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Conducting-Polymer-Based Chemical Sensors: Transduction Mechanisms

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Conducting organic polymers show great promise as sensory materials. The transport of charge in these systems imparts the ability to attain high sensitivity to analytes of interest. This contribution reviews a number of different mechanisms by which analytes can interact with organic conducting polymers to create changes in their resistivity. New sensor systems based upon triaryl-methyl carbocations are also reported for the first time. The design of specific molecular recognition can impart selectivity in this process and in addition the nature of the conducting polymer can also lead to selectivity for different analytes.

Introduction

The ability to bind to specific molecules (or classes of molecules) of interest, molecular recognition, plays an important role in nature, for example, in mammalian olfactory and gustatory systems. These sensory functions help animals to perceive dangers as well as locate food. Artificial chemical sensors that effectively mimic these natural systems, and the principles that underpin them, have many applications in the detection of pollutant and chemical warfare agents as well as bioimaging.

The basic strategy for the design of a chemical chemosensor is to connect a molecular recognition site (receptor site) with a signaling unit in such a way that these two functional components communicate.[1] In such a system, a binding event between the receptor site and a target analyte triggers a change in the measurable properties of the materials. Hence, simply stated, factors that can be modified by molecular design are (1) the affinity between the receptor site and the target analyte (i.e. binding constant (K) and selectivity) and (2) the transduction efficiency of the binding event into an observable signal.

Numerous studies on molecular recognition have been devoted to fabricating sensitive chemical sensors. Preorganization is important to consider when designing a receptor site, because this minimizes the entropic penalty for complexation. This factor is critical to factor (1) and leads to a specific and stronger receptor/analyte complex. Although this concept has proved to be successful, the binding constant is ultimately dependent on the free energy change with complexation. In practice the ability to design receptor/analyte complexes is limited to enthalpy gains that are far less than covalent chemical bonds and this element alone cannot always deliver the required sensitivity of a chemical sensor. The features that are important to factor (2) are complex and go beyond consideration of the communication between the signaling unit and the receptor site. In practice the signal can be optical (fluorescence, absorption) or electrical (redox, capacitance, resistive) and the medium can be molecular or a collective material (solid or nanoparticles). The sensitivity limits are clearly dependent on the type of signal used and the background signal, which can often be related to the specificity and binding constant (i.e. factor (1)). However, in the case of systems with collective properties, binding can influence the greater surroundings and produce signal amplification.

The transport properties of materials can provide these types of amplification and both the mobility of excitons (excited states) and charge carriers (electrons/holes) in conjugated polymers are dramatically influenced by small perturbations.[2–5] Schematically we consider these conjugated polymer-based sensors to have receptor sites that are wired together such that a signal (exciton or charge carrier) can interrogate multiple receptor sites. The first report demonstrating that single molecular wires amplify was published in 1995 using poly(phenylene ethynylenes) (PPEs) possessing cyclophane receptors.[6,7] In this case the binding of a quenching viologen analyte to a single cyclophane receptor could effectively quench the entire chain. In this case, the amplification due to the transport was determined by comparison to the monomeric sensor and it was found that one binding event causes 67 times larger signal change than a single receptor/analyte system. In other words, up to a threshold molecular weight the exciton samples every receptor site along the conjugated polymer backbone and thereby increases the probability of encountering the viologen quencher. The amplification in this process

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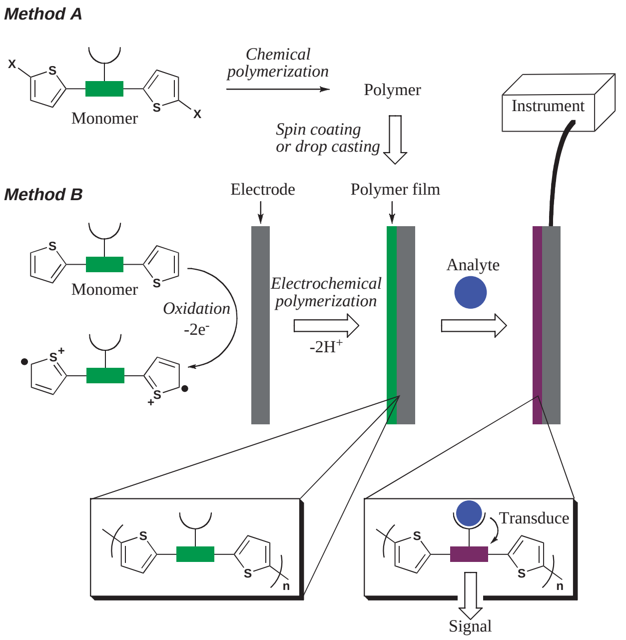

Fig. 1. Schematic representation of conducting-polymer-based chemical sensors.

is limited to the fact that the exciton undergoes a random walk along the polymer backbone. Mathematically this can be considered a one-dimensional random-walk and in this case the exciton necessarily revisits the same receptor many times. In thin films the exciton is less restricted in a three-dimensional environment and in this case much greater amplification can be realized which has led to breakthrough technologies for explosives detection.[8,9] Our group has published a very recent review on amplifying fluorescent conjugated polymer sensors,[5] hence in this contribution we describe progress in electrically conducting-polymer-based chemical sensors.

