

INVITED REVIEW

Redox-induced actuation in macromolecular and self-assembled systems

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Because of their dynamic nature, stimuli-responsive molecules that undergo conformational changes have attracted much research interest for applications in the field of actuators and sensors. In particular, redox-active molecules that undergo redox state switching have many advantages, including electrical control and drastic conformational change that involves electrostatic interactions. In this review, we focus on the conformational changes for macromolecularly and molecularly assembled systems and evaluated their potential for use as building blocks of redox-driven soft actuators. Moreover, the current review provides insights for the design and fabrication of actuating materials by considering changes in redox state.

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INTRODUCTION

Stimuli-responsive molecular switches that are capable of changing their conformation and their physical properties have attracted considerable interest for the construction of molecular devices, sensors and actuators. A wide variety of conformational changes triggered by external stimuli such as light^{1–3} and pH⁴ have been extensively demonstrated in the recent literature. However, a limited number of redox-induced conformational changes in switchable molecules have been reported, despite their importance in biochemical and electrochemical systems.^{5–20} The use of significant conformational changes of redox-active molecular switches should enable us to achieve novel electrically triggered soft actuators^{21–31} exhibiting high deformation properties. Nevertheless, few examples have been demonstrated for the construction of actuators comprising single molecular switches.³² The dimensional change is small because of the expansion or contraction of covalent bonds upon redox control. As such, constructing actuators driven by conformational change is of great interest for organic chemists.

Redox-active molecules can undergo electronic state (redox state) switching, which induces alternation of properties such as color, luminescence and hydrophobicity. In particular, color change in response to environmental change is a key property in sensing devices. In the future, the electrical (redox) control of material properties should be favorable for the fabrication of molecular devices because of their accuracy and controllability.

The major challenge for amplification of small molecular motions is the lack of effective means to assemble functional molecules such that the motion of single molecules can cause transformations in the volume or shape of bulk materials. In this context, it is necessary to exploit molecularly assembled systems on the basis of their self-organization or through the polymerization of individual molecules.

Ordered self-assembled molecular systems, as seen in biological systems, have a key role in specific and amplified functions.

The purpose of this review is to provide insights for the design and fabrication of redox-triggered soft actuators. First, we introduce several examples of redox-responsive conformational changes of single molecules. We then focus on assembled systems comprising redox-switchable single molecules and their actuation behavior. Finally, we discuss a strategy for the design and fabrication of redox-active molecular actuators and their assembled systems.

CONFORMATIONAL CHANGES IN POLYMERIC SYSTEMS

Although the conformational changes of molecules triggered by various stimuli have been extensively reported, the application of these changes in individual molecules for the construction of actuators remains challenging because actuation requires macroscopic changes in molecular order or orientation in bulk materials. It is important to amplify the conformational changes of each molecule as an integrated change in an assembled molecular system. Several attempts to introduce molecules that undergo conformational change directly into polymeric systems have been reported. If the conformational changes of actuating molecular units cooperate with changes in free volume or chain conformation of polymers, remarkable deformation in bulk materials can be expected.

Incorporating conformational changes of a cyclooctatetraene scaffold¹⁵ in the fabrication of electromechanical actuators has been proposed by Marsella *et al.* (Figure 1a).³³ As shown in Figure 1b, polymer **1**, bearing a cyclooctatetrathiophene repeating unit, was prepared, and its electrochemical properties were investigated. To evaluate the conformational change of the repeating unit in a simple system, monomeric cyclooctatetrathiophene **2** was synthesized. A drastic conformational change was revealed by calculating the structure of **2**, **2**⁺ and **2**²⁺ using the semi-empirical AM1 method and

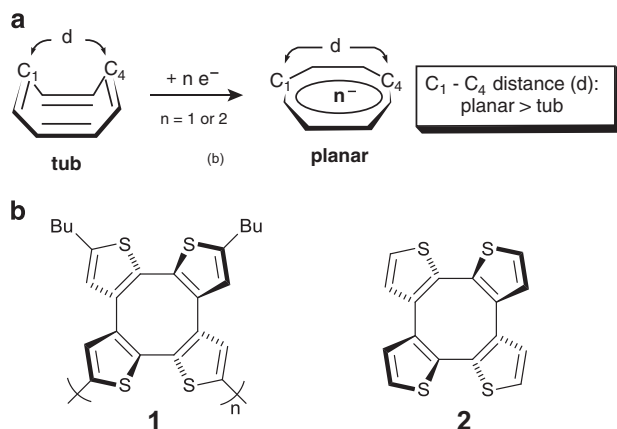


Figure 1 (a) Redox-induced conformational change of cyclooctatetraene and (b) chemical structures of polymer **1** and cyclooctatetrathiophene **2**. Reprinted with permission from reference 33, Copyright (1999) American Chemical Society.

X-ray crystallography. The S–C–S dihedral angle (ϕ) changed from 45.9° to 29.7° upon oxidation. Conversely, the change in dihedral angle in the polymeric system was estimated by calculating the structure of 2-dimer and 2-dimer⁺, revealing a change in ϕ from 44.1° to 40.5° . On the basis of conductivity measurements and an estimation of the band gap of **1**, the backbone nonplanarity of **1** was predicted as reported for regiorandom poly(3-alkylthiophene)s and showed potential significant conformational change driven by a redox process. Such predictions are of great importance for constructing polymeric electromechanical actuators.

For decades, the conformational control of poly(aniline)s (PANIs) has been widely investigated because of the strong conductivity dependence of PANIs on their conformation.^{34,35} Their conductivity has been altered by the incorporation of sulfonate groups into the PANI backbone.³⁶ Moreover, poly(2-methoxyaniline-5-sulfonic acid) (PMAS) (**3**),³⁷ in which methoxy and sulfonate groups are incorporated into the PANI backbone (Figure 2), has attracted considerable interest due to its high conductivity and solubility in water. Hirao and colleagues systematically investigated the influence of various metal ions on the conformational change of the PMAS chain.³⁸ When PMAS forms a complex with metal ions, the main chain adopts a compact coil structure, which is then reduced, resulting in an extended coil structure. Among various transition metal ions, copper ions exhibit the most remarkable conformational change. To investigate the two conformations, the authors focused on the absorptions at 475 and 750 nm, which correspond to the extended and compact coil conformations, respectively. The authors proposed a mechanism for the reversible conformational change of PMAS copper complexes. As illustrated in Figure 2, Cu^{II} oxidizes extended coil PMAS, forming reduced Cu^I, which is then oxidized by oxygen to regenerate Cu^{II}. This was confirmed by a control experiment carried out under an argon atmosphere. The oxidized compact PMAS is reduced by N₂H₄·H₂O in the presence of ethylenediaminetetraacetic acid, capturing Cu ions. When this occurs, regeneration of the extended coil is observed. This cyclic reaction involving oxidation by Cu^{II} and reduction by N₂H₄·H₂O was observed, thus confirming the repeatability of the redox cycle of the copper-coordinated PMAS system. Though the detailed mechanism of macroscopic conformational change of PMAS is still unclear, the authors attributed this to the effect of the sulfonate counteranion. Both conductivity and solvent solubility are important factors in the fabrication of electrochemical actuators. The structural

