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Semiconducting Conjugated Polymers. A  
Personal Perspective on the Past and the Future*

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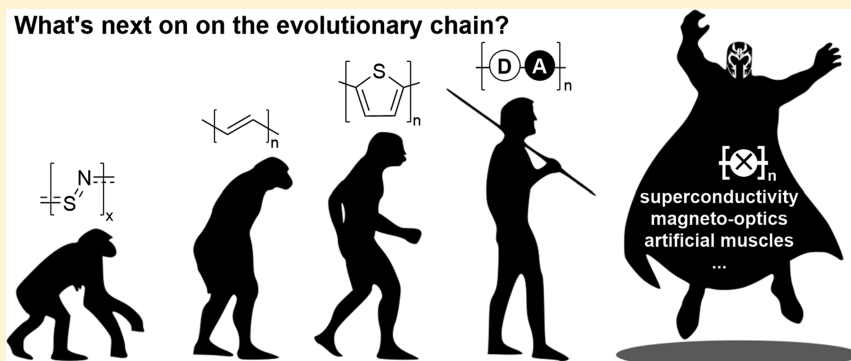
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# 50th Anniversary Perspective: Conducting/Semiconducting Conjugated Polymers. A Personal Perspective on the Past and the Future

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**ABSTRACT:** It has been about 40 years since the field of organic conducting polymers was ignited by the demonstration of metallic conductivity in polyacetylene. A retrospective view of this research area suggests some areas remain ripe for discovery/innovation. The breadth of activities is too large to be comprehensive; hence, selected seminal, as well as some personal, contributions will be used to illustrate concepts and anecdotal ways to think about conducting polymer systems. This Perspective can serve as a tutorial for newcomers to the field and will also remind experts about results from the past. It begins with some history and simple views of electronic structure, with selected examples. Segmented polymers containing isolated redox units will be discussed as well as how these materials can be made to have high conductivity. Key examples illustrating the matching of redox potentials are transition metal hybrid structures. Interchain interactions are emphasized along with their role in determining the nature of the charges. Recent results that demonstrate dramatic magneto-optical properties wherein the transmission of polarized light through conjugated polymers displays dramatic sensitivity to applied magnetic fields (Faraday effect) will also be discussed.

## INTRODUCTION

My friend and former colleague, the late Alan G. MacDiarmid, used to frequently say “We live in a materials-limited world.” The implication is that most, if not all, technologies are limited by the available materials. New functional materials continue to have a profound impact on emergent technologies and our quality of life. The unexpected opportunities arise when new properties are introduced into a class of materials that have established applications. This is where the conducting polymer story began, with the profound realization in the late 1970s that “plastic” could display electrical conductivities that rival those of metals such as aluminum and copper.

I began my intrigue with conducting polymers more about 35 years ago when the scientific community was still grappling with the revelations that organic polymers could exhibit conductivities more than 1000 S/cm. The cynical scientist today would look back and consider that it was obvious such things were possible. Graphite is a semimetal, is made of carbon, and has an extended  $\pi$ -conjugated system. However, graphite was not as versatile as polymers for the fabrication into mechanically or structurally useful objects. Hence, in the late

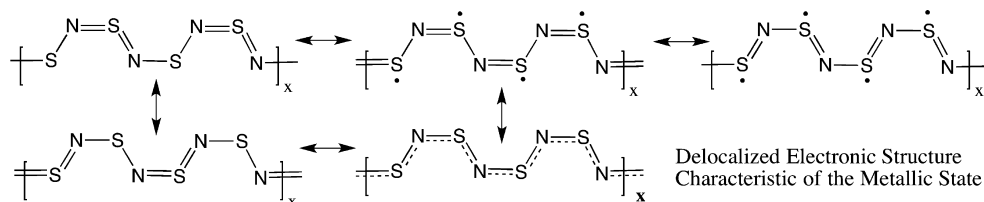
1970s and early 1980s, many were excited to contemplate the anticipated applications-of-the-day that included low-loss polymer-based power transmission lines, lightweight motors, conductive textiles, and possibly even new approaches to superconductivity. Those were very exciting times for the researchers who attended the then smallish meetings on conducting polymers and synthetic metals.

