ARTICLES

The Molecular Wire Approach to Sensory Signal Amplification

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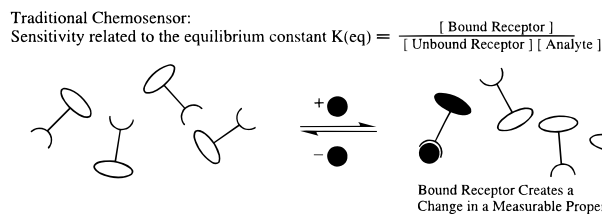*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

Introduction

A chemosensor is a molecular device designed to detect a specific molecule or class of molecules.[1a,b] Research in this field is poised for considerable advances in the coming years with the advent of diverse methods for analyte detection and new developments in the field of molecular recognition. To date, the most common signal transduction schemes utilize optical or electrical methods.[1c] Fluorescence is a highly sensitive optical transduction method, and analyte binding events that produce an attenuation, enhancement, or wavelength shift in the emission can be used to produce a functional sensor.[1d] Changes in absorption spectra, while less sensitive, have also been extensively used.[1e] Redox processes are widely used in electrical-based transduction methods, and typical systems function in either potentiometric or amperometric modes.[1f] Conductometric detection schemes based on SnO_2,[1g] conducting polymers,[1h] and phthalocyanines[1i] have also been investigated.
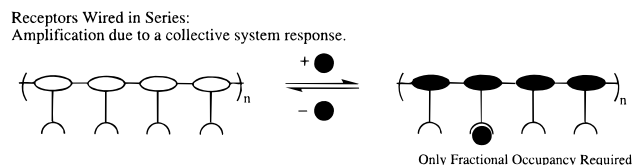
As shown in Scheme 1, a chemosensor is composed of two functional elements, a receptor and a reporter group, which need not be separate in identity. When the equilibrium between the analyte and receptor is rapid, sensors can be produced that provide a real-time response, which continuously varies with the concentration of the analyte. The detection sensitivity is determined by both the ability to measure the transduction event and the association constant of the receptor—analyte complex. As a result, when pursuing higher sensitivity one may seek instrumentation improvements and/or endeavor to increase the magnitude of the association constant of the receptor—analyte complex. The standard approach to higher association constants is to design highly preorganized receptors that do not pay a high entropic penalty for complexation. The downside of this approach

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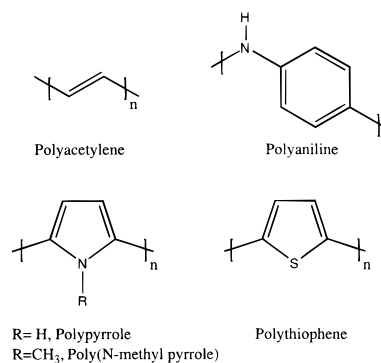
Scheme 1

Traditional Chemosensor:
Sensitivity related to the equilibrium constant $K(eq) = \dfrac{[\text{ Bound Receptor }]}{[\text{ Unbound Receptor }][\text{ Analyte }]}$

Bound Receptor Creates a Change in a Measurable Property

Scheme 2

Receptors Wired in Series:
Amplification due to a collective system response.

Only Fractional Occupancy Required

Scheme 3

Polyacetylene   Polyaniline

R= H, Polypyrrole   Polythiophene
R=CH₃, Poly(N-methyl pyrrole)

is that preorganization and high association constants generally result in slow dissociation kinetics. A molecular chemosensor with slow kinetics or an irreversible response cannot yield a reversible real-time response. Molecular systems displaying irreversible or slow behavior are nonetheless useful, but are properly called dosimeters or indicators. Methods may be developed to allow irreversible systems to function in a sensory device. For example, the device can be "reset" by chemical, electrochemical, photochemical, or physical events. These processes can cause the analyte to dissociate from the receptor or can result in the replacement of the indicator (chemosensor) molecules. Such approaches have the disadvantage of introducing additional complexity into the sensor devices.

This Account describes an approach to enhancing the sensitivity of chemosensors in effect by "wiring chemosensory molecules in series" (Scheme 2). Recent work from my research laboratory has shown that this *molecular wire* approach provides a universal method by which to obtain signal *amplification* relative to single molecule systems. I will use the term molecular wire interchangeably with conducting polymer. For the sake of clarity, some representative conducting polymers are shown in Scheme 3. These materials are insulators in their neutral (undoped)

states and become conductive with oxidation or reduction (p- or n-doped, respectively). My choice of the molecular wire terminology is pedagogical and is intended to establish a conceptual framework. However, I must also add that it is proper to describe these systems as molecular wires since the key feature of the conducting polymer is that it provides extended electronic communication and transport. Indeed, these are properties that we typically associate with macroscopic wires. I employ the terms amplification and sensitivity enhancement to indicate where a single event, the binding of an analyte, in a supramolecular polyreceptor system produces a response larger than that afforded by a similar interaction in an analogous small monoreceptor system .

