CONDUCTING POLYMERS AS BUILDING BLOCKS FOR BIOMIMETIC SYSTEMS

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Abstract

In Nature, systems are created from the cellular level to build machines with complex structures and behavior. Nature's cells are fabricated entirely from organic materials (amino acids, lipids, carbohydrates) and yet are able to sense light and chemicals, measure temperature and position, compute, store energy and convert energy to motion. Rather than separately manufacturing and assembling systems (as in existing engineering system construction) nature grows systems by 3D cofabrication. Intrinsically conducting polymers can perform each of these tasks and so are perfectly suited for growing lifelike systems from a single class of materials. For example, our existing conducting polymer muscles are grown in 3D and can exert maximum stresses of 35 MPa, 100 times greater than mammalian skeletal muscle. We have grown conducting polymer ribbons that can carry currents of over 10^7 A/m^2 (similar to copper wire) and have fabricated conducting polymer supercapacitors (for energy storage and recovery) having very high charge densities (10^5 F/kg).

We have also created conducting polymer transistors with switching speeds similar to neurons. New conducting polymer materials we are working on may exhibit strains as high as 20% with stresses of around 0.5 MPa, closely matching the performance of human muscle. The building blocks for biomimetic systems (artificial lifeforms) are actuators (muscles), computation (neurons), information transmission (nerves), energy transmission, energy storage (fat), structural elements (bones), energy absorption and storage (tendons and ligaments), and sensors (eyes, ears, tactile and temperature).

Critical to successful designs will be new simulation and modeling environments (Biomimetic CAD). We present such an environment and demonstrate its use in predicting the electrochemical impedance transfer function of conducting polymer actuators over greater than 7 orders of magnitude change in frequency.

Introduction

Nature's biological systems demonstrate an incredible diversity, sophistication, and range of abilities that engineers have yet to emulate. Subsystems for sensing, movement, computation, energy storage and energy delivery are constructed from four basic organic materials: fatty acids, sugars or carbohydrates, amino acids, and nucleotides. These subsystems are cofabricated in place during development from embryo through to adulthood.

In seeking to emulate Nature, humankind has relied on a diverse set of material types (metal, ceramics, semiconductors) to mimic the different functions of a life system. Almost exclusively, these materials are low molecular weight, isotropic materials. An alternative approach which promises

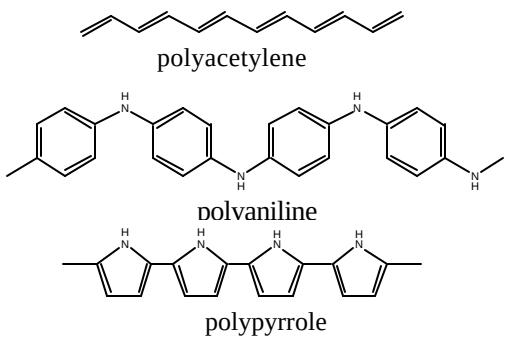

Figure 1: Chemical structure of some common conducting polymers.

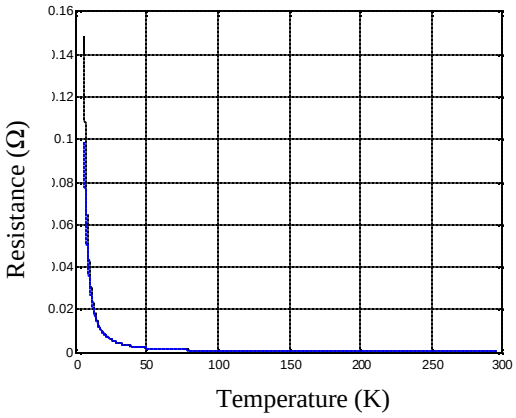

Figure 2: Mott model (dashed line) fit to the resistivity of PPy synthesized at -20 C. As the temperature approaches absolute zero, the resistance goes to infinity.