I hope to convince you of the value in looking back at the evolution of a scientific area. In doing so, this Perspective seeks to provide the reader with inspiration and insights that she/he can use to project forward and anticipate new sets of properties and opportunities. Presently, the field of  $\pi$ -conjugated polymers is dominated by a massive worldwide effort to achieve high power conversion efficiencies for organic photovoltaic applications. This area continues to evolve and has also in part driven dramatic improvements in carrier mobilities for field effect transistors (FETs), and it is safe to expect there will

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Scheme 1. Resonance Structures of  $(\text{SN})_x$ 

continue to be frequent reviews on these subjects. So, in this Perspective, I am taking a different tact. Rather than doing the usual core-dump of information with up-to-date summaries of the literature, I offer my perspective on selected aspects of  $\pi$ -conjugated polymers. Specifically, I will take a couple of walks down memory lane, recalling some contributions that shaped my thinking/research, highlight some recent innovations, and suggest how we might leverage this information to create the advances of the future. In doing so, I am purposely not comprehensive but hopefully provide a point of view on how to discuss concepts that differ from, but are not unrelated to, the hot topics of the day. So, I offer my apologies up front for the omissions of many key contributions from scientists who I know and respect. I will also keep things simple and conceptual rather than getting deep into the physics. Interested readers should follow the philosophy of “drinking directly from the spring of knowledge”, by which I mean, read and study the primary literature. This should be a quick read for those who know the conducting polymer area well and provide a tutorial for those less familiar. When possible, I have included intuitive descriptions and connections to related areas, such as emphasizing the many opportunities afforded by inorganic chemistry, that have inspired me over the years. I hope to succeed in drawing attention to opportunities, reconnect researchers to key (largely forgotten) references, and encourage new innovations with  $\pi$ -conjugated polymers.

## ■ METALLIC POLYMERS

The metallic state is often generated with a material that has a partially filled conduction band wherein the electrons are free to move with large ballistic path lengths with the occasional scattering from phonons or defects. A simplest manifestation of a metallic state is that there is increasing conductivity (decreasing resistivity) with decreasing temperature. The latter can be rationalized by simply considering that thermal fluctuations (vibrational and conformational) in a soft molecular lattice will disrupt the periodic potential and decrease the electronic coherence. Additionally, nonlocal translational vibrations (properly called phonons in solids) scatter the electrons and impede their transport in the direction of conduction (i.e., cause resistance). Ironically, although much of the early field of organic  $\pi$ -conjugated polymers was focused on achieving metallic levels of conductivity, the basic feature of increased conductivity with decreased temperature, a true signature of a metal, was only first reported for polyaniline in 2006 after this material had been studied for more than 30 years.<sup>1</sup> Semiconductors or conductors with variable range hopping conduction mechanisms require the electrons to be excited to transition between states or jump over barriers. The difficulty in producing classical metallic behavior is not hard to rationalize when you consider the inherent disorder in polymer solids. Remember, polymers seldom reach an equilibrium conformation, whereas metals are highly crystalline and often

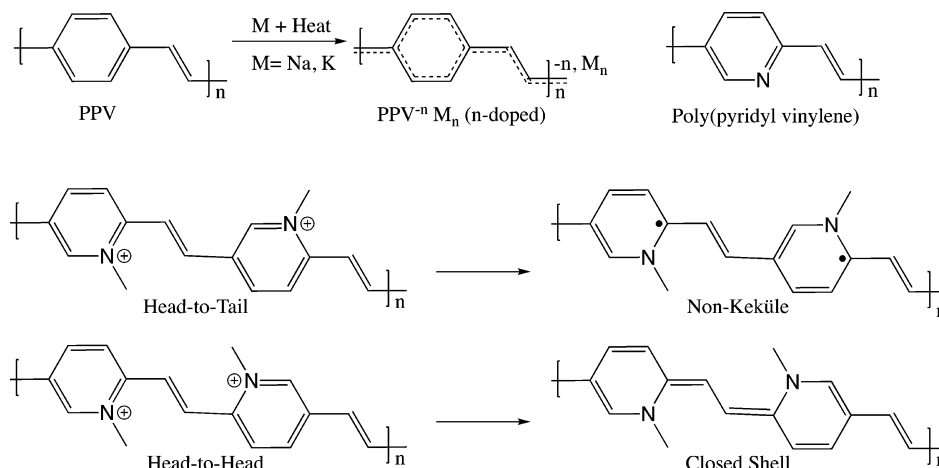
fabricated from a molten state. In any case, the best temperature conductivity profiles observed for conducting polymers were previously those that showed less temperature dependence than you would expect for a semiconductor. This behavior is described as arising from metallic polymer islands that are separated by nonmetallic domains that electrons must traverse.<sup>2</sup>