Conducting-Polymer-Based Chemical Sensors: Transduction Mechanisms

An advantage of polymeric materials is that sensory devices can easily be fabricated from these materials on electrodes either by spin coating and/or drop casting from solution (Method A in Fig. 1) or anodic electrochemical polymerization from an electrolyte solution (Method B).[2] The electrode configuration of the sensor will vary according to the sensing mechanism. A potentiometric and amperometric signal can be read through a single electrode. Conductometric sensory devices, on the other hand, are most easily monitored by passing charge between two electrodes. The conductance of a material is a bulk transport property and as a result is more sensitive than potentiometric and amperometric methods that are dependent on local electronic structure. The collective system is responsible for carrier transport in conducting polymers and molecular level perturbations anywhere along the carrier's path can impede the bulk mobility, thus giving rise to high sensitivity. Conductance sensors also have the advantage that high-precision resistance measurements can readily be made with inexpensive electronics. In our investigations, we have made extensive use of a method developed by Wrighton et al. for the in situ determination of a polymer's conductivity using an interdigitated microelectrode (IME) (Fig. 2).[10,11] In this configuration, the device can function in a transistor mode wherein a drain current (I_{drain}) flows between the two electrodes (WE1 and WE2) with a small offset potential (V_{drain}, typically 20–50 mV) and by sweeping base electrochemical potential of both the source and drain electrodes (i.e. gate voltage: V_{gate}) relative to a reference electrode, the I_{drain} profile can be determined. The observed I_{drain} is directly proportional to the polymer's conductivity thereby allowing the polymer's relative conductivity to be determined.[12,13]

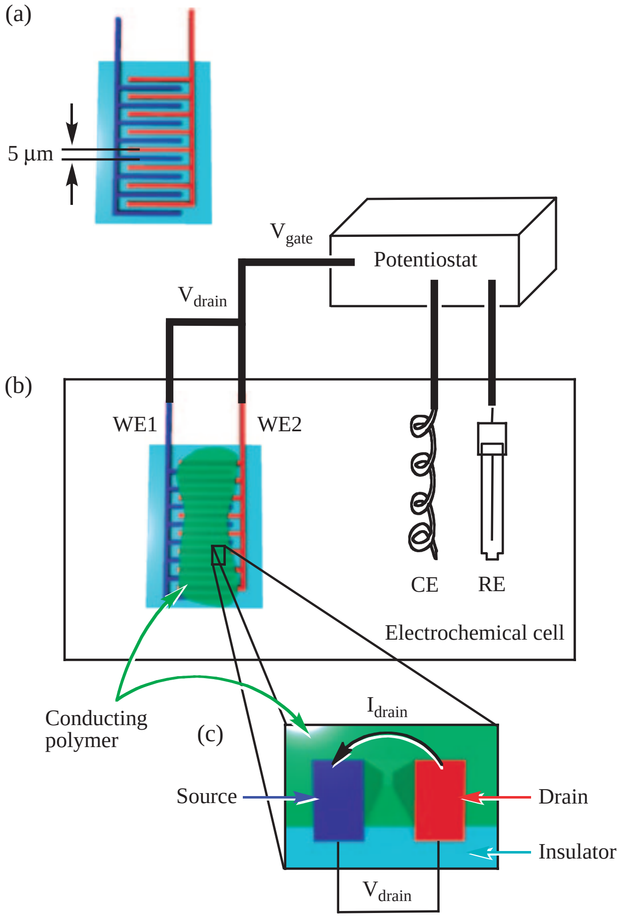

Fig. 2. Schematic representation of (a) an interdigitated microelectrode (IME), (b) an electrochemical diagram for the determination of a polymer's conductivity as a function of analyte and applied electrochemical potential (V_{gate}), and (c) cross section of IME wherein WE, CE, and RE refer to working, counter, and reference electrodes, respectively.

IMEs can be inexpensive enough to be disposable and have minimal external hardware requirements. Furthermore, all of the necessary electronics for high-precision measurements can in principle be placed on a single chip, which enables sensor arrays.[14]

By design conducting polymer-based chemical sensors transduce chemical information from the analyte, such as pK_a, redox potential, electrical charge, structure (size and shape), etc. into observable signal. Chemically induced changes in the conductivity of a material (σ) can be brought about by changes in the density (n) and mobility (μ) of charge carriers,

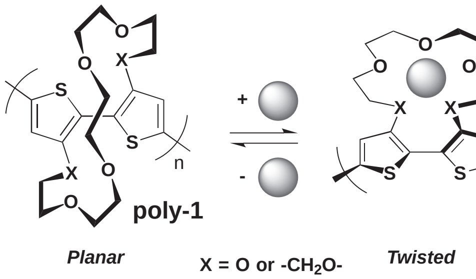

Fig. 3. Twisting mechanism of crown ether-appended polythiophene **poly-1** for the detection of alkali metal ions.

as simply shown in the following equation where e is the charge of an electron.

$$\sigma = ne\mu. \quad (1)$$

Therefore, conducting polymer-based sensory materials in which a chemical stimulus induces a change in n and/or μ, will give a conductivity change ($\Delta\sigma$). One approach is to associate a dopant analyte that changes the density of charge carriers (n).[15] This approach is limited to reactive analytes and in fact, the earliest examples of conducting polymer-based sensors were aimed at detecting oxidizing gases such as SO_2, NO_2, I_2, etc., which can oxidize (dope) the polymer. Similarly, an analyte can be involved in coupled redox reactions such as enzymatic reactions. The analyte is then detected after products of the reaction reduce or oxidize the conducting polymer. This idea has been successful and some of these chemical sensors are already commercialized in the form of pH and glucose sensors. However, this approach is limited to analytes that show or trigger redox activity or acid-based response in the case of proton-dopable polymers (e.g. polyaniline). Due to these limitations, it is important to develop conducting polymer-based chemical sensors wherein the conductivity can be affected by chemically induced changes in the charge carrier mobility (μ).

With this in mind, we initially focused on controlling the conformation of the conducting polymer's backbone because it is well-known that twisting the conjugation from planarity can result in conductivity drops of 10^5 or greater. Our initial idea, as shown in Fig. 3, was to produce a polythiophene that has the β-bridged oligoethylene glycol which can bind alkali metal ions similar to a crown ether.[16] This molecular recognition produced large spectroscopic changes and with metal complexation, **poly-1** underwent a large absorption blue-shift ($\Delta\lambda_{\max} = -91$ nm), consistent with the bithiophene axis twisting upon complexation with alkali metal ions. Twisting reduces π-orbital overlap and the effective conjugation length. This amount of blue-shift is related to the size of alkali metal ions. However, low binding constants and problematic solubility complicated thin film electrochemical studies of this system.

