc⁺ at a rate of 100 mV/s).

3.3. Techniques and instrumentation

Electrodepositions and electroactivations were carried out with a potentiostat (Amel⁴, Model 2049). Bulk conductivity measurements were conducted on a custom built four point measurement apparatus connected to a multimeter (Keithley⁵, model 2001). *In situ* conductivity measurements where acquired using interdigitated microelectrodes [21].



Figure 6: 12 cell high throughput deposition system, allowing synthesis of as many as 12 films in parallel.

To enhance productivity of synthesizing films, parallel high throughput electrochemical synthesis methods were developed. The purpose was to reduce the time necessary to scan through a large synthesis parameter space. In addition, such a small volume parallel system allowed us to utilize minimal quantities of monomer compound as possible. In a typical parallel synthesis setup as shown in Figure 6, up to 12 polymers can be synthesized at the same time. Considering that single polymer film synthesis may take as much as 5 hours of deposition time, the high throughput synthesis technique enabled acceleration of material discovery time. The parallel deposition system is based around a 12 well tissue culture plate (Falcon⁶, 35,3225) typically used for biological studies. Each well can contain up to 5 mL of solution. This volume can be increased to 20 mL by using tall vials (VWR⁶). Details of this system have been previously described [22].

⁴ <u>www.amelsrl.com</u>

⁵ www.keithley.com

⁶ www.vwr.com

4. POLYMER SYNTHESIS RESULTS

Poly(calix[4]arene-bithiophene) films were synthesized with 0.1M TEAP in dichloromethane under galvanostatic conditions (1.25 A/m², (0.125 mA/cm²)). A typical cyclic voltamogram (100 mV/s) of the deposition process is shown in Figure 7. Note that the oxidation voltage is +0.65V versus Fc/Fc^+ . Additionally the increase in current after each potential scan shows that material is being added to the working electrode.



Figure 7: Cyclic voltamogram of an acetonitrile solution containing 5 mM calix[4]arene-bithiophene and 0.1 TEAP at a gold coated PET electrode. Scan rate is 100 mV/s.

Figure 8: Cyclic voltamogram of an acetonitrile solution containing 5 mM quaterthiophene and 0.1 M TEAP at a gold coated PET electrode. Scan rate is 100 mV/s.

Similarly, poly(QT) films used for in-situ conductivity measurements were synthesized with 0.1M TEAP in acetonitrile under galvanostatic conditions (1.25 A/cm²). A typical cyclic voltamogram (100 mV/s) obtained during the deposition process is shown in Figure 8. Note that the oxidation voltage is +0.9 V versus Fc/Fc⁺.

Poly(calix[4]arene-bithiophene)/S-PHE free standing composite films were grown galvanostatically (1.25 A/m^2) from a solution containing 5 mM calix[4]arene-bithiophene, 2 % weight S-PHE (MR = 1) and 0.1M of TEAP in acetonitrile. Similarly, poly(QT)/S-PHE free standing composite films were grown galvanostatically (1.25 A/m^2) from a solution containing 5 mM QT, 2 % weight S-PHE (MR = 1) and 0.1M of TEAP in acetonitrile. Figure 9 compares the morphologically superior characteristics of a poly(QT)/S-PHE polymer composite film with a simple QT film. Notice that the simple QT film has the form of a brittle (powder like) material with absolutely no mechanical strength. On the other hand the QT/S-PHE composite exhibits a tensile strength of 20 MPa (dry).

5. BULK ACTUATOR PROPERTIES

Films of poly(QT) were prepared as described in the previous Section. The parallel synthesis system allowed us to vary the deposition concentration of S-PHE or salt within a batch of films and to quickly find optimal deposition parameters towards mechanically strong films. Initial observations indicate that films made from a deposition solution containing at least 2 % by weight S-PHE (MR = 1) and 0.1M TEAP show better mechanical integrity than films made at lower S-PHE or salt concentrations. No mechanically stable films were achieved at very low concentration of S-PHE (0.02% weight, MR = 1).



Quaterthiophene/SPHE composite film

Figure 9: Effect on poly(QT) polymer film strength of blending with the S-PHE polyanion.

Such films of Poly(QT) demonstrated a tensile strength of 20 MPa when dry. The value of the tensile strength is decreased by more then an order of magnitude to 1.2 MPa when the films are immersed in 0.1M TEAP in acetonitrile. Such behavior can be attributed to partial softening of the S-PHE polyanion matrix when placed in acetonitrile. Observations indicate that the S-PHE polyelectrolyte is acting as a matrix, holding the polymerized monomers together. In fact, at too low S-PHE concentrations (0.02% weight, MR = 1) the QT monomers initially polymerize on the substrate surface (in inhomogeneous domains) but do not adhere to the surface (see Figure 9) forming a thin powder of polymer at the bottom of the deposition cell. A soft polyanion matrix is desirable to allow molecular conformational rearrangement of the polymer backbone upon electrochemical activation in bulk polymer films. Greater conformational freedom allows the conducting polymer

molecule to expand in contract at the molecular level, allowing for larger active strains.