Amplification by Polyreceptor Assemblies

It is implicit that in order to obtain the ultimate amplification by the polyreceptor assembly shown in Scheme 2, one must utilize a collective system response. In other words, properties that are influenced only by a molecule's immediate surroundings will not yield significant amplification, whereas properties determined by the collective system will display amplification. As an example, consider NMR chemical shifts. Because chemical shift is generally sensitive only to the immediate environment, such signals will not yield dramatic sensitivity enhancements in polyreceptor chemosensor systems. Similarly, in conjugated polymers it has been established that the optical band gaps are determined by a relatively small number of repeating units. For example for thiophene oligomers greater than 7 units long, the band gap is constant.[3] Hence, changes in the absorption spectrum alone are inadequate to give large enhancements in a chemosensory response. Transport properties, on the other hand, reflect the bulk characteristics of a system and display an exponential dependence. Hence these properties are dramatically influenced by small numbers of binding events. By way of illustration, consider the polyreceptor assembly shown in Scheme 2 to be a molecular wire which is capable of transporting electrical current. If analyte binding produces a resistive element in the wire, then all the electrons flowing through the molecular wire will experience an impediment. Hence, the transport of many conducting electrons can be reduced by a single binding event. This process in which a single binding event influences many events also provides signal enhancement. There is also amplification due to the fact that the binding constants of all the receptors are additive. Hence the effective binding constant of a polyreceptor system can be very high while still maintaining reversibility.

There have been a number of studies utilizing a conducting polymer's electrical properties in detection schemes which cannot be covered in this account.[2] Noteworthy examples include acid−base responses and enzyme-mediated doping reactions.

## Chemoresistance as a Highly Sensitive Transduction Signal

Conductometric sensory devices are among the most simple and versatile. High-precision resistance measurements can be readily made with simple electronics. A limitation to these types of sensors, which have traditionally been inorganic solids, has been their lack of selectivity. Organic conductors with receptors directly affixed to the backbone offer a viable approach to selectivity.

Researchers in the area of conducting polymers have long understood the sensitivity of conductivity to molecular structure and composition. Indeed, the ultimate conductivities of the prototypical conducting polymer, polyacetylene, were realized only when procedures were developed which minimized the number of saturated defect sites.[4] Saturated sites in polyacetylene represent resistive elements that impede electrical transport in the system. The high sensitivity to defects is a manifestation of the previously mentioned amplification. Conformational defects can also reduce electronic delocalization and are well known to produce resistive elements. In fact, early attempts to make soluble polyacetylenes by appending side chains to the polymer backbones produced nonplanar structures that displayed very low conductivities.[5] A classical example of the high sensitivity displayed by conducting polymers to conformation was demonstrated by comparing the conducting properties of polypyrrole with those of poly(*N*-methylpyrrole).[6] Polypyrrole in its oxidized form exhibits maximum conductivities in the range of 10^2 S/cm. Poly(*N*-methylpyrrole), on the other hand, exhibits conductivities in the range of 10^{-3} S/cm. The almost 10^5 difference between these polymers emanates from the steric repulsion imposed by the *N*-methyl group. Crystallographic structure determinations of oligomers showed that the methyl group prevents the polymer backbone from a rigorously planar geometry. This nonplanarity not only reduces the conjugation along the polymer backbone, but also serves to decrease the electronic communication between polymer chains. The latter effect can be understood by considering a macroscopic analogy: Flat sheets of paper pack efficiently with a high degree of contact between neighboring sheets; however, the physical packing of sheets of paper that have been crinkled is much less efficient. Hence, the intermolecular charge transport between polymer chains will be greatly reduced in nonplanar structures.