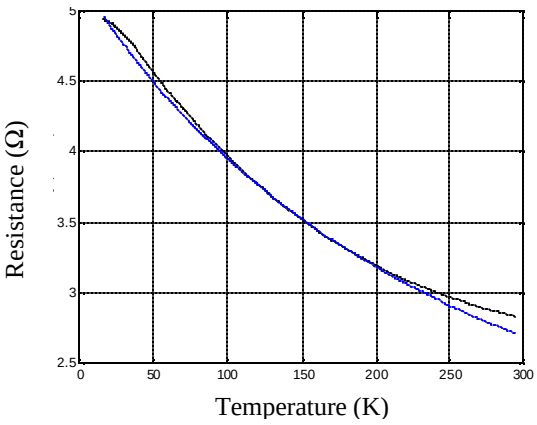

Figure 3: Sheng Model (dashed line) fit to data for polypyrrole synthesized at –40 C. As the temperature approaches absolute zero, the resistivity stays finite.

simpler manufacturing and assembly is to mimic Nature's use of high molecular weight anisotropic materials.

We use the material class of conducting polymers to build actuators (muscles), transistors (computation), wires (information transmission and energy delivery), supercapacitors (energy storage), and strain gages (position sensing) thereby building most of the elements needed for creating a biomimetic lifelike system.

Traditional polymers are electrically insulating. In a conducting polymer, the polymer backbone structure is conjugated (alternating single and double bonds). Some typical conducting polymer chemical structures are shown in Figure 1. As a pure polymer the backbone is insulating but the addition of ionic dopants to the polymer results in a delocalisation of the double bond electrons giving near metallic conductivity.

In electrochemical synthesis, as the monomer is polymerized, salt ions from the electrochemical solution are incorporated into the solid to maintain charge neutrality. The doping level can be changed after synthesis by shifting the electrochemical potential of the polymer in solution to drive ions into (or out of) the polymer. The changes in the level of ion intercalation are used to build conducting polymer transistors (conductivity change), actuators (volume change), and capacitors (charge storage).

Mechanisms of Conductivity

The temperature dependence of conductivity gives important information about the electrical conduction mechanism. In a metal, the valence bands and conduction bands overlap and so neglible thermal energy is needed for an electron to move into a vacant state. In both insulators and semi-conductors there is an energy gap between the valence and conduction bands. In the absence of thermal energy, no electrons are excited to the conduction band and the materials become insulators.

Polypyrrole synthesized at –40 ºC exhibits metallic (finite) resistivity near absolute zero while an identical synthesis at –20 ºC gives ∞ resistivity (see Figure 2 and Figure 3).

Several models have been proposed to describe the observed temperature dependence of conducting polymer conductivity.

Mott[1] developed a model to describe electron conduction in amorphous metals. Mott balances the likelihood of tunneling between random energy electron potential wells with the likelihood of gaining enough thermal energy to move to a nearby site and finds that:

$$r = r_o \exp\left(\frac{B}{T^{1/4}}\right)$$

where r is the resistivity, r_o and B are constants, and T is the absolute temperature. In Mott's model, as the temperature falls to zero, the resistivity rises to infinity.

A second model developed by Sheng[2] treats the polymer as conductive metallic domains that

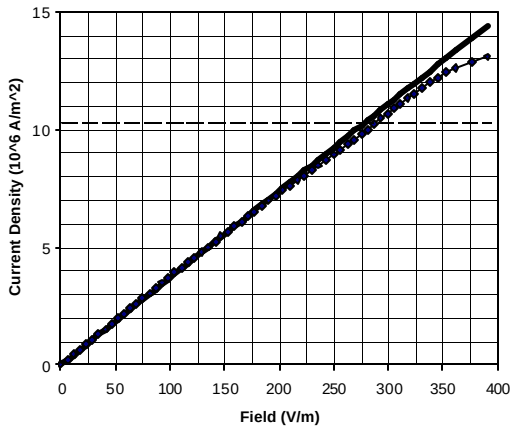

Figure 4: Measured current density vs. electric field for polypyrrole. The maximum current density of $13 \cdot 10^7$ A/m^2 is greater than the generally quoted maximum current density of 10^7A/m^2 for copper wire (dashed line). The slope of current density vs. electric field is the conductivity of the sample (37000 S/m). PPy sample grown at –40 ºC, 2.5 mm by 10 mm by ~50 mm long.

are separated by insulating barriers that electrons must tunnel through. Sheng finds that:

$$r = r_o \exp\left(\frac{T_1}{T+T_o}\right)$$

where r is the resistivity, T is the temperature, and r_o, T_0, and T_1 are constants. At high temperatures ($T >> T_o$), the resistance goes down as temperature rises. At low temperatures, there is little temperature dependence, giving a 0 K conductivity of $s_o \exp(-T_1 / T_0)$.