On the other hand, Poly(QT)/S-PHE composite film conductivity is low (10^{-1} S/m) , compared for example to polypyrrole $(3 \cdot 10^4 \text{ S/m})$ [23]. A possible explanation for such a low conductivity might be due to the size of the S-PHE molecule preventing high doping levels in poly(QT)/S-PHE films. In fact, we observe an increase of conductivity by an order of magnitude between films that have been synthesized with addition of a smaller salt ion such as TEAP vs. films that contained only the S-PHE polyanions.



Figure 10: Poly(QT) film in actuation electrochemical cell test setup as seen under the microscope. The film is held by a pair of stainless steel tweezers which also act as a working electrode. The micrograph shows the oxidized state (contracted) and expanded state (expanded) overlaid on the same frame.

Initial activation studies using the beam-bending method [24] were conducted under а stereo microscope (Zeiss). A strip of poly(QT) (2.25 mm long, 0.375 mm wide and 80 µm thick) was held in between a pair of stainless steel tweezers. Potentials of ±5V vs. Ag/Ag^{+} were applied to the working electrode for 4 seconds in an electrochemical cell containing 0.1M TEAP and a stainless steel counter electrode. The resulting actuation was monitored with a digital video camera (Sony DFW-V300).

Our initial actuation experiments (Figure 10) show that the poly(QT) system exhibits reversible strains in levels of $20 \pm 3\%$. These high strains are observable close to the pair of tweezers where the bilayer bends to a large radius of curvature. It is speculated that low film conductivity prohibits contractions far away of the point of electrical

contact. Note that this result is not a direct confirmation of molecular actuation, but serves to demonstrate that poly(QT) is electroactivable.

6. NOVEL ACTUATION PRINCIPLE

The actuators we report herein use reversible molecular conformational transitions to generate controllable displacements and work. One possible physical effect leading to such molecular rearrangements is the formation of π -dimers (e.g. the tendency of π orbitals to align due to Pauli's exclusion principle) upon oxidation of the material. π - π stacking interactions between aromatic units in supramolecular structures help to create robust macroscopic conglomerates. In the case of polymer 1 and polymer 2 it is energetically more favorable for two adjacent quaterthiophene units to have their π -orbitals overlap and rearrange in π -dimers, potentially leading to large molecular conformational changes [15].

In situ conductivity measurements allow probing polymer film conductivity as function of oxidation state hence giving an insight into electrochemical processes taking place at the molecular level. Films of poly(QT) prepared as described in Section 4, were cycled at 25 mV/s at potentials between 0 V and 1 V vs. Ag/Ag⁺ and their conductivity measured against a bias of 40mV using interdigitated microelectrodes. Figure 11 shows the relative conductivity of a poly(QT) film vs. oxidation potential, overlaid with a cyclic voltamogram. Notice the large relative conductivity hysteresis in Figure 11, where a potential difference of 0.6 V is required to revert the relative conductivity of poly(QT) from conducting to insulating during the reverse sweep.

Such a large hysteresis indicates that more energy is required to switch poly(QT) from its oxidized state to its reduced state and vice versa, giving strong evidence that a more stable structure (possibly the π -dimer) has been formed as a result to the initial anodic potential sweep in which the quaterthiophene groups were oxidized. In other words, the higher stability of the π -dimer in poly(QT) makes the aggregated state harder to reduce, causing the large hysteresis in the current voltammogram. On the other hand, such a behavior could be also attributed to electrochemical kinetic limitations such as electron transport or ion diffusion. However film relative conductivity is high over the entire potential range of the reduction sweep, indicating that such kinetic limitations do not take place.



Figure 11: Cyclic voltammetry (25 mV/s) / *in situ* conductivity combined experiments of a poly(QT) at an interdigitated microelectrode.

Now that we assume that $\pi - \pi$ stacking of quaterthiophenes redox units is the driving force for actuation, let's consider how much energy can be produced during such a contraction. From theoretical and experimental studies on quaterthiophene dimers in solution, the barrier of dissociation of π -stacks is found to be 1.3.10⁻¹⁹ J (0.8eV or 18.5 kcal/mol) [25], [26]. Notice that this energy value is an order of magnitude larger then the Van der Waals bonding energy. It is also equivalent to 31 k_BT (where k_B is Boltzmann's constant and T is the absolute temperature; at room temperature 1 k_BT is $4.1 \cdot 10^{-21}$ J). Hence the π -dimer is considered to be an electro-reversible chemical bond. It is interesting to notice that molecular actuators found in nature operate within the same energy range. The ATP synthase, for example - which is a 10 nm rotational ATP synthesizing molecular motor found in mitochondria,

bacteria and chloroplasts - produces 20 k_BT of work per ATP synthesized (1/3 of rotation) [27]. Similarly, single actinfilament /myosin-head interaction in human skeletal muscle produces between 3 and 15 k_BT of work.