Electrostatic factors are also known to produce dramatic changes in a conjugated polymer's conductivity. An early example of this effect was observed in n-doped polyacetylene.[7] It was determined that at very low doping levels, the polymer's conductivity was a very low (2.5×10^{-8} S/cm). Exposure to THF vapor raised the conductivity to 2.5×10^{-4} S/cm. The explanation for this factor of 10^4 increase is that, in the THF-free state, strong electrostatic interactions pin the anionic soliton carriers to the Na^+ counterions. Coordination of THF to the Na^+ ions reduced this interaction, thereby liberating the carriers to provide a higher mobility and consequently enhanced

conductivity. Other observations in conducting polymers may also be attributable to similar solvation or screening effects. Polyaniline has been long understood to have a conductivity that is critically dependent upon the degree of hydration.[8] Dehydration of this polymer results in a reduction in conductivity. More recently, the interaction of *m*-cresol with polyaniline has been shown to give large enhancements in conductivity.[9] Changes in the amount of *m*-cresol in polyaniline films can also produce reversible changes in the conductivity. However, irreversible effects are also operative, such as *m*-cresol mediated crystallization of the polymer. Higher degrees of crystallinity generally produce greater conjugation as well as interchain interactions, both of which lead to higher conductivity.

To produce large resistive elements in conductive polymer sensors, we designed receptor systems that induce both electrostatic and conformational perturbations. The first structure investigated incorporated simple crown-ether macrocycles into a polythiophene structure.[10] As shown in eq 1, we envisioned that ion coordination

$$(1)$$
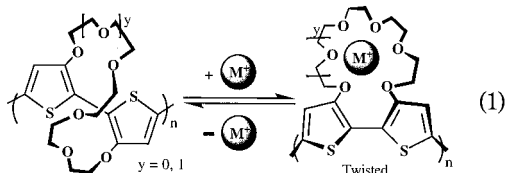
should produce conformational changes in the polymer's backbone. This premise is based on the fact that the crown-ether moiety will prefer to distribute the oxygen atoms in a spatially uniform manner around the ion. Polymers **1** and **2**, which are 15-crown-5 analogues, are expected to produce the largest effects with Na$^+$. Likewise polymer **3**, a 18-crown-6 analogue, should display the
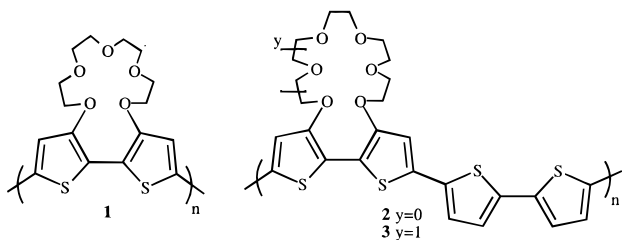
largest response with K$^+$. These expected results were realized with polymers **1** and **2**, which display 91-nm and 63-nm blue shifts, respectively, when exposed to 0.1 mM Na$^+$ solutions. While blue shifts were observed for both K$^+$ and Li$^+$ (0.1 mM) in these polymers, the shifts due to these ions are considerably lower, confirming the selectivity for Na$^+$. Likewise, polymer **3** shows the largest shift in its λ_{max} for K$^+$ (45 nm) and a smaller blue shift for Na$^+$ (30 nm). These optical changes are all consistent with the proposed twisting mechanism. Additional features of this system are the electronic perturbations due to the coordination of the metal ion to the oxygens that are directly attached to the thiophene and the charged nature of the metal cations. This interaction should decrease the donation of the oxygen lone pairs to the polymer's π
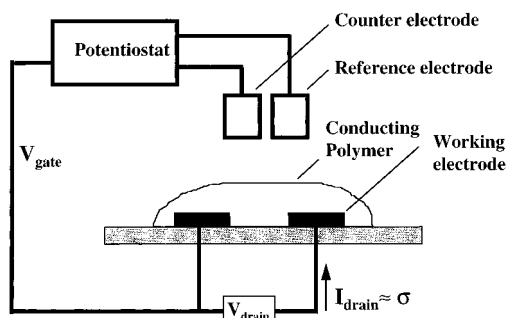

FIGURE 1. Schematic respresentation of an electrochemical device for the determination of a polymer's conductivity as a function of analyte and applied electrochemical potential.[13] A cross-sectional view is shown of microelectrodes (spaced at 1−5 μm) covered with an electroactive polymer. When there is no voltage applied (or voltage offset) between the microelectrodes ($V_d = 0$), then sweeping the applied electrochemical potential (V_g) produces a cyclic voltamogram. When V_d is finite (0.01−0.05 V), sweeping the applied potential will produce a current between the microelectrodes which is proportional to the polymer's conductivity.

system and hence compromise the ability of the complexed repeating units to stabilize positive charge. The conductive state of most conducting polymers (particularly electron-rich thiophenes) is generally produced by oxidation or p-doping. The resultant carriers are cationic, and the decreased ability of repeating groups with occupied receptors to stabilize positive charge, as well as the electrostatic repulsions with the charged cations, create barriers to electronic transport. Although we observed predictable shifts in λ_{max}, polymers **1**, **2**, and **3** displayed relatively low binding constants, which were in the range of 10^5 M^{-1}. Low binding constants and problematic solubility properties complicated electrochemical studies.