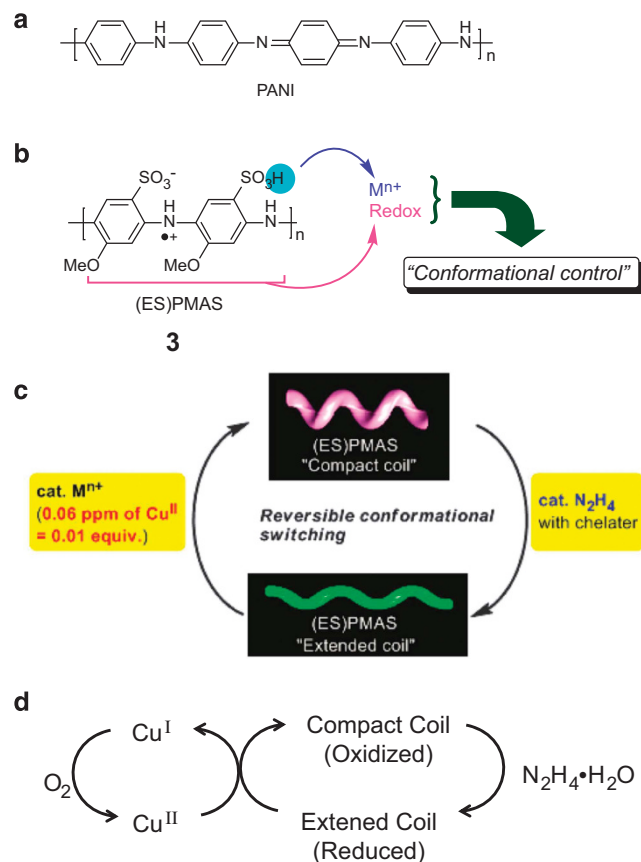


Figure 2 Structures of (a) PANI and (b) (ES)PMAS (**3**). (c) Schematic representation of the reversible conformational switching and (d) its redox cycle. Reprinted with permission from reference 38, Copyright (2010) American Chemical Society. (ES)PMAS, poly(2-methoxyaniline-5-sulfonic acid) emeraldine salt; PANI, polyaniline.

interconversion between an extended coil and a compact coil, as demonstrated by the authors, is simple; however, it is important in the preparation of redox-driven ‘polymer springs.’ This work provides useful information to improve the performance of conductive polymer-based electrochemical actuators.

Electron transfer from myoglobin or hemoglobin has been extensively studied due to its importance in the construction of biocompatible electrochemical systems. To achieve effective electron transfer between these proteins and the electrode, steric factors of the heme unit need to be optimized. Thus, investigation of protein conformational changes upon redox control is of great interest. Approximately two decades ago, Mäntele and colleague examined the redox-induced conformational change in myoglobin and hemoglobin through a combination of Fourier transform infrared spectroscopy and a surface-modified electrode.³⁹ In this case, Fourier transform infrared spectroscopy difference spectra were used to detect structural changes through the detection of individual bonds in proteins, which was possible due to the extreme sensitivity of Fourier transform infrared spectroscopy. The authors assigned the following characteristic bands of myoglobin or hemoglobin to discuss the structural change: (i) $1630\text{--}1670\text{ cm}^{-1}$ as C=O stretching of the polypeptide backbone; (ii) $1680\text{--}1700\text{ cm}^{-1}$ as symmetric vibration of the COOH groups; (iii) $1578\text{--}1610\text{ cm}^{-1}$ as vibration of the aromatic or vinyl CH=CH or C=N– of histidine; and (iv) $1490\text{--}1500\text{ cm}^{-1}$ as ring vibration of phenylalanine. The infrared difference spectra

provided information regarding the local heme environment and interactions and on the interactions of protein subunits. The authors successfully established an electrochemical technique combining the innate electrochemistry of proteins with infrared spectroscopy to evaluate structural changes upon redox reactions at high protein concentration, enabling us to obtain structural information under conditions close to native reactions.

Although stimuli-responsive polypeptides and protein materials that undergo interconversion between ordered and disordered chain conformations have been widely studied, many have different solubilities in water, which makes it difficult to design materials to mimic biological systems. To overcome this challenge, Deming and colleague developed water-soluble glycol polypeptides **4a** and **4b** (Figure 3a), which undergo interconversion between α -helix and random coil structures. Conformational switching of polypeptide chains from α -helix to random coil upon oxidation was detected by circular dichroism (CD) spectroscopy.⁴⁰ Side-chain polypeptides bearing an α -D-glucose or α -D-galactose unit as a pendant group were prepared by living polymerization of α -D-glucose-L-cysteine or α -D-galactose monomers, respectively. Polypeptides that undergo helix to coil switching have been previously reported to alter their solubility in water through protonation or deprotonation. It is not favorable to investigate structural changes in biological systems; thus, conformational changes inducing water solubility are desirable. The authors focused on the polar glycoside group and incorporated a glycoside moiety into the polypeptide backbone. Both **4a** and **5a** are water

soluble and show CD-active properties characteristic of an α -helix, as indicated by the CD minima at 208 and 222 nm. Even after the oxidation of **4a** and **4b** by H_2O_2 , the corresponding sulfones remained water soluble and showed a loss of CD minima at 208 and 222 nm, which indicated that the resulting polymer adopted a random coil structure (Figure 3b; data for **4b** and **5b** are not shown). The authors attributed this conformational change between α -helix and random coil to the transformation of the thioether groups to polar sulfones, which may cause the destabilization of the α -helix. No conformational change could be seen when a methylene unit was inserted between the thioether group and peptide backbone. The polymer maintains an α -helical structure even after oxidation, suggesting that the change in the molecular structure of the repeat units has an important role in determining the stable chain conformations. The authors concluded that the conformational switching induced by oxidation of the thioether moieties may serve to detect oxidative environments in biological systems.

Efficient charge transfer is a crucial factor for redox-driven actuators. For this reason, extensive studies on the utilization of conductive polymers in soft actuators have been carried out for several decades.^{27,41} Swager and colleagues prepared segmented conductive polymers **6a** and **6b** (Figure 4a), wherein a calix[4]arene scaffold could bridge conductive quaterthiophene units.⁴² Calix[4]arenes, which can undergo drastic structural changes, have been widely studied for their application to mechanically active materials.^{43,44} In this case, calix[4]arene acts as a hinge by connecting the electroactive quaterthiophene units. The authors investigated the mechanism of this redox process by cyclic voltammetry and electron paramagnetic resonance measurements. The neutral *p*-dihydroquinone state underwent a one-electron oxidation that produced an extended *p*-diquinone radical cation, and it was further oxidized to the extended *p*-diquinone salt state. The authors explained that this conduction is primarily due to electron exchange between the radical cations and *p*-diquinone salts. The change in stacking interactions between oxidized quaterthiophenes combined with conformational changes of flexible calix[4]arene scaffolds are expected to induce remarkable conformational changes in polymer chains. The authors experimentally demonstrated that changes in π -stacking interactions can be converted to actuation by conformational changes of flexible molecular hinges such as calix[4]arene.

Scherlis and Marzari⁴⁵ examined the optimized architecture of quaterthiophene-functionalized calix[4]arenes and their polymers on the basis of electronic and structural simulation (Figure 4b). They focused on (1) the performance of calix[4]arenes as molecular hinges, (2) the electronic structure of the polymer in oxidized and neutral states, (3) the effect of oxidation state on stacking interactions of oligothiophene moieties and (4) the dynamic response of intermolecular interactions of oligothiophene moieties. To evaluate calix[4]arene units as flexible molecular hinges, the potential energy surface was estimated as a function of the distance between C_a and C_b . Dimethyl calixarene is the most convenient structure, as it does not hinder the intermolecular interactions of oligothiophene units, thus preserving the proper arrangement. The effects of oxidation state on the electronic structure of polymers were investigated. The change in electronic density was limited within the oligothiophene moieties, whereas that of calixarene units was not affected by oxidation. This implies the clear division of roles for oligothiophene and calix[4]arene moieties. The intermolecular interaction was evaluated as a function of the interplanar distance between oligothiophenes. This was achieved by calculating the potential energy of charged or neutral bithiophene dimers. This was conducted in the singly charged state, demonstrating