Previous AM1 (Austin Model 1) molecular simulations [18] show that two arms of the poly(calix[4]arene-bithiophene) molecular actuator can theoretically contract by 1.39 nm upon oxidation [32]. Dividing the amount of work generated per monomer unit of $1.28 \cdot 10^{-19}$ J by the active molecular displacement, it is estimated that a single molecule of calix[4]arene-quaterthiophene will produce at most 92 pN of average active force.

Let's now analyze the theoretical maximal efficiency of such a molecular actuator. As each QT arm needs to be oxidized to form a π -stack we can assume that the removal of 2 electrons per calix[4]arene-quaterthiophene unit is required to achieve π -stacking. From the poly(QT) film electroactivation cyclic voltamogram (Figure 11) we observe that there is a potential difference of 0.6 V between the oxidation and reduction wave. Therefore the electrical energy that is brought into the system during oxidation of a single polymer **1** molecule is $1.92 \cdot 10^{-19}$ J. Thus the proportion of energy converted to work (the electromechanical coupling efficiency) of polymer **1** as molecular actuator is potentially as high as 66.7%.

Finally, let's consider the poly(calix[4]arene-bithiophene) as a bulk material, and try to estimate the upper bound on the average stress produced by molecular contraction. This is computed, given that stress times strain is the work per unit volume. The novel molecular muscle materials are designed with the goal of achieving 20% strain contraction on average. We assume a bulk density of 1300 kg/m³, a molecular weight of 781 g/mole and an energy for π - π stacking of 18.5 kcal/mol. Considering that the two calix[4]arene-bithiophene monomer molecules are needed to achieve contraction, the maximal average stress is found to be 321 MPa.

7. DISCUSSION

While *in situ* conductivity measurements combined with electrochemical potential sweep technique provide indirect evidence for electrically triggered molecular conformational of the backbone of polymer 1 and 2, direct evidence of molecular actuation is difficult to obtain from bulk film actuation experiments. Ultimately, knowing the force and stress generated by a single conducting polymer molecular chain or by a thin polymer fiber will give tremendous insights into the nano and the macro scale mechanical behavior of polymer molecular actuators

Such direct measurements of the mechanical properties of a single molecular chain or a thin polymer fiber could be achieved by using optical tweezers [28] or single molecule AFM techniques [29].



Figure 14: Single molecular muscle actuator testing apparatus using optical tweezers

In the case of optical tweezers, a single polymer chain is attached to a functionalized sub-micrometer sized dielectric particle trapped in a 3 dimensional force field produced by a laser beam (Figure 14). By modulating the intensity of the laser beam and using system identification, the stiffness of the optical trap is easily and accurately determined, thus making this instrument a sensitive force sensor (0.2 $pN/Hz^{1/2}$ [30]). In addition, mechanical forces over a large dynamic range $(1-10^4 \text{ pN})$ and a microsecond time scale can be generated and monitored by using this instrument, [31]. We estimated that a single molecule of calix[4]arene-quaterthiophene will produce at most 92 pN of average active force, making optical tweezers ideal to monitor contractions of polymer 1.



Figure 15: Single molecular muscle actuator testing apparatus using an AFM.

Similarly, an Atomic Force Microscope (AFM) can be used to carry single molecule actuator characterization (Figure 15). A single conducting polymer molecule is attached both to a substrate and an AFM cantilever tip by means of functionalized receptor/ligand interactions such as biotin/streptavidin or covalent bonding resulting from thiol/gold interactions. Soft AFM cantilevers typically have a spring constant of 0.01 N/m. Considering that a single hinged dimer unit of polymer 1 is expected to contract by 1.39 nm, the minimum force that is required to bend the cantilever to monitor a full contraction is 13.9 pN, which is below the average maximal force produced by a hinged dimer of polymer 1. The key advantage of AFM techniques, however lies in the fact that rigid molecule/cantilever coupling (compared to soft coupling in optical tweezers) allows high frequency probing of the single polymer molecule. In other words the AFM can be considered a single molecule dynamic mechanical analyzer (M-DMA). Optical tweezers on the other hand are better suited to probe low force, low frequency regimes.

8. SUMMARY

Synthesis of novel thiophene based conducting polymer molecular actuators has been reported. These novel compounds are designed to utilize the effect of π - π stacking as a driving force for actuation. The hypothesis of active molecular conformational changes is supported by *in-situ* electrochemical data. Initial actuation studies of poly(QT)/S-PHE bulk films seem to indicate that large strains are observable in these novel materials. Single molecule techniques are considered for molecular actuator characterization. The creation of such muscle-like actuators will enable advances in autonomous and life-like robotics, artificial organs and prostheses, and micro/nanosystem fabrication.

9. ACKNOWLEDGEMENT

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