The calix[4]arene framework provides a highly organized arrangement of oxygen atoms and therefore is an ideal scaffold for the design of ionophores.[11] As a result, we extended our design to create the more rigid (preorganized) receptor, **4**, which does not suffer from the limitations of **1**−**3**.[12] Receptor **4** displays association constants (eq 2) for K$^+$, Na$^+$, and Li$^+$ of 7.3 × 10^5, 7.6 ×

$$(2)$$

M$^+$ =K$^+$, Na$^+$ or Li$^+$
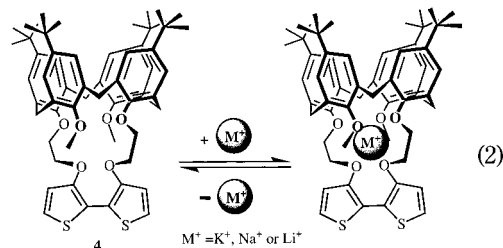
10^7, and 1.9 × 10^6, respectively. Hence, this system exhibits a binding constant that is about 10^3 greater than that of **1** and **2**, and almost a 100-fold selectivity for Na$^+$ relative to K$^+$ and Li$^+$.

Polymer **5** was synthesized from **4** by first iodination and polymerization by a Stille coupling. This material exhibits a very specific colormetric response to Na$^+$ with no detectable changes in response to Li$^+$ and K$^+$. The
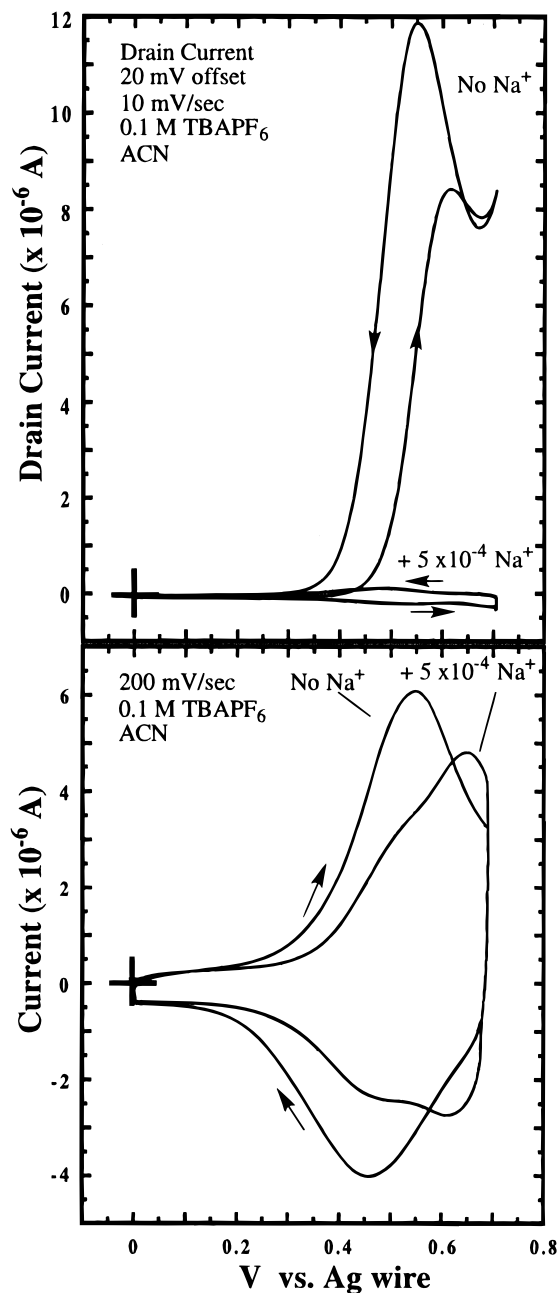
FIGURE 2. CV and corresponding conductivity profile (drain current) as a function of electrochemical potential for polymer **6** in the absence and presence of 0.5 mM Na⁺.