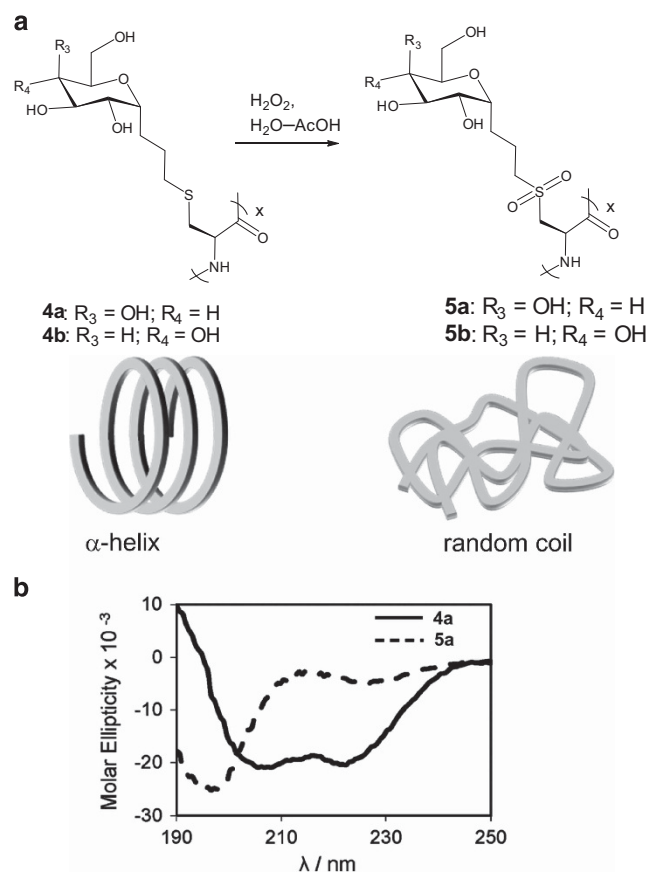


Figure 3 (a) Conversion of **4a,b** to **5a,b** and schematic image of structural change. (b) Circular dichroism spectra of **4a** and **5a**. Reprinted with permission from reference 40, Copyright (2012) American Chemical Society. A full color version of this figure is available at *Polymer Journal* online.

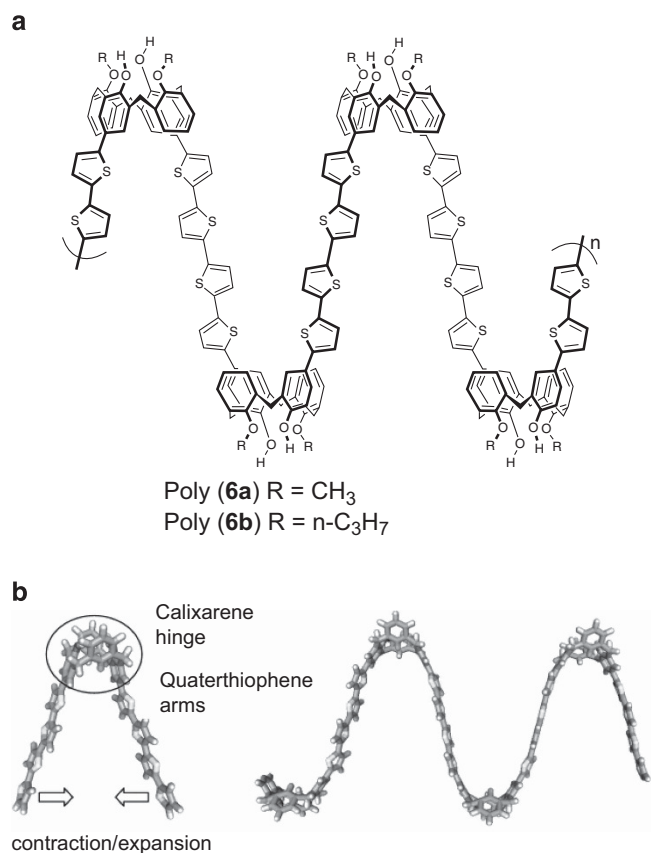


Figure 4 (a) Chemical structures of conductive polymers based on the calix[4]arene units. Reprinted with permission from reference 42, Copyright (2003) American Chemical Society. (b) Structure of a calix[4]arene-thiophene molecular actuator: actuating unit and a polymerized assembly. Reprinted with permission from reference 45, Copyright (2005) American Chemical Society.

that neutral and singly charged bithiophenes interact strongly with a binding energy of ~ 12 kcal mol⁻¹ and intermolecular distances of 3.5 Å. Moreover, molecular dynamics simulations demonstrated that the response time required to reach the maximum angular opening of quaterthiophene units (65°) upon oxidation was 2.5 ps. The authors demonstrated the potential of oligothiophene-functionalized calix[4]arenes as building blocks to fabricate deformable materials. This was accomplished by estimating the flexibility of calix[4]arene, the difference in potential energy of stacked oligothiophene dimers upon oxidation, and the dynamic response of oligothiophene intermolecular forces.

When developing nucleic acid-based diagnostics, precise and reversible control of nucleic acids is crucial. Bachmann and colleagues focused on electrochemically controlled hybridization of DNA.⁴⁶ In this case, daunomycin **7** was used as a redox-active intercalator,^{47,48} which underwent interconversion between the hydroquinone and quinone form via a two-electron redox cycle (Figure 5a). The insertion of **7** stabilized the DNA structure through specific molecular interactions, such as H-bonds and van der Waals interactions. Such molecular interaction-based intercalation of **7** in DNA can be switched in response to the redox state of **7**. Spectroelectrochemical studies revealed that the characteristic absorption band for **7** appeared at 435 nm upon reduction. Conversely, upon oxidation at 0.3 V, the absorption at 260 nm drastically decreased, indicating transformation of ssDNA to dsDNA. This suggests that the observed change in UV

spectra can be attributed to the structural change between dsDNA intercalated with **7** and ssDNA with free **7**. When **7** is in the oxidized state, DNA adopts a double-stranded hybridized form, whereas it adopts a single-stranded form when **7** is in the reduced state (denatured). Moreover, no evidence of DNA degradation or fragmentation could be seen upon redox cycling, which confirmed that structural interconversion is due to the effect of redox cycling of **7**. The reproducibility of the interconversion between intercalated **7**/dsDNA and free **7**/ssDNA was confirmed by UV and CD spectroscopy, which demonstrated stable redox switching signals.

Although this mechanism of DNA conformational change mediated by redox switching of **7** is not completely understood, the authors speculate that the protonation/deprotonation process of **7** is strongly related to the hybridization/denaturation switching of DNA (Figure 5b). Intercalation of **7** between stacked base pairs leads to the stabilization of dsDNA, possibly through molecular interactions (Figure 5c).

For reduction of **7**, electrostatic repulsion between deprotonated **7** may promote deintercalation from DNA, resulting in denaturation of the DNA. The approach presented in this study provided motivation to investigate the control of DNA hybridization for molecular diagnostic analysis. This method (i) provided a method to electrochemically control the DNA denaturation/renaturation cycle without drastically changing the solution composition; (ii) enabled shorter denaturation/renaturation cycle times compared with other electrochemical approaches; and (iii) demonstrated promising insights into the control of the cycles at elevated temperatures.

It is difficult to achieve effective deformation of polymer materials by simply incorporating molecular units that display conformational change in the polymer chain. As such, the following two points should be carefully considered and optimized:

- (1) Avoid relaxation of conformational change of the molecular units in the polymer chain. The polymer chain should be sufficiently stiff to propagate the conformational change of the molecular units over the entire polymer chain but remain soft enough to exhibit deformation.
- (2) Maximize the efficiency of the redox reaction. All molecules should respond to stimuli, as the degree of deformation is proportional to the number of molecules oxidized (or reduced). Thus, electron transfer is important not only on the surface of the electrode but also in the bulk material.

ACTUATION INDUCED BY MOLECULAR INTERACTIONS

Specific molecular interactions such as ionic bonds, π - π interactions, ion-dipole interactions and hydrogen bonds have been widely exploited in the fields of molecular recognition and molecular assembly. Molecular interactions can function as a driving force capable of triggering conformational changes in molecular structures and nanostructures of assembled molecular architectures. For redox-active molecules, switching the redox state (charge) leads to an alternation of stable assembled structures in response to each redox state. The macroscopic structural changes of polymeric materials that are induced by varying ionic interactions have been widely demonstrated.