A second generation sensory polythiophene was designed to further optimize sensitivity and selectivity to alkali metal ions with a calix[4]arene receptor (**poly-2** in Fig. 4).[17] The binding site for alkali metal ions in this system is strongly selective to Na^+ over K^+ and Li^+ due to a highly preorganized architecture.[18] The absorption maximum of **poly-2** is red-shifted ($\Delta\lambda_{\max} = +80$ nm) with the addition of Na^+, which is opposite to **poly-1** and indicates that effective conjugation length was increased. Nevertheless, a conductometric study revealed that the conductivity of **poly-2** is completely (>99%) diminished upon complexation with Na^+ (Fig. 4b). It is interesting to note that this response is the opposite of what would be expected, based on purely conformational effects. We therefore attribute this conductometric response to electronic perturbations, such as an electrostatic repulsion between the cationic alkali metal ions and positively charged carriers (polaron and/or bipolaron) as well as a decrease in the electron donation ability of terminal oxygens in the polyether tether. These elements combine to increase the energy of a carrier at the site of an occupied receptor.

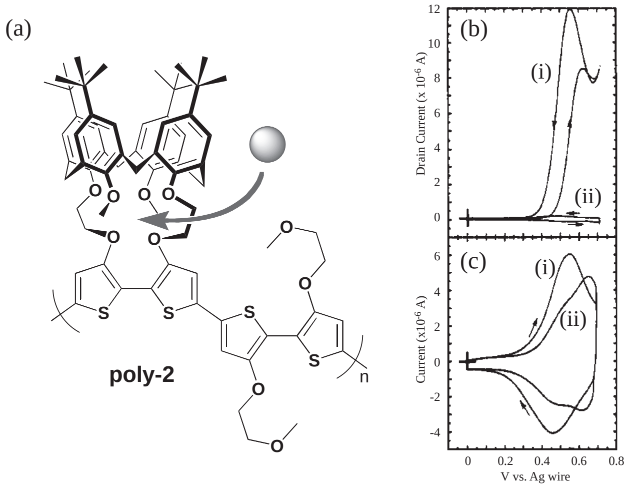

Fig. 4. (a) Structure of calix[4]arene-appended polythiophene **poly-2**, (b) conductivity profile (drain current) and (c) CV of **poly-2** (i) without and (ii) with 0.5 mM of Na^+.

Other calix[4]arene receptors have been integrated into thiophene-containing polymers that operate to detect metal ions (Fig. 5a).[19] Sensory films of **Poly-3** can readily be prepared on electrodes by electrochemical polymerization. **Poly-3** is different from the other polymers just discussed in that it is not fully conjugated and is a "segmented" conducting polymer, where charges hop between electroactive segments (in this case, quarterthiophenes) to give bulk electrical transport. Protonation/deprotonation of lower-rim phenol groups play an important role in electron conduction (Fig. 5b).[20] Upon deprotonation the conductivity was dramatically reduced. Interestingly, the conductivity of **poly-3** increased to its highest levels with the addition of divalent cations (Ba^{2+} and Ca^{2+}), whereas the conductivity decreased with monovalent cation (K^+). This selective conductivity response is understood by considering the charge-hopping mechanism in segmented conducting polymers. In a charge hopping (self-exchange) mechanism, the hopping rate will be optimal when each segment has the same environment to ensure isoenergetic character. As shown in Fig. 5c, each calix[4]arene moiety can bind one divalent cation (Ca^{2+}), however, two monovalent cations (K^+) are required (Fig. 5d) in order to balance the anionic charges of two phenol groups. As a result, the quarterthiophene moieties in K^+–**poly3** have different redox potentials that prevent charge carriers from rapidly hopping through quarterthiophene stacks. As a result, this system shows remarkable discrimination