Na⁺-induced blue shift of 24 nm exhibited by **5** is consistent with our initial design. Again, we believe that the polymer conformation adjusts to produce the most spherically symmetric disposition of the oxygens around the ion. However, there can be complications, and this trend is not always observed from polymers derived from **4**. Receptor **4** exhibits multiple (at least three) major conformations in solution, which were shown by NMR to slowly interconvert. An X-ray crystal structure of **4** shows a nonplanar conformation for the bithiophene moiety.[12] As a result, in the absence of other factors we anticipate a nonzero dihedral angle between the thiophene residues. The competitive stability of multiple conformations manifests different results when **4** is incorporated into polymer
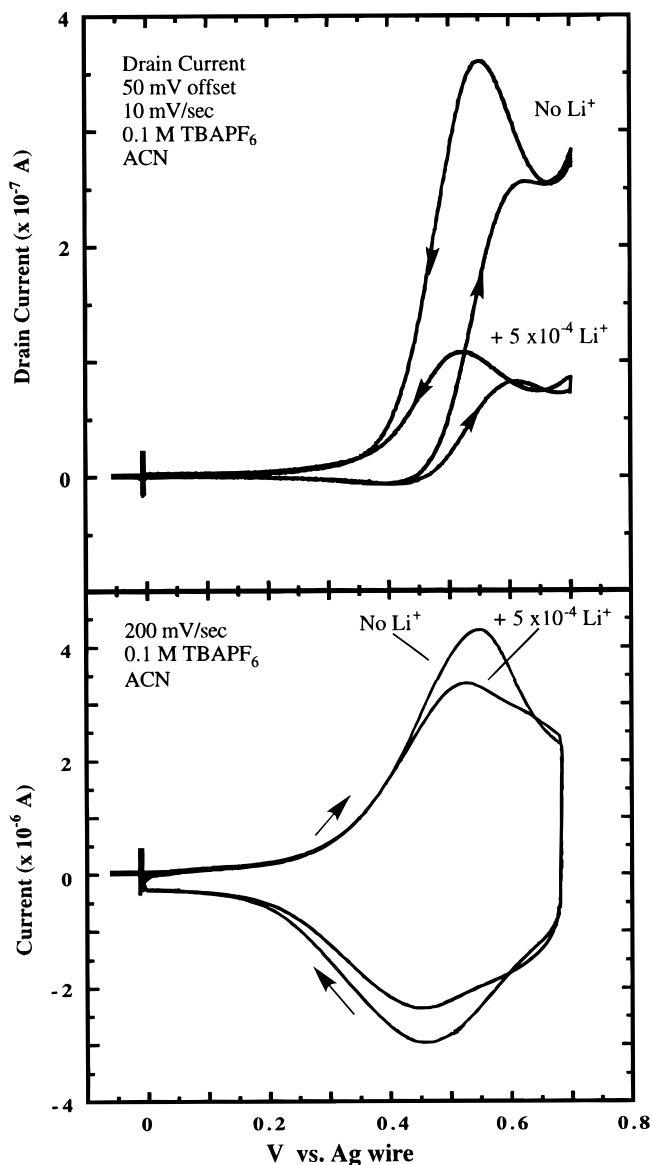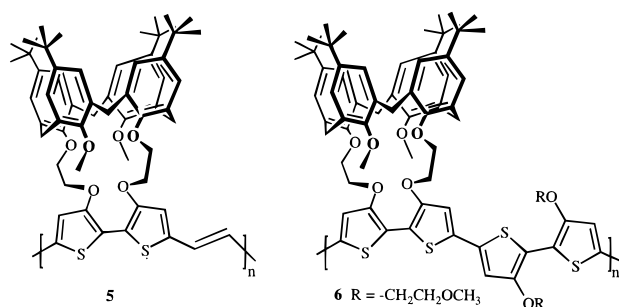

FIGURE 3. CV and corresponding conductivity profile (drain current) as a function of electrochemical potential for polymer **6** in the absence and presence of 0.5 mM Li⁺.

6. In the case of **6**, we again observe no response

whatsoever in the optical absorption spectrum upon exposure to Li⁺ or K⁺. However, Na⁺ produces a red shift in the absorption onset of **6**. Hence, Na⁺ appears to induce a more planar conformation in **6**, which is the opposite of what was observed for polymers **1**, **2**, **3**, and **5**.