Linear polymer chains can be converted to macrocycles via end-to-end coupling caused by external stimuli.^{49,50} Deffieux and colleagues prepared dimeric functionalized poly(ethylene oxide)s (PEOs) to which iron(III) tetrphenylporphyrin (TPP) derivatives were attached. They reported the formation of macrocycles through intramolecular cyclization by oxidation with oxygen and reproduction of linear

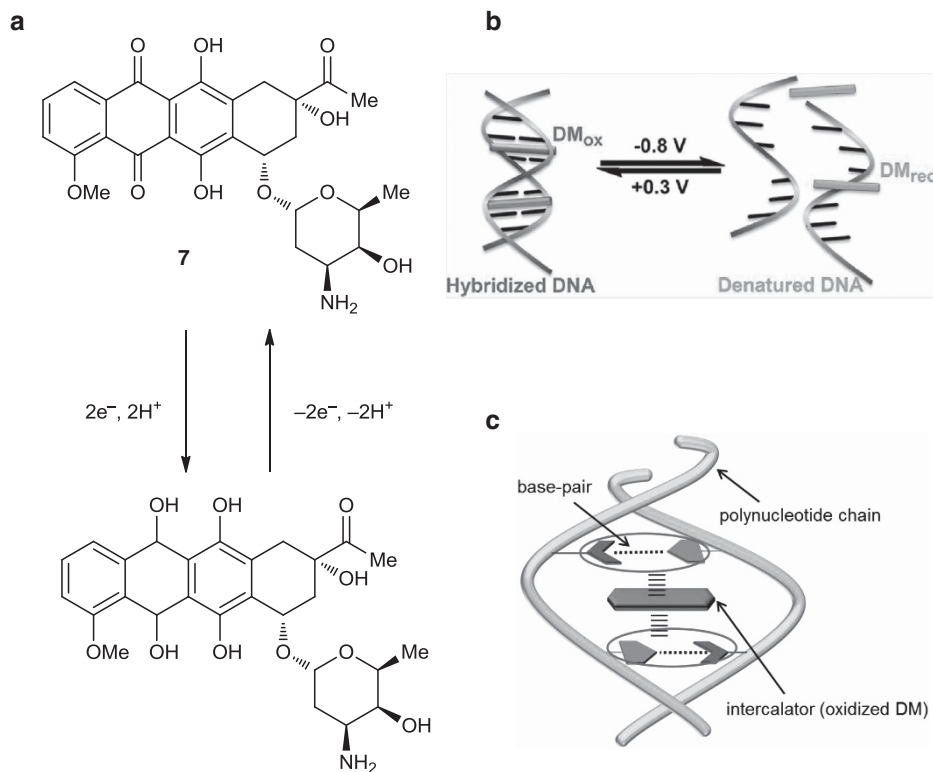


Figure 5 (a) Reversible reduction and oxidation of **7**, as postulated to be involved in the electrochemical control of DNA hybridization. (b) Schematic illustration of redox-triggered interconversion between hybridized DNA and denatured DNA. (c) Plausible mechanism for the stabilization of hybridized DNA through molecular interaction of oxidized intercalator with base pairs of DNA. Reprinted with permission from reference 46, Copyright 2013 American Chemical Society. A full color version of this figure is available at *Polymer Journal* online.

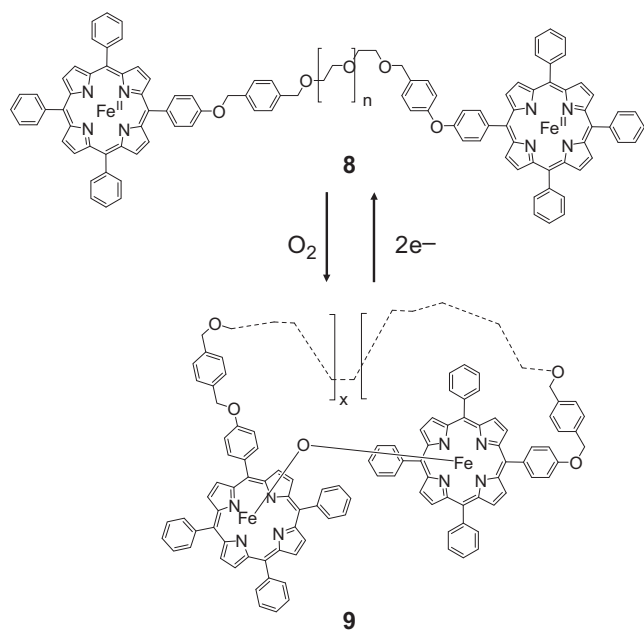


Figure 6 Reversible interconversion between **8** and **9** by oxido-reduction.

polymers by reduction with aqueous sodium dithionite. The formation of an $Fe(III)$ porphyrin dimer can be explained by the autoxidation of the six-coordinate $Fe^{II}TPP(THF)_2$ complex **8** to μ -oxo-bis($Fe^{III}TPP$) **9**, in which an oxygen atom bridges two porphyrin rings on the same polymer chain (Figure 6).^{51–53} The reverse reaction,

that is, the reduction of macrocycles with sodium dithionite, was achieved quantitatively. Similar interconversion was observed by applying other stimuli, such as variation of solvent polarity or pH. If such TPP-functionalized polymers are properly assembled into well-ordered nanostructures, structural interconversion between the linear and cyclic forms can be transformed into significant mechanical deformation of the polymers. Moreover, the function of the redox-triggered bridging/dissociation switching of TPP units, if incorporated into the polymer backbone, can be applied to switchable cross-linkers for polymer gels. This class of materials will be capable of tuning the Young modulus by redox stimuli and is expected to be applied to shape-memory polymers.⁵⁴

Redox stimuli can induce switching of not only Coulomb interactions but also host/guest interactions for β -cyclodextrin (β CD) and ferrocene (Fc) units. β CD is a cyclic molecule comprising six to eight glucose units and can form inclusion complexes with various molecules.⁵⁵ The unique nature of CDs has attracted much interest in the field of supramolecular chemistry, as have rotaxanes and catenanes.^{56,57} In particular, inclusion complexes of CDs and Fc exhibit inclusion/exclusion switching in response to the redox states of Fc,^{58–61} which leads to a sufficient conformational change to induce macroscopic deformation of polymeric materials and gels. Volume changing behavior of redox-responsive hydrogels on the basis of inclusion complexes between β CD and Fc units attached to the polymer backbone has been reported by Harada and colleagues (Figure 7a).⁶² In the case of poly(acrylamide)-based systems, inclusion complexes of β CD and Fc units function as redox-triggered reversible cross-linkers. As illustrated in Figure 7b, in the oxidized state, the affinity of Fc^+ for β CD is low, and dissociation of the inclusion

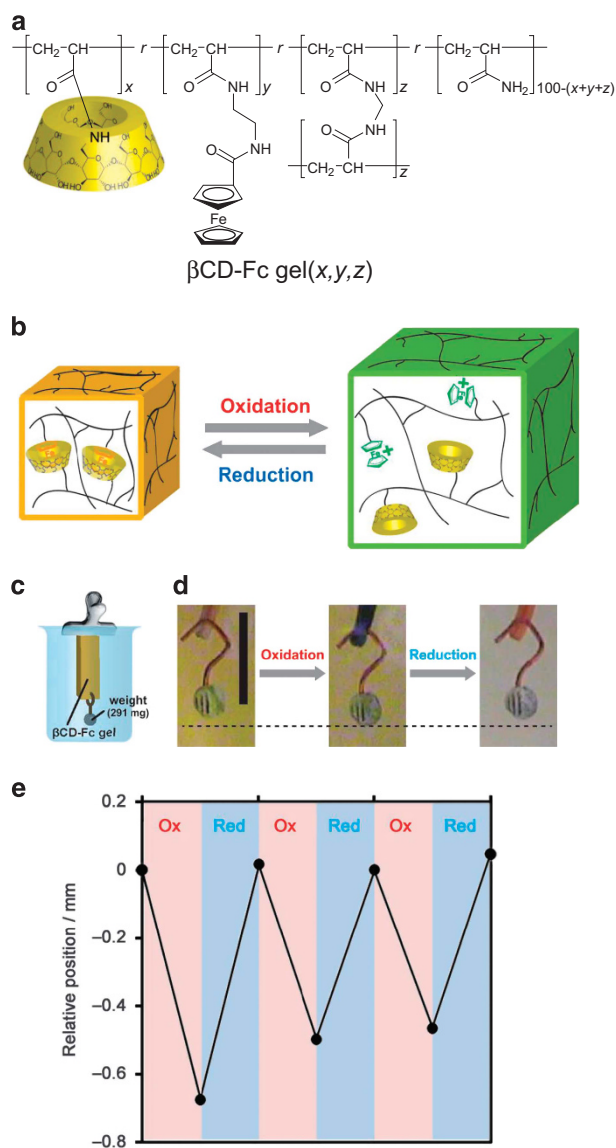


Figure 7 (a) Chemical structure of the $\beta\text{CD-Fc gel}$. (b) Illustration of redox-responsive expansion–contraction of the $\beta\text{CD-Fc gel}$. (c) Schematic illustration of the hydrogel actuator. (d) Photographs of a $\beta\text{CD-Fc gel}$ actuator in response to redox stimuli. (e) Plot of the relative position of the weight versus immersion time for $\beta\text{CD-Fc gel}$ with a weight. Reprinted with permission from reference 62, Copyright (2013) Wiley-VCH Publishers.