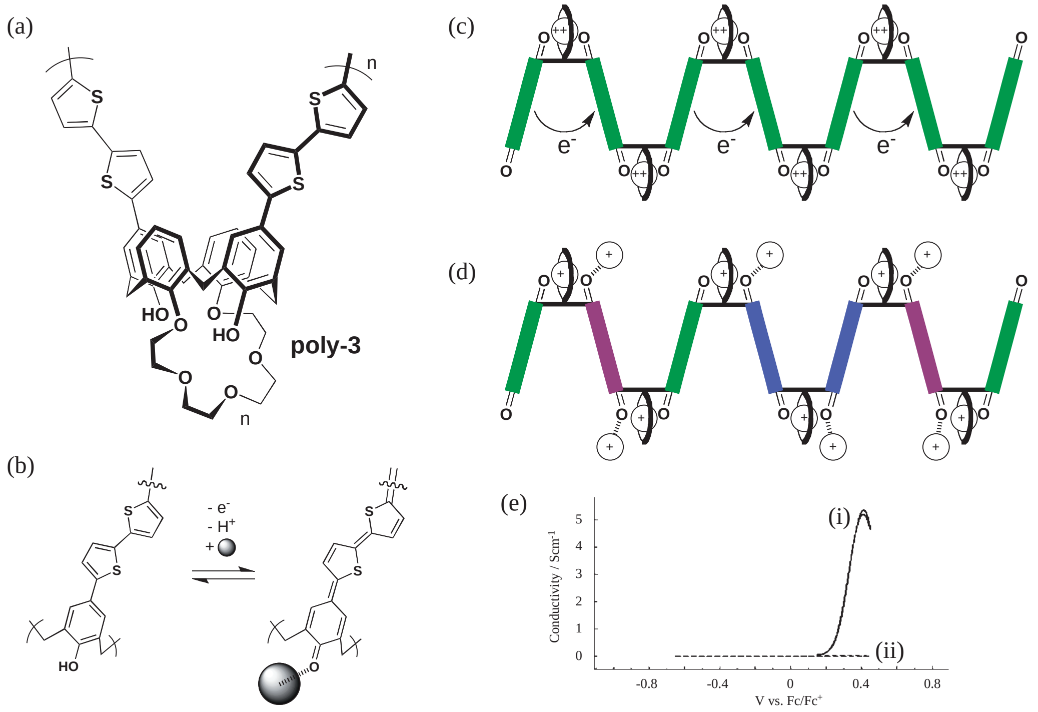

Fig. 5. (a) Structure of calix[4]arene-appended "segmented" polythiophene **poly-3**, (b) coupled equilibria between electrochemical process and proton–ion exchange, and the schematic representation of (c) Ca^{2+}–**poly3** and (d) K^+–**poly3** where different redox states are shown with different colors, and (e) conductivity profile of **poly-3** with (i) Ca^{2+} and (ii) K^+ ions.

between divalent and monovalent cations. It should be noted here that the binding of K^+ and Ca^{2+} ions to the calixarene crown produced extremely similar NMR spectroscopic and cyclic voltammetric behaviors. However, the conductivities show more than three orders of magnitude difference (Fig. 5e).

We have further confirmed the high sensitivity of chemoresistivity in systems that respond to electron-deficient organic analytes via an electronic/electrostatic perturbation mechanism (Fig. 6a).[21,22] The binding of paraquat dications (Fig. 6b) to the macrocycle-containing polythiophene **poly-4** to give a rotaxane structure resulted in attenuated conductivities, whereas a reference polymer that does not have the macrocycle moiety did not show a conductivity response. As shown in Fig. 6c, we attributed this effect to charge-transfer interactions between the polymer and paraquat. This perturbs the local redox potential and creates "barriers" to charge transport. The barriers are best considered as resistive elements that impede charge transport.

Another system utilizing the electronic perturbation mechanism makes use of a doubly strapped porphyrin substituted with electrochemically polymerizable bithiophene groups (Fig. 7).[23] This highly rigid structure defines a very small cavity containing hydrogen-bond-donating amide and pyrrole groups which appear to exclusively bind fluoride anions, as observed by absorption spectral changes. Specifically, we observed no binding to larger anions, including Cl^-, Br^-, I^-, NO_3^-, etc. Monomer **5** has two fluoride binding sites, one on each face of the porphyrin plane. Plots of the absorbance changes versus fluoride concentration showed a sigmoidal curve,[24,25] indicating that binding of F^- to **5** is cooperative with the binding of a first F^- facilitating the binding of a second F^-. This allosteric binding process was analyzed with the

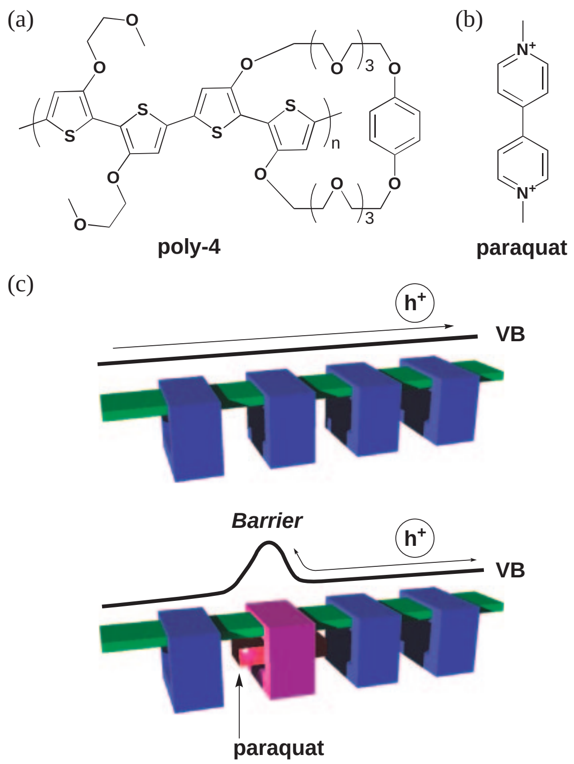

Fig. 6. Structure of (a) macrocycle-containing polythiophene **poly-4** (b) paraquat, and (c) creation of a barrier to electronic conduction by cationic carriers in **poly-4** with the binding of paraquat.

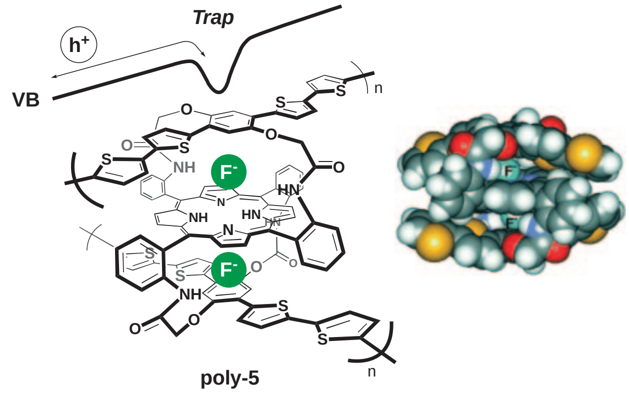

Fig. 7. (a) Electrostatic "trap" mechanism of the doubly strapped porphyrin-containing polythiophene **poly-5** for the detection of fluoride anion and (b) energy-minimized structure of $(F^-)_2$–**5** complex.