To demonstrate chemoresistive effects, we utilized a method developed by Wrighton for the in situ determination of a polymer's conductivity as a function of an applied electrochemical potential (Figure 1).[13] This method allows for rapid determination of both the cyclic voltammogram and the conductivity. The conductivity is directly proportional to the drain current when the test devices are functioning in a transistor mode. Figure 2 shows the chemoresistive response of **6** to Na$^+$. As shown, the polymer's cyclic voltammetry displays a pronounced anodic shift upon treatment with 0.5 mM Na$^+$. The conductivity in the Na$^+$-free state is large and easily detected; however, this conductivity appears to be totally absent after Na$^+$ treatment, indicating a >99% reduction in the conductivity.[12] As shown in Figure 3, Li$^+$ produces slight changes in the shape of the cyclic voltammogram, but does not significantly alter the peak potential of the polymer's oxidation. Nevertheless, treatment with 0.5 mM Li$^+$ produces a 69% drop in the polymer's conductivity.

Li$^+$ binding to polymer **6** must produce only a weak electrostatic perturbation and not change the conformation. This is concluded because Li$^+$ treatment did not result in a change in the polymer's oxidation potential or optical characteristics. We consider this result to be particularly important because it is direct proof that *chemoresistivity provides a higher sensitivity than do other measurable signals*. It should also be noted that the amplification confirms the advantages of the polyreceptor system (Scheme 2). The polymer's band gap and hence optical characteristics are determined by the local electronic structure, which is equivalent to a low molar mass chemosensor (Scheme 1). Additionally, the charged states (polarons or bipolarons) introduced by oxidation are also localized to a few repeat units. Hence, the optical and electrochemical properties are local properties and are not as sensitive as conductivity, which is a bulk transport property.

We have further confirmed the generally high sensitivity of chemoresistivity in other systems that respond to electron-deficient organic species.[14,15] The binding of viologen dications **7** to the macrocycle-containing polymers **8** and **9** also resulted in attenuated conductivities.
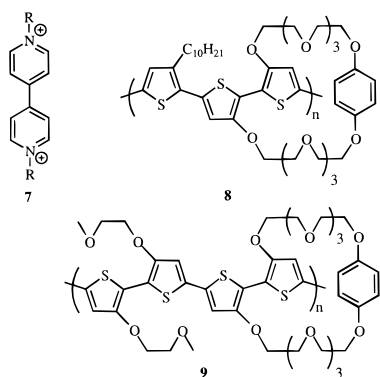
We find that, while the potentiometric response of these polymers exhibits no direct correlation with the binding events, the conductivities are uniformly decreased with
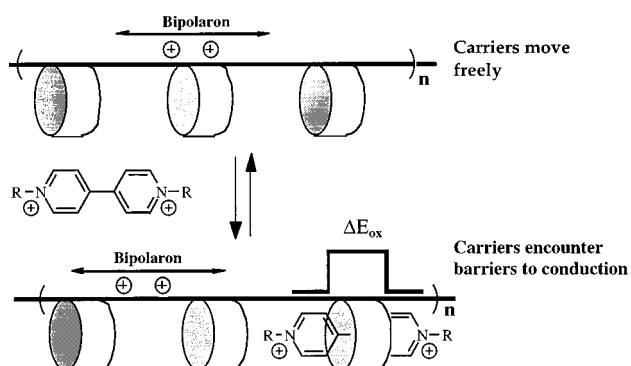

FIGURE 4. Proposed mechanism for attenuation of conductivity by viologen binding to cyclophane receptors.

viologen binding. Polymers with the same electronic structure but that lack the cyclophane were also investigated. However, these polymers did not display significant changes in conductivity with exposure to viologen analytes. As shown in Figure 4, we attribute these effects to charge-transfer interactions between the polymer and the viologen, which perturb the local redox potential and create barriers to carrier transport. This barrier can be considered a resistive element that impedes charge transport. Consistent with this interaction, we found the most electron-rich polymer, **9**, to exhibit the largest effects.

It is important to note that conducting polymers and conducting polymer blends which lack receptors have been investigated in array detection schemes such as artificial nose devices.[16] Conducting polymer materials show great promise in these applications and display resistive responses to organic vapors. The formation of many polymers with varying response factors to different vapors produces an array device that mimics mammalian olfaction. The responses to various vapors can be either positive or negative (enhanced or attenuated conductivity) and are dependent upon the method of preparation, the composition, and the counterion. The response mechanism may be the result of enhanced/reduced screening of electrostatic interactions between the carriers and the counterions. Alternatively, it could be due to volume expansion of the polymer films, conformational changes, or a mixture of effects. In either case, a nonspecific but different array response is obtained for exposure to analyte vapors. The array response provides a fingerprint to the analyte and can be deconvoluted to provide a measurement. These arrays have been principally limited to gas detection. The systems described here have well-defined receptors that create highly specific responses which can in principle be used to create highly accurate array devices. Additionally, the molecular recognition-mediated changes function in solution, and as such open the possibility for the formation of an artificial tongue.