However, before the field of organic conducting polymers got rolling, there was another, largely forgotten, polymeric material that exhibited a true metallic state.<sup>3</sup> The material is called poly(sulfur nitride) or  $(\text{SN})_x$ , and it is an intrinsic metal. I refer to it as an intrinsic metal because in its pure unmodified state it displays rigorous metallic electronic properties.  $(\text{SN})_x$  was studied by many people, but perhaps Mort Labes deserves special attention for this scientific advance that demonstrated the first true metallic polymer conductor.<sup>3</sup> This work predated and, according to Alan MacDiarmid, inspired the polyacetylene research<sup>4</sup> that was recognized by a Nobel Prize.<sup>5</sup>

Interest in  $(\text{SN})_x$  was not enduring because it is a relatively exotic material that is produced by subliming  $\text{S}_4\text{N}_4$  through silver wool to give an unstable, occasionally explosive,  $\text{S}_2\text{N}_2$  that then undergoes a solid-state ring-opening polymerization to give  $(\text{SN})_x$ . Hence, this material is not conducive to classical polymer synthesis and processing. However, it still has taught us that unusual types of materials hold promise, and, in fact,  $(\text{SN})_x$  is the only polymer to display superconductivity.<sup>6</sup> The superconductive transition temperature of 0.3 K ( $T_C$ ) is too low to be of technological interest. However, it is clear that superconductivity is still not a completely understood phenomenon, and potentially a discovery of historic significance is yet possible. Perhaps the most exciting and provocative proposals for new superconductors relevant to organic electronic materials were provided by Little more than 50 years ago with his theory of excitonic superconductivity.<sup>7</sup> Little proposed that higher energy excitations involving large polarizations (charge transfer electronic excitations) could be used to provide the coherent coupling of the mobile electrons needed to sustain a bulk superconductive state. Note this was about two decades before superconductivity had been demonstrated in crystalline organic charge transfer compounds<sup>8</sup> or alkali metal doped  $\text{C}_{60}$ ,<sup>9</sup> which both conform to the classical BCS theory<sup>10</sup> of superconductivity. Indeed, there is still hope that exciting, new types of superconductors will be discovered that, like the copper oxide high- $T_C$  materials, do not conform to the BCS model with its prediction of phonon-limited  $T_C$ 's.<sup>11</sup>

Just like continued research on high- $T_C$  polymer superconductors, testing new designs that can generate intrinsically metallic  $\pi$ -conjugated polymers is a challenge worth pursuing. The fact that the only known polymer superconductor is also an intrinsic metal suggests that this is best hunting ground for new superconductors. The earlier emphasis on high conductivity has given way to a deserved focus on organic electronics, wherein we need semiconductors that can be

Scheme 2. n-Doping of PPV and the Structure of Poly(pyridyl vinylene) and Its Charged and Neutral Methylated Regioisomers