We have made measurements of the electrical resistivity of polypyrrole from about 5 K up to 300 K. We fit the measured resistivity to both the Mott model and the Sheng model and found that samples synthesized at –20 ºC (Figure 2) are very well described by Mott's equation for resistivity. The samples synthesized at –40 ºC (Figure 3) are quite well described by Sheng's model (fits are shown in Figure 2 and Figure 3). The large change in behavior as a function of synthesis conditions points to an important change in the structure of the polypyrrole. By better understanding how the different synthesis conditions lead to differences in structure we can optimize the properties of conducting polymers that we grow.

Conducting Polymer Wires

The densities of most metals (copper 8910 kg/m^3, silver 10500 kg/m^3) are high compared to organic materials (typically 1000 to 2000 kg/m^3). We expect that because of their lower density, conducting polymers will be able to equal or exceed the current carrying capacity per unit mass of metals such as copper and silver.

In Figure 4, the current density in a polypyrrole strip is plotted against the electric field. The strip was destroyed at a current density of 1.3 x 10^7 A/m^2, slightly higher than the typically quoted maximum safe current density of 10^7 A/m^2 for copper wire[3].

For applications in robotic and prosthetic limbs where reducing weight improves the performance, the current density per unit mass is a useful measure of a material. The densities of copper and silver are 8 to 10 times higher than conducting polymers (density of polypyrrole = 1300 kg/m^3) so conducting polymers will be very competitive.

Conducting polymers are also potentially cheaper and can be biodegradeable, leading to disposable electric motors.

Strain Gages

Strain gages provide a mechanism for measuring a position or force. When a material is stretched it becomes longer and generally the cross-sectional area decreases. In a conductive material, the dimensional changes affect the electrical resistance as well.

We have fashioned strain gages from polypyrrole strips and tubes. A plot of the output (changing resistance) versus the strain is shown in Figure 5. These conducting polymer strain gages have several properties that open new applications where traditional strain gages are impractical. In particular, because they are made of flexible plastic, the PPy gages can undergo maximum strains of several percent whereas silicon or metal film gages are limited to ~0.1 or 0.2%. PPy gages can also be used in applications that not only require large strain but that also require bending or flexing of the gage itself. In much the same way, the mammalian muscle spindles transduce position yet are as flexible as the muscle fibers themselves.

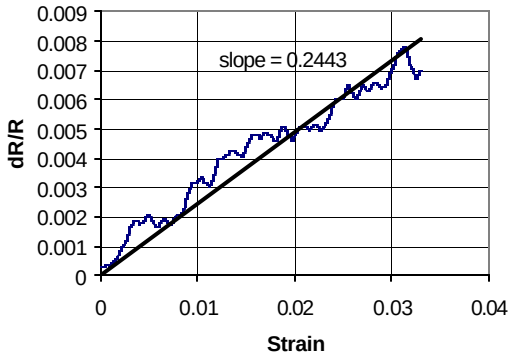

Figure 5: Conducting polymer strain gage output versus strain. dR/R is the change in resistance divided by the initial resistance. The strain gage used is a 190mm long by 0.6 mm diameter tube of polypyrrole. The maximum strain shown here of over 3% is far beyond the range of most existing strain gage technologies.

Conducting Polymer Muscles

Nature has evolved a very impressive actuator that converts chemical energy to mechanical energy. Mammalian skeletal muscle exerts 350 kPa and undergoes contractions of up to 20% at rates as high as 100%/s. Muscle is flexible and because of its cellular nature can be built up fiber by fiber into a wide range of different shapes and sizes for different applications (e.g. quadriceps vs. finger muscles).

Artificial conducting polymer muscles exert forces per cross-sectional area of up to 35 MPa, over 100 times the force per cross-sectional area of skeletal muscle[4]. So far, the maximum strain we have measured is 7% and is more typically around 2%. We have achieved contraction rates of up to 3%/s.