complex takes place, decreasing the crosslinking density and swelling the hydrogel. However, the formation of inclusion complexes proceeds due to the increased affinity of Fc, increasing the crosslinking density and shrinking the hydrogel. The rheological change of the gel in response to redox stimuli was confirmed by the change in stress–strain curves. This can be attributed to the alternation of the degree of crosslinking involving inclusion/exclusion switching of the βCD and Fc units. As shown in Figure 7c, a weight was attached to the βCD hydrogel, which was subjected to oxidation and reduction, resulting in expansion and contraction of the gel, respectively (Figure 7d). The position of the weight oscillated upon repeated oxidation–reduction cycles (Figure 7e). The mechanical work to lift the weight (291 mg) attached to the hydrogel was estimated to be $20 \mu\text{J}$. Changes in

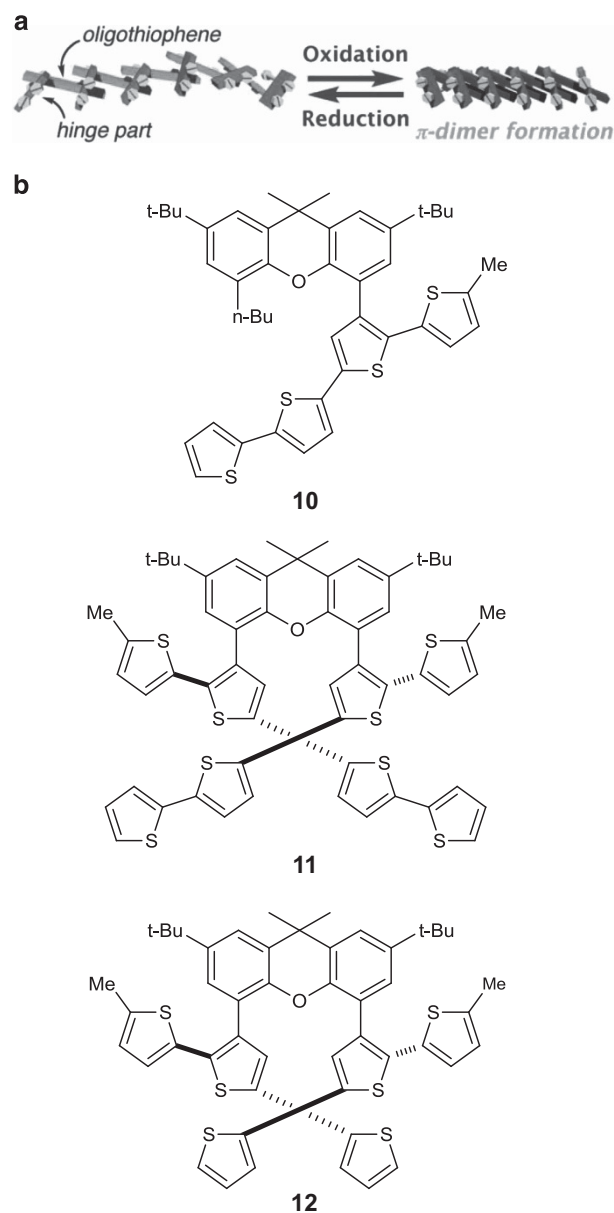


Figure 8 (a) Schematic illustration of a molecular actuation triggered by a π -dimer formation of oligothiophene moieties connected with electronically inactive hinge molecular units. (b) Chemical structures of **10**, **11** and **12**. Reprinted with permission from reference 86, Copyright (2008) American Chemical Society. A full color version of this figure is available at *Polymer Journal* online.

oxidation state of the molecular units led to rheological changes due to the highly specific and selective supramolecular interaction between βCD and Fc units.

Inclusion complexes comprising CD and Fc units can be applied to shape-memory polymers. Zhang and colleagues demonstrated the shape-memory behavior of cross-linked βCD and chitosan ($\beta\text{CD-CS}$)/ferrocene modified poly(ethyleneimine) networks upon redox control.⁶³ The shape-memory polymer contains two components: $\beta\text{CD-CS}$ and ferrocene modified poly(ethyleneimine). Two types of crosslinks (covalent and reversible bonding) were formed to achieve redox-active shape-memory polymers. Covalent bonds were formed by the reaction of glutaraldehyde with amino groups and were stable

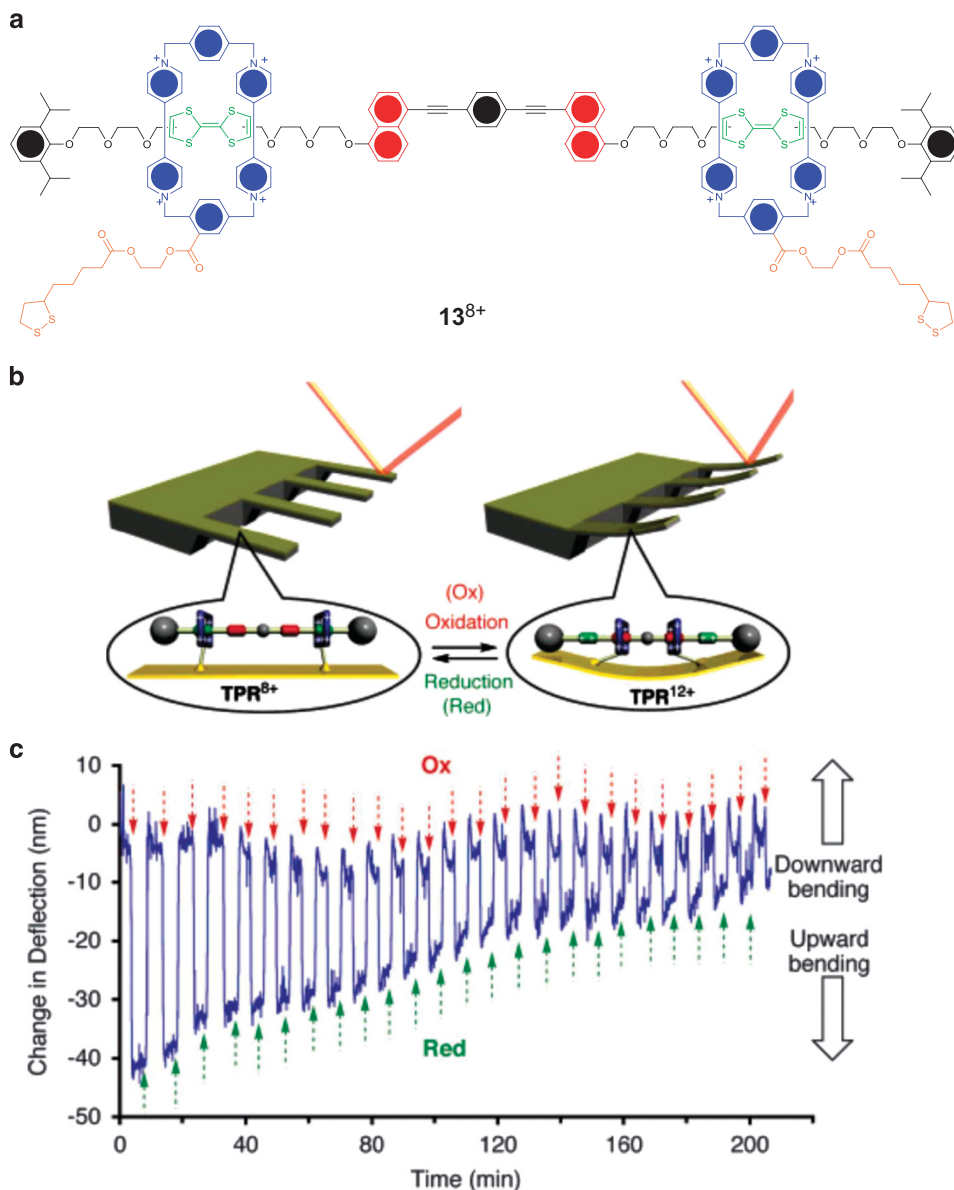


Figure 9 (a) Chemical structure of disulfide-tethered molecular muscle 13^{8+} . (b) Schematic diagram of the proposed mechanism of the device's operation. (c) Experimental data showing 25 cycles of the upward and downward bending of one cantilever beam coated with 13^{8+} . The red and green arrows indicate the time when oxidant or reductant solution is injected into the fluidic cell. A negative deflection corresponds to an upward bending of the cantilever beams. Reprinted with permission from reference 87, Copyright (2005) American Chemical Society.