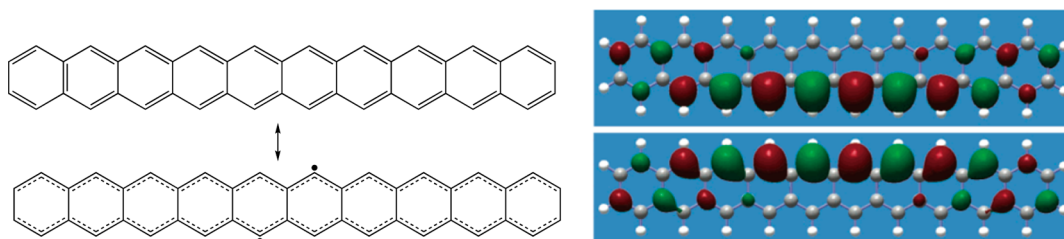
switched on and off in a field effect transistor (FET). In fact, it is commonly said that the problem with graphene is that it is *too* conductive, and this has led to the popular idea of creating semiconducting graphene nanoribbons,<sup>12</sup> wherein constraining the width of strips of graphene produces semiconductor materials.<sup>13</sup> It is not clear how best to search for materials that have a pure metallic ground state, and in this vein both (SN)<sub>x</sub> and organic charge transfer salts offer important teachings. First, (SN)<sub>x</sub> has an open shell electronic state. As shown in Scheme 1, it is possible to draw a number of Lewis structures. Some have the sulfur atoms in different oxidation states, and we might suggest these are minor resonance forms. However, when we consider the resonance structures with  $\pi$ -bonding similar to an alternating polyene, we find that we have an unpaired electron on each sulfur atom. This electron is effectively in a  $\pi^*$  orbital leading to a half-filled band, the signature of a metal. Clearly, this is an oversimplification, but our chemical intuition is correct here, and structural studies show the N–S bond lengths to be similar in length (1.593 and 1.628 Å) and intermediate between typical N=S and N–S bond lengths, indicative of a delocalized structure.<sup>14</sup> Another feature from the structural studies of (SN)<sub>x</sub> is the fact that there are short noncovalent S...S and S...N contacts between adjacent chains (3.476 and 3.256 Å, respectively) that are less than the respective van der Waals radii of 3.70 and 3.35 Å. The polarizability of sulfur and invoking S...S interactions to explain structures has been pervasive throughout the field of molecular and polymeric conductors. In fact, these interactions are central to the understanding of the band structures that led to superconductors based on bis(ethylenedithio)tetrathiafulvalene,<sup>8</sup> which was nicknamed ET, although I am quite sure that it was not left on the planet by aliens.<sup>15</sup>

One might ask, is creating a metallic state as simple as creating materials with half-filled bands? Clearly there are other considerations, not the least of which is stability. I suggested for (SN)<sub>x</sub> that we could think of the electronic structure as having a half-filled  $\pi^*$  band, which intuitively must be reactive. Open shell molecules and polymers are challenging targets, and it is tempting to think that they will not have sufficient stability for real-world applications. In fact, some years ago my research group targeted polymers that would have, at least using simple resonance formalisms, half-filled bands. We were inspired by work that had shown that the alkali metal intercalated (n-doped) poly(phenylenevinylene) (PPV) could display con-

ductivities greater than 10<sup>4</sup> S/cm.<sup>16</sup> Detailed structural studies of the high-conductivity PPV materials, as well as ordered n-doped polyacetylene, revealed that ordering of the counterions served to promote greater organization between adjacent polymer chains. To target an isoelectronic analogue of highly n-doped PPV, we synthesized the different regioisomers of poly(pyridyl vinylene) and by aggressive alkylation reactions (neat methyl triflate with heat in a sealed tube) produced poly(*N*-methylpyridinium vinylene)s as shown in Scheme 2.<sup>17</sup> The head-to-head regiomers when reduced creates a neutral closed shell electronic structure. However, the head-to-tail form is topologically prevented from displaying a closed shell Kekulé structure when reduced to its neutral state. Consistent with expectations, we found that the head-to-tail structures for both the n-doped poly(pyridyl vinylene) and poly(*N*-methylpyridinium vinylene) display higher conductivities than their head-to-head analogues. However, the conductivity of the reduced poly(pyridinium vinylene) is far lower (10<sup>-4</sup> S/cm) than expected. The problem is perhaps obvious from the open shell non-Kekulé structure; this polymer was highly unstable even under inert atmosphere. The reduced head-to-tail polymer became extensively cross-linked after reduction, and its reaction upon exposure to air was so rapid that it resulted in physical movement of polymer films. Clearly, there were many reactive radicals in a small volume that react fast with molecular oxygen. Perhaps pseudo-rotaxane assembly can prevent the intermolecular coupling or radicals in these systems,<sup>18</sup> but the sensitivity to molecular oxygen prevented practical applications of these materials as conductors.