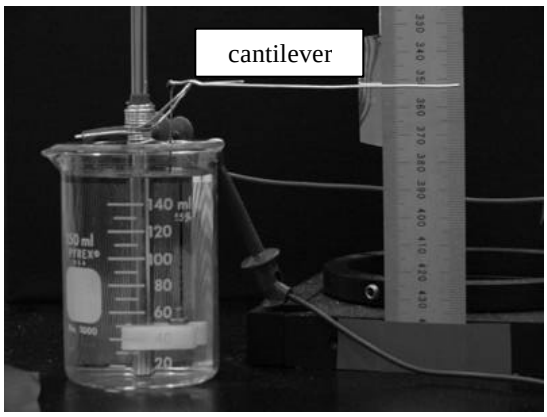

Figure 6: Photograph of a one of our conducting polymer actuator test platforms. The conducting polymer muscle (polypyrrole) is the thin black strip (0.7 mm diameter) to the right inside the beaker. A cantilever can be used to amplify the contraction and expansion.

Figure 6 shows a photograph of a typical actuator test platform as used in our laboratory. The polypyrrole muscle and a counter electrode (which can also be polypyrrole) sit in an electrochemical bath. As the voltage between the electrodes changes, ions are driven into or out of the polymer electrode, causing it to expand or contract.

At constant stress, the amount of expansion or contraction is proportional to the amount of charge transferred:

$$e = a \cdot r$$

where e is the strain, r is the charge transferred per unit volume, and a is the strain to charge ratio[5]. a is experimentally measured and is roughly related to the size of the ions.

In order to predict the strain rate, we have developed a model relating the current flow into the polymer to the potential applied to the cell[6]. Expressed as a function of the Laplace frequency variable $s = jw$, the admittance Y is:

$$Y(s) = \frac{s}{R} \cdot \frac{\frac{\sqrt{D}}{d} \cdot \tanh\left(\frac{a}{2} \cdot \sqrt{\frac{s}{D}}\right) + \sqrt{s}}{\frac{\sqrt{s}}{RC} + s^{3/2} + \frac{\sqrt{D}}{d} s \cdot \tanh\left(\frac{a}{2} \cdot \sqrt{\frac{s}{D}}\right)}$$

where R is the resistance of the solution and contacts, C is the double layer capacitance of the solution polymer interface, d is the thickness of the double layer, D is the diffusion coefficient of the ions in the polymer, and a is the thickness of the polymer.

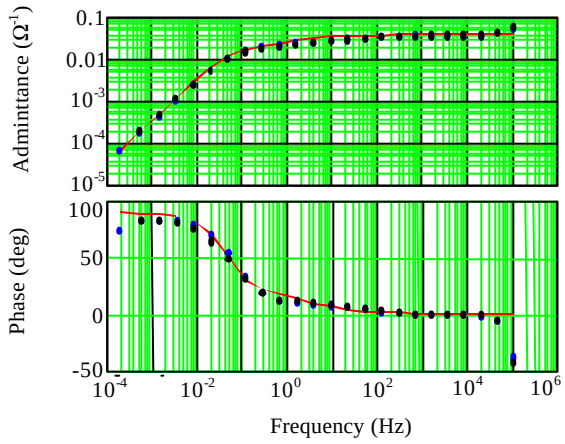

Figure 7: Electrochemical impedance of a polypyrrole muscle. The solid line was fit to the data by varying only a single parameter. Experimental data is extremely well described by the model between 10^{-3} Hz to over 10^{4} Hz. (Admittance is for a polypyrrole strip 8.5 mm thick).

One of the important limits to speed of the polymer is the diffusion rate of ions into the solid material. As a result, thinner films have faster response because the diffusion distance is smaller. As we aim for better performance, we have been electrochemically growing films as thin as 8-10 μm.

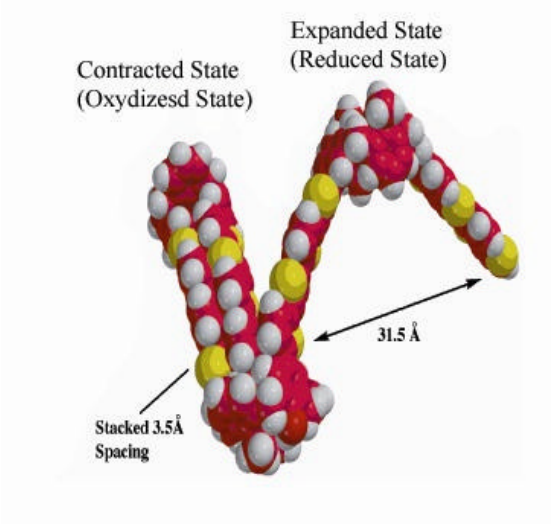

Figure 8: Structure of a molecular actuator. The calix[4]arene bithiophene monomeric compound. The left side of the figure represents the molecule in its contracted state (oxidized) and the left side its expanded state (reduced).