Hill equation, which gave $\log K = 6.6$ and $n = 2.0$, where K and n are the binding constant and Hill coefficient, respectively. It is likely that the allosterism and the small cavity size both contribute to fluoride selectivity. Electrochemical polymerization of monomer **5** was effective, probably due to the highly cross-linked structure, and gave a thick **poly-5** film after a few CV cycles. In situ conductivity measurements revealed that **poly-5**'s conductivity was dramatically and irreversibly reduced by the addition of F^-, although there is no direct interaction between F^- and the conjugated polymer backbone. The irreversible behavior can be attributed to the large binding constant, which results in slow kinetics for the removal of fluoride from the film. The strongly bound anionic charges can trap the charge carrier, which decreases the charge carrier mobility, μ.

Metal complexes have both the ability to bind to some ligating molecules and to produce interesting redox systems. We have been interested in conducting metallopolymers in which the redox activity of the transition metal complex and the conducting polymer backbone are coupled such that the conductivity of the material can intimately involve both elements (so-called "redox matching").[26–35] When this redox-matching condition is met, the metal essentially provides additional electroactive pathways for transporting charge throughout the material. Analyte binding events that produce a change in the metal's redox potential can enhance or decrease the conductivity depending upon whether binding produces a better or worse match between the redox characteristics of the transition metal and the organic conducting polymer. Building upon this understanding we developed conducting metallopolymers that behave as gas-phase nitric oxide (NO) sensors by using cobalt salen complexes as the active elements in the conducting polymer systems (Fig. 8).[35] Monomer **6** can readily be electrochemically polymerized on IMEs for conductometric NO sensing. When the polymer film was subjected to ppm levels of NO in a stream of dry N_2, we observed reversible resistance responses. As a reference, simple polyEDOT, which lacks the metal centers, did not show any change in resistance upon NO exposure. The kinetics and intensity of the resistance response of **poly-6** can be optimized by electrochemical treatment of the film in electrolyte solution after electrochemical polymerization. For example, a film conditioned for 2 min after film growth at a voltage corresponding to its peak conductivity/oxidation potential showed a 2-fold signal change and rapid response compared to the unconditioned film. The film morphology and the density of the incorporated electrolyte are important factors in diffusion of analyte molecules into the sensory polymer. This system displays high selectivity to NO over other possible interfering gases (i.e., O_2, CO, and CO_2). An exception is NO_2, and the **poly-6** film, which displayed a large, irreversible resistance decrease due to a one-electron-transfer reaction between the NO_2 analyte and the cobalt-conducting metallopolymer, resulting in the formation of a Co^{3+}–nitrite complex. This difference in resistance response between NO and NO_2 will enable specific differentiation of NO vs. NO_2 using sensor arrays.

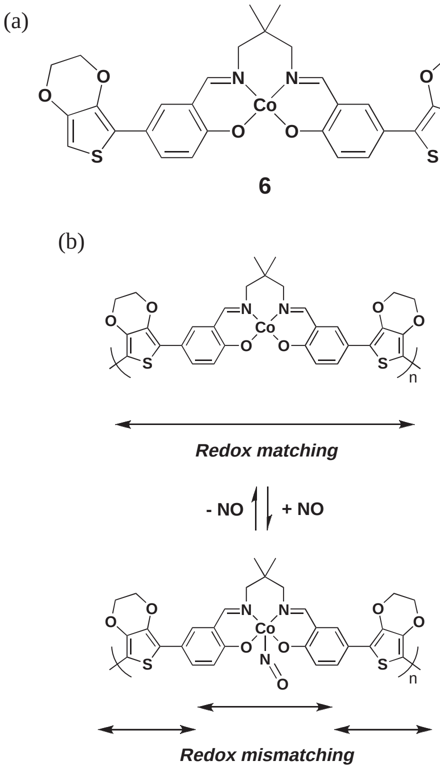

Fig. 8. (a) Structure of Co–salen complex-containing monomer **6** and (b) schematic representation of redox matching mechanism for the detection of NO gas.

The aromaticity of a conducting polymer is one of the important factors that affects its electronic properties.[36,37] This feature was used more than two decades ago by Wudl and co-workers for the design of poly(isothianaphthene) as a low band-gap polymer wherein the quinoid resonance structure is stabilized by a fused benzene ring.[38] We envisioned that switching the aromaticity in a conducting polymer backbone can also be used to change its electronic properties, which would offer a new mechanism for sensory devices. To demonstrate this idea, we concentrated on tropone, a nonbenzenoid conjugated carbocyclic compound that can gain aromaticity when protonated (Fig. 9).[39] **Poly-7** film on electrode was easily prepared by electrochemical polymerization in electrolyte solution. Interestingly, in situ conductometric measurements revealed that the conductivity of **poly-7** can be reversibly switched in response to protonation and deprotonation pro-

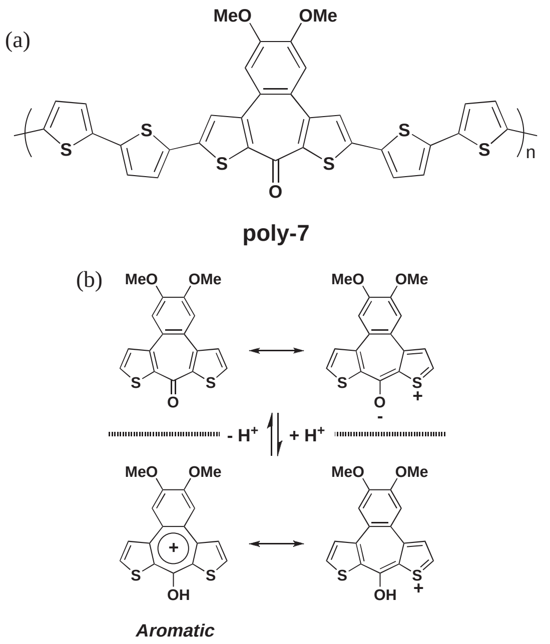

Fig. 9. (a) Structure of tropone-containing polythiophene **poly-7** and (b) schematic representation of aromaticity switching mechanism. The aromatic tropylium cation is the dominant resonance contributor to the delocalization.