There were other earlier predictions of structures that would behave as intrinsic metals. In particular, Kivelson and Chapman suggested that polyacene should behave as an intrinsic organic metal.<sup>19</sup> The polyacene structure does not have a topology that enforces a non-Kekulé electronic structure, but it was suggested that it should have an intrinsically metallic state. This bold prediction has never been completely tested as a result of the fact that linear acenes tend to be unstable beyond 5–7 repeating units.<sup>20–22</sup> However, the idea that acenes have special properties has been borne out in a number of related studies. In particular, higher acenes deviate from typical polycyclic aromatics and have singlet biradical character.<sup>23</sup> In this case classical thinking of electrons residing in two-electron orbitals (Kekulé structures) is inadequate. Specifically, the frontier electrons in these systems start to behave more like a coupled



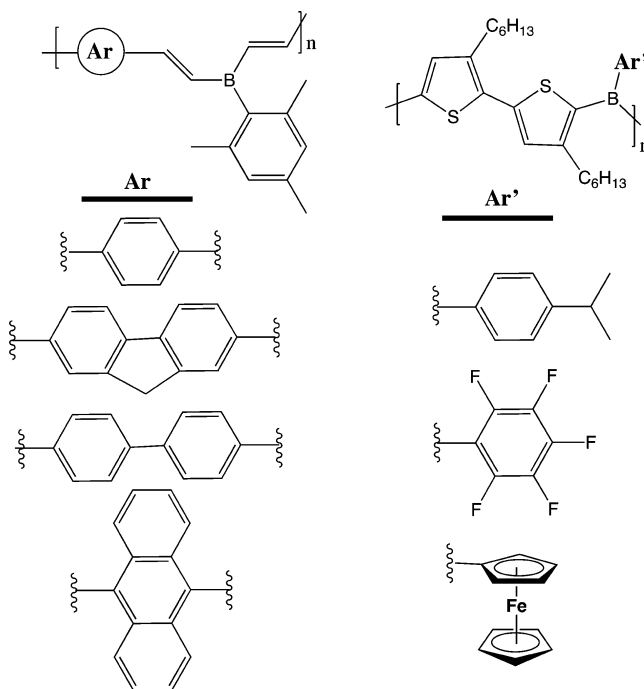


**Figure 1.** Closed shell and open shell resonance contributions (left) and computed highest energy singly occupied orbitals (right) for decacene. Reproduced with permission from ref 19. Copyright 1983 American Physical Society.

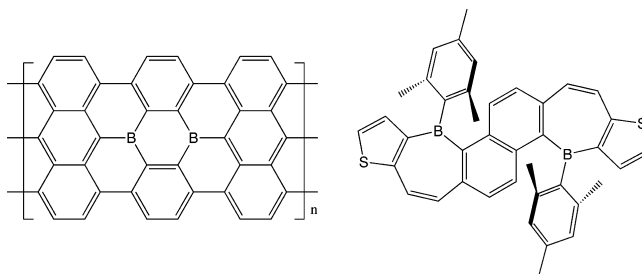
“electron gas”, and perhaps we should think about extended acene systems more as if we were physicists describing a metallic state. The higher acenes represent a high-symmetry situation, and one cannot help but be captivated by the beauty of their computed highest energy singly occupied orbitals (Figure 1). Importantly, although computational insights are extremely valuable, it is still useful to think in terms of resonance structures. In fact, there is a contribution from the closed-shell (spin paired) Kekulé structure, which suggests correctly that the diradical state should have singlet spin parity. It is also no coincidence that in armchair carbon nanotubes one can carve out an acene motif that is coincident with the long axis, and all diameters of this type of nanotube are metallic. Polyacene remains as a holy grail target for the taking. In the meantime, there have been a number of studies on isoelectronic equivalents with nitrogen substitution, which through a higher electron affinity reduces oxygen sensitivity and provides for n-type semiconductive behavior.<sup>24</sup> Indeed, this area has been very productive, and key steps in the syntheses make use of classical condensation reactions.<sup>25</sup>