against oxidation and reduction, whereas reversible bonds were based on the inclusion complex of β CD and Fc units. The coexistence of reversible switching bonds and stable fixed bonds is an important factor for exhibiting the shape-memory effect.⁶⁴ When the ferrocene moiety is in the reduced state, the polymer network contains both covalent bonds and physical binding based on ferrocene and β CD; however, in the oxidized state, Fc^+ is excluded from β CD and only covalent bonds exist. Switching of the crosslinking density caused changes in mechanical properties of the polymer network.⁶⁵ In the oxidized state, the sample was easily bent by external stress due to low crosslink density and treated with a reducing agent. The sample maintained its bent shape, even after removing the external stress, but recovered its original shape upon oxidation. Thus, mechanical properties were successfully tuned by controlling the crosslink density. The shape-memory effects demonstrated by the authors, if combined with

continuous redox cycles, will enable application of this function to the development of soft actuators.

Similar actuation based on association/dissociation between metal ions and ionic functional groups of the polymer chain was demonstrated by Tatsuma and colleagues.⁶⁶ Moreover, the expansion and contraction behaviors of such polymer complexes comprising poly(acrylic acid) and Cu^{2+} ions were transformed into a bending motion. A poly(acrylic acid) hydrogel incorporated with Cu^{2+} ions was immobilized on a Au-sputtered polyimide film, and the degree of bending of the modified flexible electrode was monitored to quantitatively evaluate the strain of the film. The authors suggested that in the oxidized state of Cu^{2+} , carboxyl groups strongly bind to Cu^{2+} , leading to contraction of the polymer chain of the gel, whereas in the reduced state of Cu^0 , the carboxyl groups dissociate from Cu^0 , which led to the expansion of the polymer chain. The dependence of the stretching

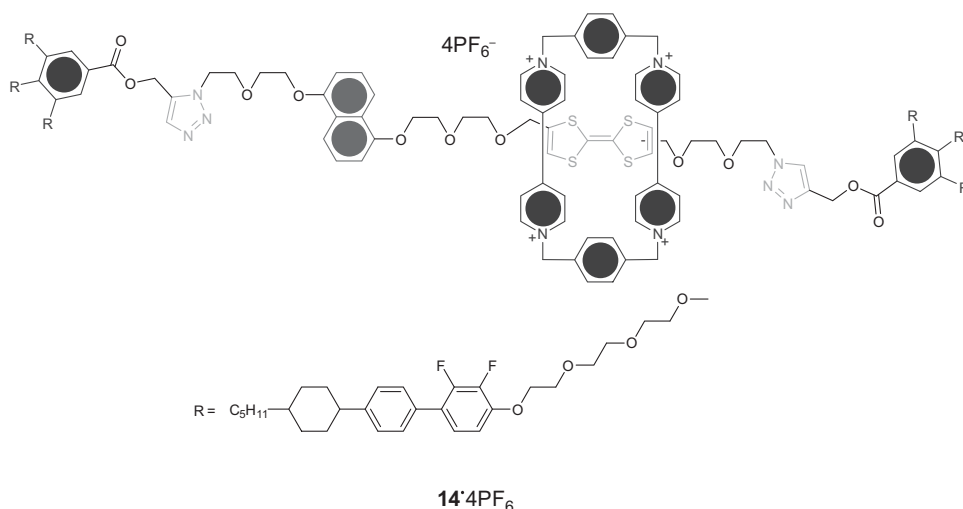


Figure 10 Chemical structure of bistable LC rotaxane **14·4PF₆**. A full color version of this figure is available at *Polymer Journal* online.

ratio on the concentration of loaded copper ions strongly suggests that the binding of metal ions to carboxyl groups has a major role in the change in volume of the polymer gel. The contraction of the gel was up to 0.15%, and good reproducibility was observed. The energy conversion in this system was estimated to be $10^{-3}\%$. On the basis of electrochemical studies, the authors proposed a mechanism for swelling/shrinking switching of the polymer gel complexes and provided several further suggestions for improvement of the gel for use as an actuator component. For improved performance, the authors have proposed the use of a porous gel to increase diffusion of Cu^{2+} and inclusion/exclusion of water. Moreover, potential introduction of conductive polymers was suggested to increase the reaction rate. This series of hydrogel actuators can be operated in aqueous systems and thus are expected to be applied in biomedical and biological fields.

ACTUATION OF SELF-ASSEMBLED OR IMMOBILIZED SYSTEMS

Although the Coulomb force of intra- and intermolecular interactions is one of the key factors in the construction of electrochemically driven soft actuators, it must be controlled in the ordered molecular field to enhance performance. Recently, the design of redox-active molecules focusing on self-organization was demonstrated. This strategy enables us to mimic biological systems such as myosin II in muscle contraction,^{67–69} in which small motions of each molecule are effectively amplified in highly ordered molecular systems, which leads to macroscopic deformation. A molecular level understanding and construction of synthetically integrated well-ordered systems is one of the major challenges for the fabrication of functional materials.^{70–78} In particular, a well-ordered structure is crucial to establishing sensing^{79–81} or actuating systems.^{82,83} Supramolecular architecture and liquid-crystalline properties should also be taken into account for molecular design.

Swager and colleagues suggested that conformational change can be a major driving force to produce mechanical motion and proposed a basic strategy for transforming conformational change in individual molecules into macroscopic mechanical work by the formation of well-ordered assembled structures. The authors intended to transform the formation of π -dimers of oligothiophene derivatives^{84,85} into conformational changes, thus leading to the mechanical motion of molecular actuators. They designed and prepared tweezer molecules

by incorporating terthiophene or quaterthiophene moieties to electrochemically inactive hinge scaffolds and investigated the formation of π -dimers by UV-Vis spectroscopy, cyclic voltammetry, differential pulse voltammetry and electron paramagnetic resonance.⁸⁶ In this case, π -dimer formation may cause significant amplification of rotational motion of the hinge unit. Such effect may be achieved through the formation of highly ordered self-assembled structure of the molecular tweezers (Figure 8a).

For **10** and **12** (Figure 8b), generation of new absorption bands at 660–670 nm and ~ 1100 nm were observed in the UV-Vis spectrum, which are characteristic of radical cations. However, other absorption maxima at 615 and 1011 nm were also observed for **11** by oxidation, which could be attributed to the π -dimer formation. Electrochemical and electron paramagnetic resonance studies further supported effective π -dimer formation for **11**, whereas no peaks indicating π -dimer formation were observed for **12**. These results suggest that quaterthiophene moieties are favorable over terthiophene moieties. Effective π -dimer formation of oligothiophene-functionalized tweezer molecules was demonstrated. Detailed investigation of the conformational change of the hinge and nanostructure of the molecular assembly is the next step in the development of polymeric systems.