cesses (low conductivity when protonated). In contrast, the control polymer that does not have a cyclic tropone moiety did not show a conductivity change even in the presence of excess acid. This conductivity response can be rationalized when resonance contribution is considered. With the addition of acid, the protonated tropone (tropylium cation) gains aromaticity, and as a result, the thiophene-fused tropone moiety destabilizes the quinoid resonance which reduces delocalization along the conjugated backbone, which in turn decreases charge carrier mobility. This postulation was further supported by in situ EPR measurements where it was found that the EPR intensity of **poly-7** is not affected by protonation, indicating that the density of charge carriers remains constant. Therefore, the decrease in conductivity of **poly-7** induced by protonation is attributed to a decrease in carrier mobility (μ). It should be noted that the conductivity switching mechanism of **poly-7** contrasts to that of conventional proton dopable polymers such as polyaniline.

Another strategy to directly change the properties of conducting polymers is to affect the electronic conjugation with analyte binding. Our monomer design based on this new sensory mechanism is shown in Fig. 10.[40] Monomers **8** to **10** can be easily transformed to tris(thienyl)methyl cation derivatives by acid-induced dehydration to yield **8**$^+$ to **10**$^+$, respectively.[41–44] As shown in Figs. 11a–11c, the absorption spectra of compound **8**, **9**, and **10** shift to longer wavelengths with the addition of TFA and the colorless solution of these compounds are transformed to red, blue and green-colored solutions, respectively (Fig. 11d). This significant red-shift is attributed to conjugation of the three peripheral thiophene groups via the vacant p-orbital of the carbocation center. This conjugation was also supported by molecular orbital calculations. We envisioned that the conjugation through the vacant p-orbital would be switched off by the addition of nucleophilic analytes. This approach is related to other materials wherein the vacant p-orbital of a boron center in a conjugated framework is known to bind with fluoride anion.[45–50] An especially interesting example was reported by Yamaguchi, Tamao, et al. where conjugation of peripheral aromatic molecules via the vacant p-orbital of a boron atom can be controlled by an acid–base interaction (i.e., B–F interaction).[47,48] Related boron-containing conjugated polymers have also been reported by Miyata and Chujo[49] and Jäkle.[50]

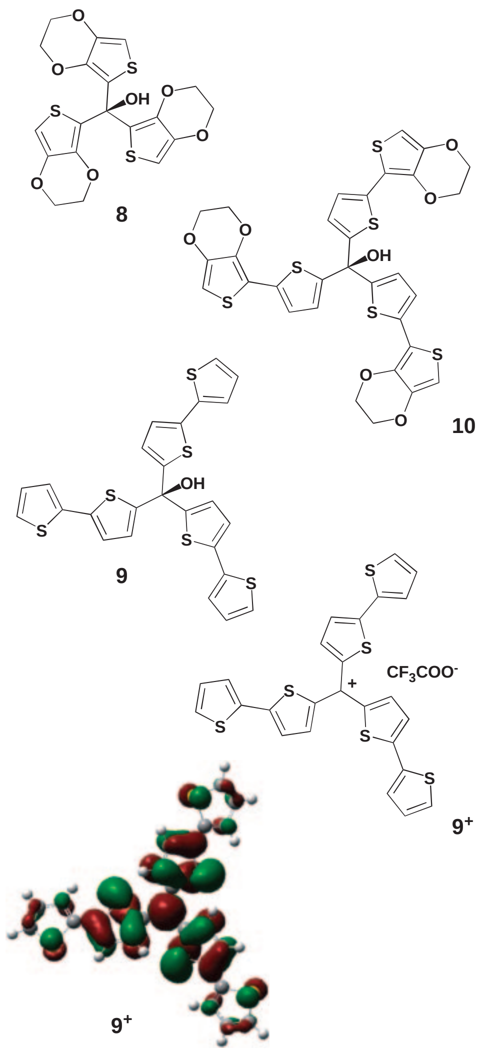

Fig. 10. Structures of monomers **8**–**10** and one of the structures of dehydrated compounds **9**$^+$. The representation of the LUMO of **9**$^+$ is based on an HF/6-31G(d) calculation, indicating that the LUMO is delocalized over three bithiophene moieties via the vacant p-orbital.

With this in mind, we added anionic species to the solutions of **8**$^+$ to **10**$^+$ and found that the colored solution turned colorless with the addition of fluoride anion (as a tetrabutylammonium salt). Using absorption spectral changes, the binding constant of **9**$^+$ with F$^-$ was determined to be $5 \times 10^5\,\mathrm{M}^{-1}$ (in dichloromethane containing 100 mM of $\mathrm{TBAPF_6}$, r.t.), which is comparable to the previously reported boron-containing fluoride sensors. The anion binding event was about 100 times more selective for F$^-$ over I$^-$, and minimal or no