A measured electrochemical admittance is shown in Figure 7. The model for admittance (solid line) was fit to the data with one free parameter. As can be seen from the plot, the model very accurately predicts the frequency response of the polymer over more than seven orders of magnitude.

Polymer Conformation Changes

While the conducting polymer actuators based on ion intercalation between the polymer chains give impressive performance, they are limited in maximum strain because the polymer molecular backbone is unable to change length. New materials with large free volume that undergo conformational changes will result in materials that can expand and contract by 10 to 20%. In this case the active properties of the conducting polymer are intrinsic to the polymer backbone[7].

These novel polymers hold the promise of generating strains of 20% or more at stresses in excess of 0.5 MPa. A number of candidate thiophene based molecular conducting polymers actuators are synthesized and characterized in our laboratories. One compound under study features an accordion like polymer formed by calix[4]arene flexible hinges separated by conducting thiophene rods (Figure 8). In this particular compound, actuation results from π-π stacking of thiophene oligomers upon oxidation, producing a reversible molecular displacement (Figure 9).

We have also observed experimentally that related polymers can undergo fast and large volume changes when solvent is removed or added, thus suggesting that these new compounds once polymerized contain a large free volume. Some of the films we have grown have been brittle and

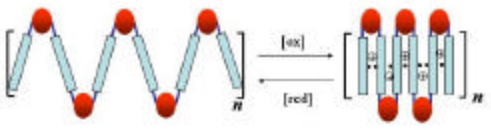

Figure 9: Reversible electrochemical molecular actuation mechanism. The thiophene oligomers are attracted to each other to form p-p stacking upon oxidation

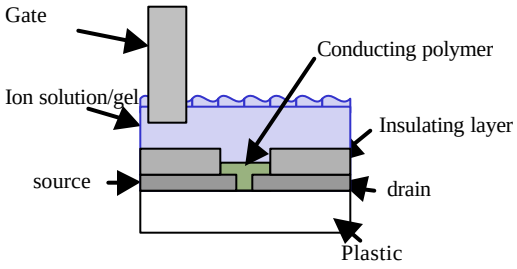

Figure 10: The conducting polymer electro-chemical transistor. The source to drain resistance is changed by raising or lowering the gate potential to drive ions into or out of the active region of conducting polymer (exposed to the solution).

difficult to handle but with improved molecular weights superior mechanical properties are expected. We have recently started to create polymer blends of the active polymer with a polymeric sulfonate to increase the mechanical robustness of the films[8]. These novel polymer composites have been successfully synthesized in our laboratory and their active and passive mechanical properties are currently being evaluated.

Electrochemical Transistors

If the ion content (or the doping level) of a conducting polymer is reduced far enough, the conductivity begins to drop dramatically. With no doping at all the backbone of conducting polymers becomes insulating and no current can flow.

Wrighton first made use of this property of conducting polymers to make transistors[9]. Conducting polymer is grown across a gap between two electrodes. By driving ions into or out of the polymer, the resistance between the two electrodes can be changed, analogous to the operation of a FET transistor (Figure 10).

We have built conducting polymer transistors based on polyaniline doped with chlorine ions. In our transistors, the source to drain resistance changes by over two orders of magnitude.

With transistors we can construct the logic, amplifiers, and feedback loop circuits that are needed to create an intelligent biomimetic system. Computations can be performed. Signals from sensors can be combined and analyzed. The output from a strain gage can be amplified to drive a muscle creating a simple reflex loop.

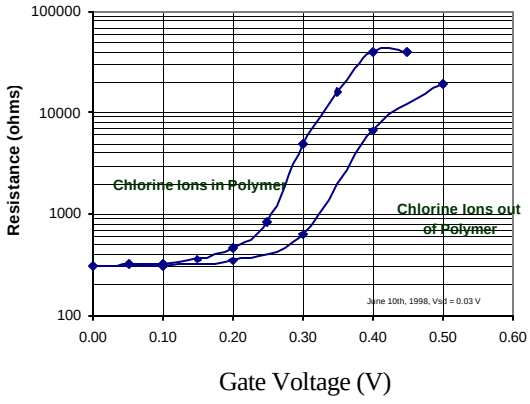

Figure 11: Source to Drain resistance of a polyaniline transistor.