## Amplification via Energy Migration

As mentioned earlier, a conductive polymer's band gap is determined by a reasonably small number of repeat units.[3] As a consequence, simple measurements of the optical absorption cannot produce large enhancements in sensitivity. To produce amplification, a transport

property must be included in the measurement. This is a natural application of conjugated polymers because they are exceptional systems for the transmission of energy over large distances. For example, poly(phenyleneethynylene), **10**, which exhibits a lower band gap at the

10
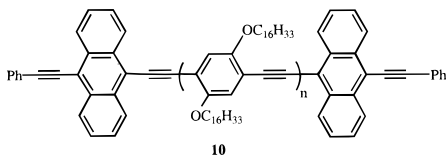
polymer's terminus, shows dominant (>95%) emission from states localized to the terminal anthracene groups.[17] Thus, in this system the excited states migrate rapidly to the anthracene groups where they are trapped. Similar effects and explanations have become commonplace in electroluminescent polymers. In multilayer systems, emission has been shown to selectively emanate from minor regions of the polymer that are energetically favored.[18] This aspect, where a small component in a mixture effectively dominates the total emission, represents *amplification*. Indeed, in the synthesis of ladder polymers my group has utilized fluorescence to reveal defect structures present in low concentration that were not readily detected by other spectroscopic measurements.[19]

To design polyreceptor chemosensors, we needed to develop analyte binding schemes that would result in reversible changes of a polymer's emission intensity or wavelength. As mentioned earlier, we anticipated that the transport characteristics of the excitations would provide amplification. As a test of this amplification method, we investigated several cyclophane polymers[20,21] that should reversibly bind electron-poor viologen analytes.[22] Given that fluorescence-based chemosensors can be developed from both single receptor and polyreceptor systems, this situation is ideal for determinations of the degree of amplification. In this context we have studied the fluorescence quenching by viologens in **11**, a single receptor chemosensor, and **12**, a polyreceptor chemosensor. As

11
R=OC$_{12}$H$_{25}$

12
R=CON(C$_8$H$_{17}$)$_2$
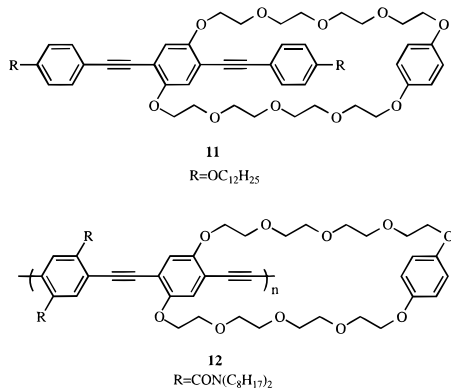
illustrated for **12** in Figure 5, an excitation is generated randomly along the polymer backbone. This excitation may be tightly bound as an exciton or may be in equilibrium with free carriers as it migrates throughout system.[23] Upon encountering a viologen occupied receptor, the excitation is quenched. As shown, the viologen
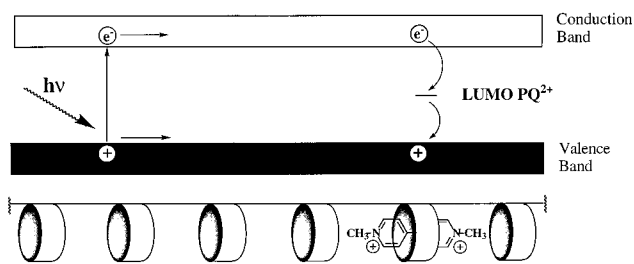
FIGURE 5. Schematic band diagram illustrating the mechanism by which the molecular wire receptor assembly can produce an enhancement in a fluorescence chemosensory response. The horizontal dimension represents the position along the conjugated polymer shown schematically at the bottom. Excitations are created by absorption of a photon (*h*ν) and then migrate along the polymer backbone. Paraquat binding produces a trapping site whereby the excitation is effectively deactivated by electron-transfer quenching.
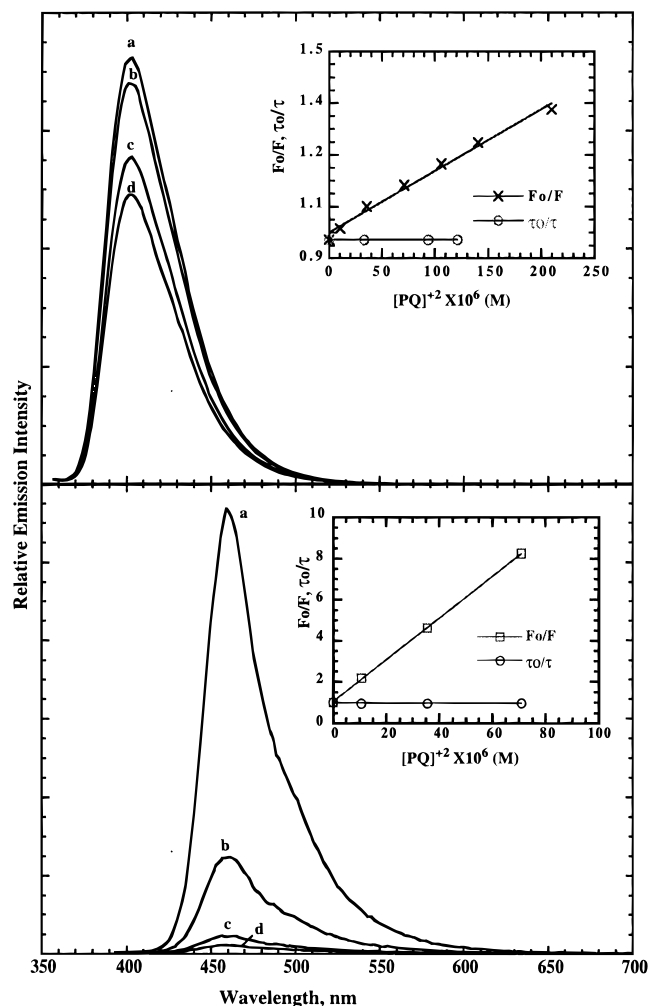