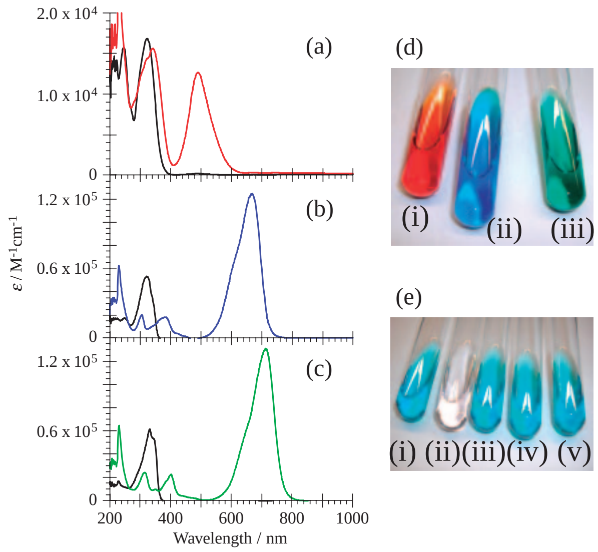

Fig. 11. Absorption spectra of monomer **8** (a), **9** (b), and **10** (c) before (black lines) and after acid treatment (colored lines). Note that materials become colorless with the addition of fluoride anion and the spectra coincide with the black lines, indicating that the fluoride adds to the center carbon. (d) Pictures of solutions of $\mathbf{8}^+$ (i), $\mathbf{9}^+$ (ii), and $\mathbf{10}^+$ (iii). (e) Picture of solutions of $\mathbf{9}^+$ (i) and $\mathbf{9}^+$ in the presence of 100 mM of $TBAPF_6$ and 100 µM of F^- (ii), Cl^- (iii), Br^- (iv), and I^- (v).

response was observed with the addition of Cl^- or Br^- ions (Fig. 11e).

The cyclic voltammograms (CVs) of compounds **8** to **10** and their dehydrated trifluoroacetate salts, $\mathbf{8}^+$, $\mathbf{9}^+$, and $\mathbf{10}^+$, were recorded in dichloromethane containing $TBAPF_6$ as an electrolyte. Monomer **8** showed an irreversible oxidation peak but did not yield a polymer film, probably due to its high solubility arising from a twisted structure with large steric hindrance. Monomers **9** and **10** gave robust films after 20 oxidation and reduction cycles between −0.27 and +0.93 V (Fig. 12a for monomer **9**). In contrast, none of the cationic compounds $\mathbf{8}^+$ to $\mathbf{10}^+$ yielded polymer films under the same condition. Instead, $\mathbf{8}^+$, $\mathbf{9}^+$, and $\mathbf{10}^+$ each showed reversible reduction peaks at around −0.4 V (Fig. 12b for monomer $\mathbf{9}^+$). **Poly-9** film deposited on electrodes was easily transformed to **poly-9**$^+$ film after immersion into an acidic solution (confirmed by the disappearance of ν_{OH} in the IR spectrum). The resulting **poly-9**$^+$ film showed new absorption bands in the near infrared region ($\lambda_{max} = 1000$ nm) (Fig. 13). This significant red-shift can be attributed to a “bipolaron-like” quinoid structure, which delocalizes and stabilizes the cationic charge on carbocation moieties over the conducting polymer network (Figs. 14a and 14b). For reference, it is reported that for boron-containing polythiophene the conjugation through the vacant p-orbital of boron shows a much higher energy transition with the absorption maximum at around 400 nm.[51]

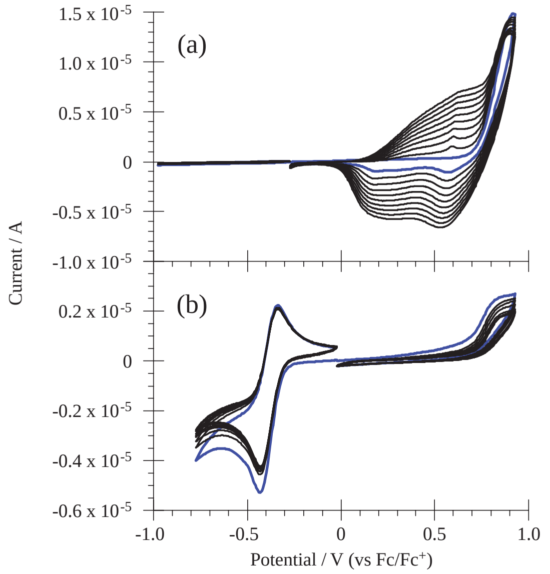

Fig. 12. Ten CV cycles of compound **9** (a) and $\mathbf{9}^+$ (b). First cycles are shown in blue lines.

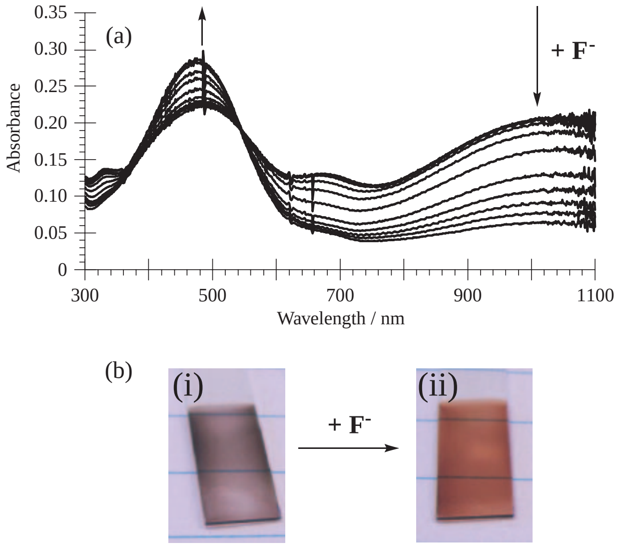

Fig. 13. (a) UV–vis–NIR spectral change in **poly-9**$^+$ film with the addition of F^- and (b) pictures showing the color change of the **poly-9**$^+$ film prepared on ITO electrode before (i) and after (ii) F^- treatment.