Supercapacitors

Animals store energy in the form of sugars and complex carbohydrates. Engineered biomimetic systems also need to store energy. At low frequencies, conducting polymers behave as supercapacitors, able to store significant amounts of charge.

The insertion of ions into conducting polymer systems as they are doped and undoped takes place over the bulk volume of the material rather than just at the surface and as a result, a very large amount of charge can be stored per unit volume.

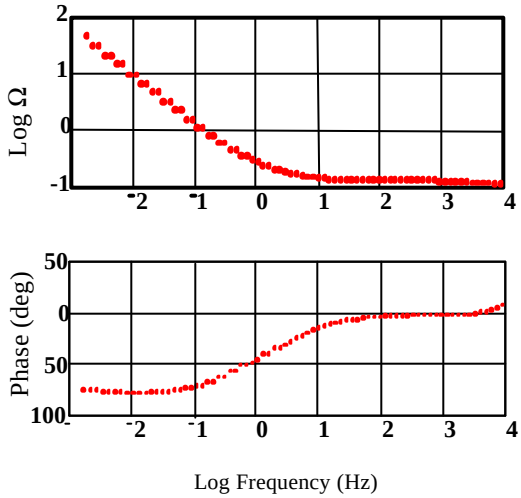

Figure 12: Plot of the measured electrochemical impedance of polypyrrole. At low frequencies, the behaviour is purely capacitive (log slope of and a phase of –90º). The material capacitance is 10^5 F/kg.

Figure 12 shows a plot of the electrochemical impedance of a strip of conducting polymer. At frequencies below 1 Hz, the behavior of the polymer is almost purely capacitive with the very high capacitance of 10^5 F/kg. A strip of material of around 10 mm square by 1 mm thick has a capacitance of near 1 F.

A conducting polymer supercapacitor could be used for energy storage for biomimetic systems, either as a local source of energy within a muscle or as an energy storage for the biomimetic system as a whole.

Modeling: Biomimetic CAD

As a first step to providing an engineer with tools to design conducting polymer based systems, we have been developing computer based models for the electrochemical performance of polypyrrole.

These models implement the description of conducting polymer electrochemical behavior and are helping us predict the performance of actuator designs.

For low current (lower contraction rates), the model of admittance described above and shown in Figure 7 has proven to be very accurate as the geometric parameters of our actuators are varied. We can accurately predict the frequency response of different geometries of conducting polymer actuators over many decades of frequencies.

At higher currents resistive drops in the polymer material begin to affect the electrochemical behavior. We are currently developing a finite difference model to include resistive (iR) drops in the polymer material so that we can extend the applicability of our model.

Ultimately we will incorporate into this model predictions of the electrical, mechanical, and chemical properties and interactions of the material. Much as engineers today rely on CAD to design and build devices with low molecular weight materials, in the future we will require tools to aid in the design of high molecular weight materials.

Cofabrication Methods

Conducting polymer materials can be grown from the monomer form through either chemical or electrochemical oxidation. In our research on polypyrrole, we have used electrochemical oxidation almost exclusively.

Actuators, strain gages, wires, supercapacitors and transistors are all fabricated by electrochemically depositing polypyrrole. Because so many different types of device can be created from exactly the same material they can be fabricated together in parallel (cofabrication), avoiding the need for later assembly.

Biological systems cofabricate in a truly three dimensional manner as cells divide and differentiate. Polymer material can be grown electrochemically using spatially localized deposition to create 3D micro scale structures[10,11,12]. Such a technique will be used to build small scale truly three dimensional conducting polymer systems that will integrate all the elements needed for a conducting polymer lifelike system.

Conclusions

Conducting polymers offer a great range of capabilities for future biomimetic applications. We have developed conducting polymer muscles, strain gages, transistors, and supercapacitors to be components of future biomimetic systems.

We are also developing the computer aided design tools that we will need to take advantage of the range of material properties that are offered in the class of conducting polymers.

Looking to the future, systems that integrate the multiple functions of conducting polymer will enable us to build truly biomimetic systems from the molecular scale.

Acknowledgements

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