FIGURE 6. Emission spectra of **11** (top) and **12** (bottom) as a function of added (PQ^{2+}). The curves are labeled to indicate the amount of PQ^{2+} added: (a) [PQ^{2+}] = 0, (b) [PQ^{2+}] = 3.56 × 10^{-5} M, (c) [PQ^{2+}] = 2.10 × 10^{-4} M, (d) [PQ^{2+}] = 3.45 × 10^{-4} M. The Stern–Volmer plots are shown as insets and the plots show τ$_0$/τ to be invariant with added PQ^{2+}.

has an empty state (LUMO) in the band gap, and the quenching occurs via electron transfer from the polymer to the viologen, followed by back electron transfer to the polymer. As planned, the cyclophane receptors endow

these materials with an affinity for viologens, and the fluorescence data yields a bimolecular binding constant for paraquat (**7**, R = CH$_3$) and **11** of 1600 M^{-1}. As shown in the insets for **11** and **12** in Figure 6, the fluorescence lifetime is invariant with added paraquat, indicating that only static quenching is operative. In other words, diffusive quenching is very small and need not be considered. The data in Figure 5 show a pronounced enhancement in the case of polymer **12** relative to monomer **11**. Indeed, a measure of the amplification can be determined by a Stern–Volmer analysis of the quenching. This analysis shows polymer **12** (M_n = 65 000 by GPC) to exhibit a quenching that is 65 times greater than that of the monomeric species **11**. Under ideal circumstances, wherein the excitation can migrate throughout the entire polymer, further increasing the molecular weight of these polymers should further increase the sensitivity.[20] Our synthetic methods have been shown to provide polymers of extremely high absolute molecular weights in the range of 5 000 000.[24] However, further increasing the polymer molecular weight of **12** did not provide significant enhancements. The short lifetimes of polymer **12** (∼0.5 ns) and the excitation mobility, which may be limited by conformational disorder in solution, prevent the diffusion throughout the entire length of high molecular weight polymers. Further studies are being directed at organizing polymers into assemblies to promote higher mobility.

The energy migration approach has considerable potential for amplifying many other fluorescent chemosensory schemes. In particular, a red wavelength shift induced by analyte binding should also display amplification. In this case, similar to what was observed for **10**, the electrons and holes become trapped at the location where the local band gap is narrowed. Selective emission from these localized trapping sites will also constitute amplification because multiple events (radiative recombination) are occurring as a result of a single binding event.

Outlook

In this article I have outlined conceptual aspects of how molecular wires (conjugated polymers) can be used to amplify molecular chemosensors. The properties that are responsible are universal and can be utilized in a multitude of schemes. The sensitivity and diversity available suggest that these materials will be important for future sensor technologies.

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