Redox-active molecular switches on the basis of binary functional components have been examined extensively as integrated, ordered molecular systems. Typical examples include rotaxane or catenane-based bistable molecular switches. In these cases, one functional unit can move within another macrocycle or linear molecule. Stoddart and colleagues reported the transformation of rotaxane motion into the mechanical work of a cantilever beam.⁸⁷ They designed redox-active, bistable rotaxane (**13⁸⁺**), as shown in Figure 9a. Tetracationic cyclophane and cyclobis(paraquat-para-phenylene) (CBPQT⁴⁺) changed their positions in response to the redox state of tetrathiafulvalene (TTF) such that the rings were in a thermodynamically stable position. Rotaxane **13⁸⁺** self-assembled on a Au-coated cantilever, and mechanical binding motion of the cantilever based on the oxidation-induced contraction of inter-ring distance was observed for 25 cycles (Figures 9b and c). Addition of oxidant and reductant solutions caused the cantilever to bend upward and downward, respectively. The authors attributed such mechanical motion of the cantilever to the collective effect of the alternation of the intermolecular distance between CBPQT⁴⁺ rings. It should be noted that the authors quantitatively calculated the force per molecule on the basis of

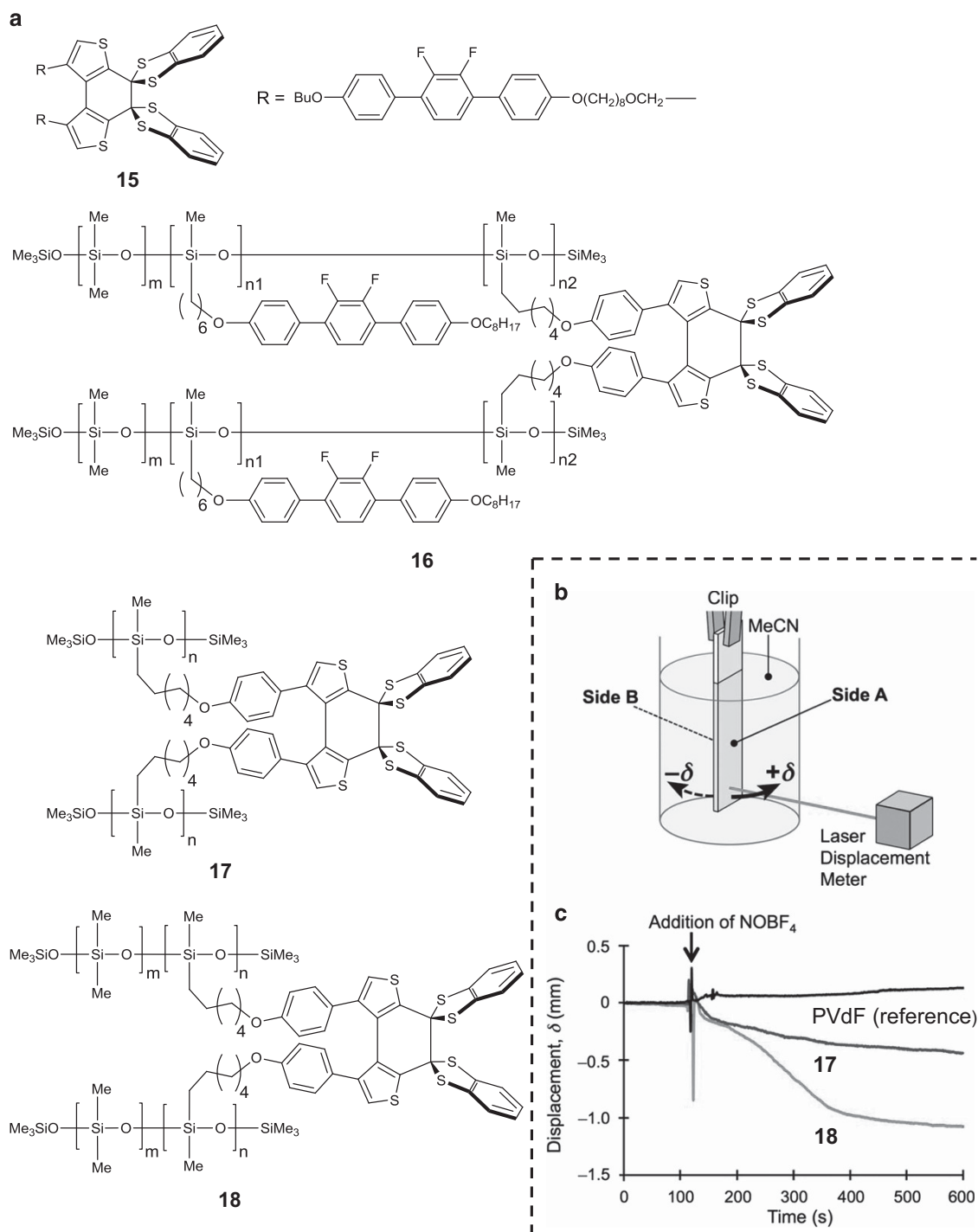


Figure 11 (a) Chemical structure of **15–18**. (b) Schematic image in detail of experimental setup for displacement measurements. (c) Changes of displacement for the PVdF films coated with polymer gels as a function of time. The curve for **17** is in red, for **18** in blue, and for bare PVdF (reference) in black. Reprinted with permission from reference 92, Copyright (2014) American Chemical Society. A full color version of this figure is available at *Polymer Journal* online.

deflection data. In this case, the Coulomb repulsion forces between tetrathiafulvalene and CBPQT units were a major driving force. On the basis of geometrical assumptions and Hooke's law, the force per molecule needed to induce a 35-nm deflection was estimated to be 10.2 pN. The calculation of individual molecular forces provides important information for the estimation of stress in assembled or bulk systems.

To amplify the motion of individual molecules for mechanical work, an ordered structure of the molecular assembly is required. For example, formation of an ordered structure of rotaxane or catenane molecules by introducing liquid crystals has been extensively explored by Kato and colleagues^{88,89} The authors prepared a bistable rotaxane incorporated with dendritic mesogenic moieties, as shown in Figure 10. The LC rotaxane (**14-4PF₆**) exhibits a smectic A phase

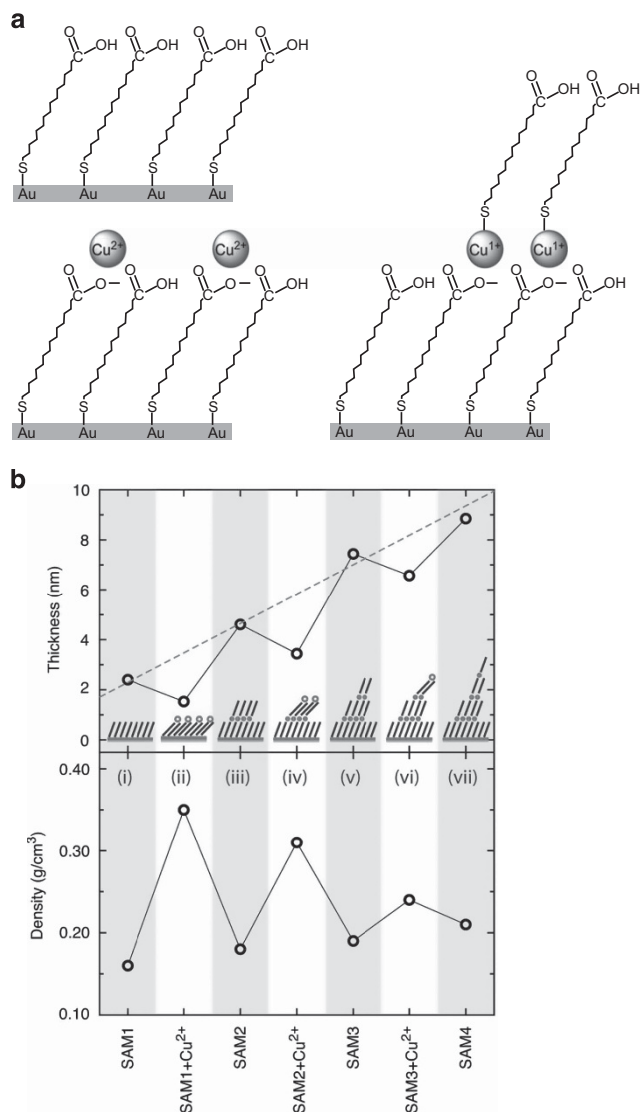


Figure 12 (a) Schematic diagram of a multilayer molecular film assembled by the sequential adsorption of *n*-alkanethiolate monolayers and divalent metal ions, here Cu^{2+} . The Cu^{2+} ion is reduced to Cu^+ following chemisorption of the upper monolayer. (b) Dual-polarization interferometry (DPI) experimental data showing the change in thickness and density of a multilayer film assembled from four MHDA monolayers. The dashed line in the upper graph shows the straight line fitted to the total film thickness measured following the assembly of each new monolayer (regions i, iii, v and vii). The assembly mechanism is shown schematically in the upper panel where open (closed) circles represent copper ions in the +2 (+1) oxidation state, respectively. Reprinted with permission from reference 95, Copyright (2012) American Chemical Society. A full color version of this figure is available at *Polymer Journal* online.