Interestingly, the NIR absorption bands of **poly-9**$^+$ and **poly-10**$^+$ films deposited on ITO electrodes are greatly attenuated with the addition of F^- (Fig. 13).[52–55] These results indicate that conjugation of the conducting polymer network was switched off by complexation with F^- (Fig. 14c). This system enables us to detect F^- in the near infrared region wherein light scattering and background absorption effects are minimal. We also investigated potentiometric sensing of F^- by cationic polythiophene networks. As shown in Fig. 15, the reduction peak for carbocation centers disappeared with the addition of F^-.[56]

We have developed several mechanisms that transduce the chemical information of analyte into observable signals using conducting polymers. A key feature of our approach is that carrier density (n) remains constant, thus no redox chemistry is required to alter conductivity. Equally crucial in designing conducting polymer-based sensors is precise control over the conduction pathways traversed by the charge carriers, as this property dictates the sensitivity of the system.[57–63] The

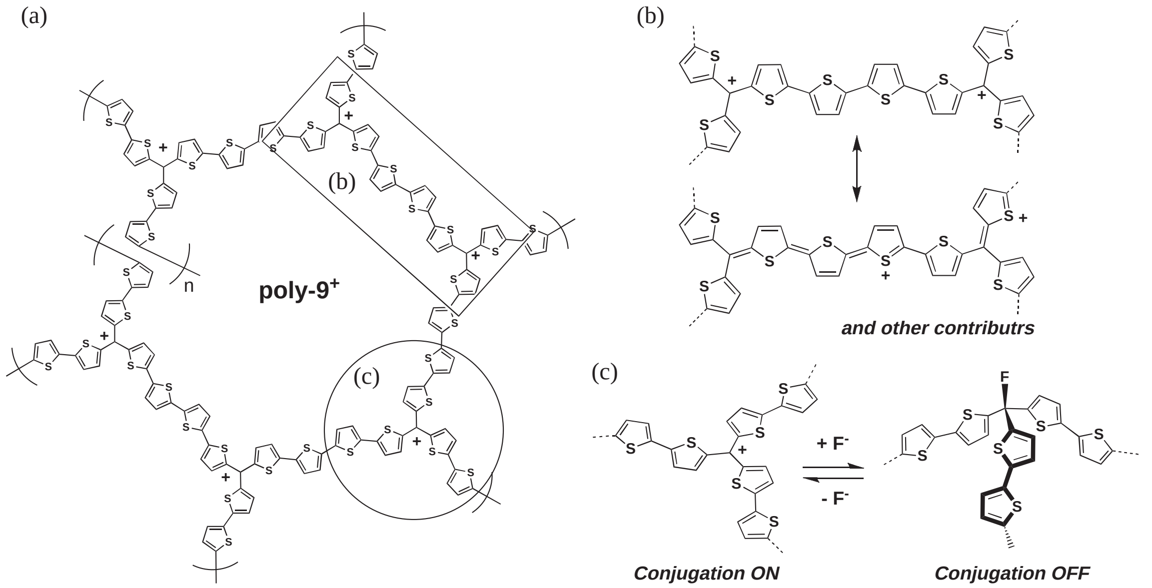

Fig. 14. (a) Structure of the conducting polymer network of **poly-9**$^+$ (b) possible resonance structures and (c) conjugation switching by F^- binding.

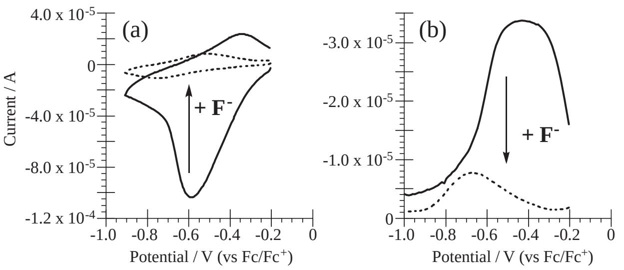

Fig. 15. (a) CV and (b) DPV (differential pulse voltammogram) changes of **poly-9**$^+$ film with the addition of F^-.

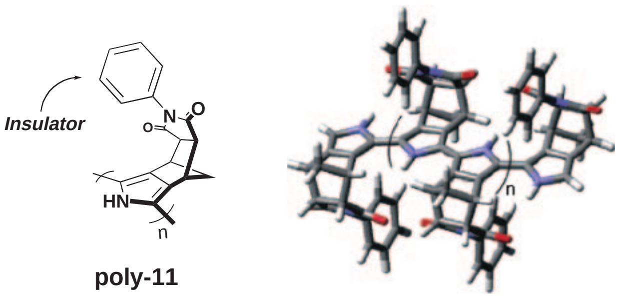

Fig. 16. (a) Structure of "canopied" polypyrrole (**poly-11**) and (ii) computer-generated model of **poly-11**.

"canopied" polypyrrole (**poly-11**), has isolated "insulated" polymer chains due to a cantilevered benzene ring (Fig. 16).[60,61] Due to the high porosity of **poly-11** films imparted by this canopy, analytes can easily diffuse into the polymer film and therefore give real-time sensing responses in solid materials. The insulation of the pyrrole chains limits interchain charge hopping and hence, this system gives large responses when the conduction along a chain that is prevented by analyte reactions. Thus, charge conduction can be dramatically reduced if confined charge carriers encounter an energy barrier or trap in these insulated molecular-wires to give a high signal-to-noise ratio. Indeed, **poly-11** was found to show a faster response and better sensitivity in protonation/deprotonation processes as compared to the parent polypyrrole.

Conclusion

We have outlined strategic aspects of how we can transduce the binding or reaction of an analyte to give observable signals in conducting polymers. When properly designed, the conducting polymer behaves as a gain medium. These systems display amplification because one analyte-triggered event can determine the transport properties of many charge carriers in the system. With restricted pathways in chemosensory materials, it is possible to design ultrasensitive chemical sensors and there are many other ways to provide unique specificity to analytes.

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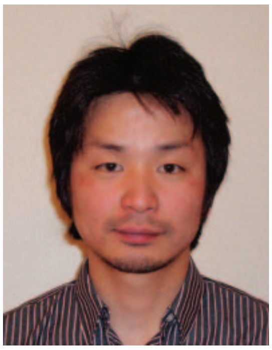

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