over a wide temperature range from room temperature to 150 °C. Formation of nanosegregated superstructures in the smectic A phase was confirmed by XRD studies. The electrochemical bistability, which was observed for normal bistable rotaxane, was observed by cyclic and differential pulse voltammetry. The reversible mechanical motion was also spectroelectrochemically examined by monitoring the absorption band at 840 nm, which is indicative of the charge transfer interaction between tetrathiafulvalene and CBPQT^{4+} . The construction of redox-active and dynamic rotaxane functionalized with mesogenic cores allowed for the development of large and complex superstructures,

which will be applied to electrochemical devices to investigate the effect of mechanical switching on nanostructures. The basic strategy demonstrated by the authors will become a benchmark to assemble functional molecules possessing dynamic nature into integrated molecular systems.

Ohta and colleagues prepared redox-active molecular switch **15** and reported that it possessed liquid–crystalline properties (Figure 11a).⁹⁰ This mesomorphic molecule and its cationic salt both exhibit smectic phases. They can be used as building blocks for the fabrication of actuating materials in which each molecule undergoes conformational change while maintaining a smectic ordered structure. Moreover, both mesogenic cores and redox-active functional units were incorporated into a polysiloxane backbone (**16**) (Figure 11b).⁹¹ Surprisingly, mesomorphic behavior was not observed for this polymer; however, redox activity was observed, associated with interconversion of the cationic and cyclic forms of bis(benzodithioly)bithienyl moieties. To form the stable, liquid–crystalline ordered structure, the mesogenic moiety content incorporated in the polymer requires optimization.

Volume change induced by oxidation of the bis(benzodithioly)bithienyl unit attached to the polysiloxane chain was observed for polymer gels **17** and **18** (Figure 11c), which do not contain mesogenic cores.⁹² The polymer gels **17** and **18** were formed on poly(vinylidene difluoride) thin films, and the deformation of the film upon oxidation was evaluated as illustrated in Figure 11d. Clear bending behaviors were observed by the addition of the oxidant (NOBF_4 ; Figure 11e), which can be attributed to the swelling behavior of **17** and **18** upon oxidation. Preparation of the polymer gel with a liquid–crystalline ordered structure and examination of anisotropic mechanical deformation will be attempted.

Microcantilever transducers have become important in the fields of chemical sensing and biosensing. Deformation of the cantilever is mainly caused by change in the surface stress arising from molecular interactions. To achieve better performance of the cantilever, an understanding of the surface tension or stress in terms of molecular interactions is crucial. Redox-active molecules were successfully immobilized on microcantilevers to transform orientational order of molecules into mechanical work.

Badia and colleague prepared a self-assembled monolayer (SAM) comprising ferrocenylalkanethiolate on a metal-coated cantilever and investigated changes in surface stress triggered by electrochemical reactions of ferrocenyl units.^{93,94} The authors examined the effects of alkyl chain length and counteranions on the microcantilever deflection.⁹⁴ In this case, the major factors dominating the deflection of cantilevers were packing density changes and stabilized orientational order. An increase in the film thickness of the SAM was detected upon oxidation, which could be ascribed to molecular reorientation involving a more perpendicular orientation of the alkyl chains and ferrocenyl groups with respect to the surface of the electrode. The change in surface stress ($\Delta\sigma$) decreased upon reduction of the alkyl spacer length. This tendency was explained by the increased tensile elastic contribution due to interplay between attractive chain–chain interactions.

The effect of counteranions is more pronounced. The $\Delta\sigma$ coincides with that of the ion-pairing tendency of the anions. Complexation with PF_6^- and ClO_4^- led to reversible deformation, which may be attributed to the stabilization of oxidized ferrocenyl units; whereas hydrophilic NO_3^- and F^- destabilized the oxidized ferrocenyl units and depressed the reversible deflection. The authors explained that the mechanism of change in surface stress was owing to complexation of ferrocenium units to counteranions, forming two-dimensional networks. Moreover, they clearly demonstrated the dominating factors

(alkyl spacer length and counteranions) that must be controlled for the improvement of redox-active SAM-based cantilevers.

Conformational change of a self-assembled multilayer system was theoretically and experimentally examined by Wälti and colleagues.⁹⁵ They prepared multiple monolayers of mercaptoalkanoic acid ligated via carboxyl and thiol groups with copper ions, as illustrated in Figure 12a. For the first monolayer, a decrease in the film thickness and an increase in the density upon complexation with copper ions were both observed by dual-polarization interferometry measurements. When the second monolayer was formed on the copper carboxylate interfaces, the orientation and density of each monolayer recovered its original state. Thus, the total film thickness was the same as that of two free MHDA monolayers. Such oscillation in film thickness and density was observed until the formation of the fourth layer (Figure 12b). On the basis of the molecular dynamics simulation, the authors investigated the mechanism of structural change in monolayers and bilayers of the SAM, focusing on the redox state of copper ions. Through exposure of the monolayer to Cu^{2+} ions, reorientation of the monolayers occurred owing to the interaction between Cu^{2+} ions. After the second monolayer was formed, the Cu^{2+} ions were reduced to Cu^+ ions, and $\text{Cu}^+ - \text{S}(\text{CH}_2)_{15}\text{COOH}$ was formed as a top layer, suppressing the reorientation of the polymethylene chains. The authors concluded that conformational change in the multilayer film was induced by differences in stability of $\text{S}(\text{CH}_2)_{15}\text{COO}^- \text{Cu}^{2+}$ and $\text{Cu}^+ - \text{S}(\text{CH}_2)_{15}\text{COOH}$. The former forms a less stable but more dynamic structure, enabling polymethylene chain reorientation such that the tilt angle of the top layer increases, whereas the latter forms a stable structure with no change in orientation. Switching the redox states of copper ions successfully converted the conformation of the SAM via drastic changes in molecular interactions and stability. Ordered structures may depend strongly on the redox state of molecules owing to Coulomb interactions. In this case, cooperation of electrostatic forces and van der Waals interactions between molecules in each redox state are crucial for maintaining self-assembled structures. This may be a key factor to exhibit enhanced molecular actuation in an ordered anisotropic field.

CONCLUSIONS AND FUTURE OUTLOOK

Conformational changes in polymers, macromolecules and molecular assemblies have been reviewed as promising driving forces to induce macroscopic actuation of bulk materials. Incorporation of molecular units that undergo conformational change in polymeric systems is the most accessible technique for amplification of small structural changes of molecular units into macroscopic deformation. Considerable studies on actuating polymer materials have been demonstrated. However, conformational changes of molecular units may be relaxed or negated owing to the flexibility of the polymer chain by simply connecting or incorporating shape changing molecular units. Moreover, changing the redox state of molecules through oxidation or reduction may induce significant changes in inter- and intramolecular interactions. Thus, it is necessary to design functional molecular units by considering the change in charge density. Such changes in molecular interaction or molecular recognition are efficient driving forces for large conformational changes of polymer chains or macromolecular scaffolds. A molecular assembly with an ordered structure may enable significant bulk actuation in a specific direction with high efficiency. We suggest the use of liquid crystals and self-assembled monolayer systems as promising options. We believe that utilizing supramolecular chemistry and molecular recognition is important for the amplification of small structural changes of

molecular units and will provide useful insights for the fabrication of stimuli-responsive materials.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

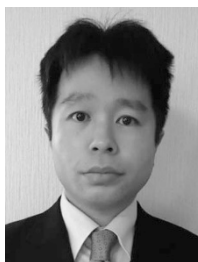
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