The consequences of substituting N: for CH just mentioned for acenes is straightforward, and we can, in effect, think of this as simply placing another proton in the C nucleus to create a more electronegative atom. However, it is tempting to target a truly half-filled band by substituting B nuclei in place of C. At first glance, this is directly analogous to classical doping of Si to give a p-type semiconductor. However, B substitution in crystalline Si does not create strong local structural distortions, and the wavelengths of the electrons are sufficiently long that any local heterogeneity in the atomic potentials does not localize the electrons. In contrast, a B for C substitution in a molecule or polymer is a large perturbation. Nevertheless, there has been great progress in placing three-coordinate boron into the  $\pi$ -conjugation pathways of electronic polymers. Stabilization of the boron centers is generally accomplished by attaching sterically bulky groups that prevent Lewis base coordination, which typically precedes hydrolysis. Representative systems have been produced by Chujo that contain divinyl- and diarylborane groups as shown in Scheme 3.<sup>26</sup> In general, these behave as weakly delocalized, closed shell systems with band gaps that produce emissions in the visible portion of the electromagnetic spectrum. Some interesting applications include the ability to create selective responses to fluoride ions. However, highly conducting polymers with boron centers in the main chain have yet to be discovered. There may be ways to accomplish this, and much like the concept of doping B into silicon, the context of the incorporation is most critical. In this case, novel surface-immobilized B-doped graphene ribbons<sup>27</sup> (Scheme 4) are inspiration for future work. Additionally, six-electron Hückel aromatic borane structures (which look like prospective monomers) reported by J. D. Tovar<sup>28</sup> promote

### Scheme 3. Examples of Conjugated Polymers with Main-Chain Boron Atoms Protected against Lewis Base Coordination by Sterically Bulky Groups

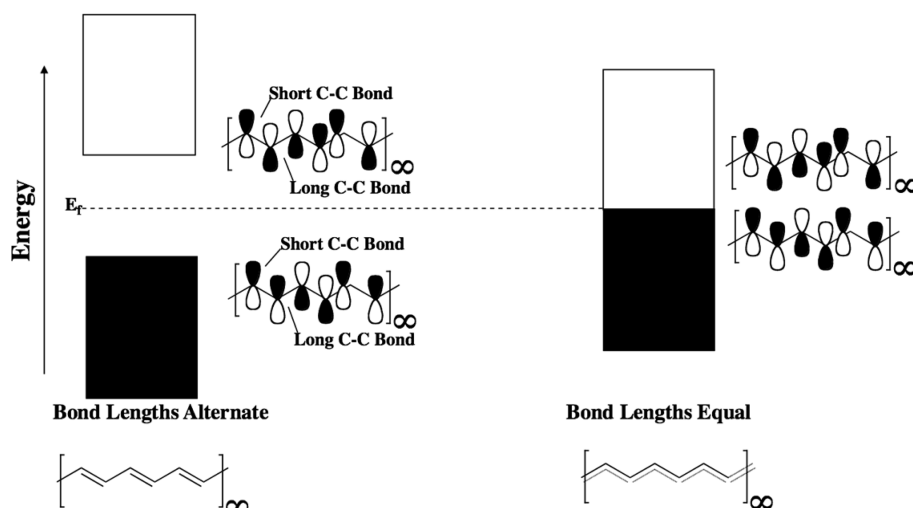


### Scheme 4. Boron Incorporation into Conjugated Systems



mixing of the B-centered p-orbitals with the carbon-centered  $\pi$ -system (Scheme 4).

I expect that new intrinsically conducting organic polymers will be produced that can have half-filled bands and radical character in the not too distant future. Indeed, we can look to recent innovations in small molecule chemistry for inspiration. Specifically, there has been an expansive growth in the design of polycyclic  $\pi$ -conjugated diradicals<sup>29</sup> with a number of topologies that are candidates for integration into electronic polymers. There is likely a sweet spot between radicals that are too unstable, and approaches we have explored wherein highly



**Figure 2.** Conceptual illustration of electronic states for an infinite polyene (e.g., polyacetylene). In the semiconductive state on the left, note that for the highest orbital at the top of the filled valence band, bonding interactions correspond with shorter C–C bond lengths and antibonding interactions match with longer C–C bond lengths. The converse is true for the lowest energy state in the conduction band. Note that if all of the bonds were equal in length (which they are not) as shown at the right, then the orbital at the top of the valence band would be degenerate with that at the bottom of the conduction band at the Fermi level ( $E_f$ ) and it would have a metallic state.

stabilized radicals placed in conjugated polymers resist long-range delocalization required for conductivity.<sup>30</sup> Indeed, some hydrocarbon open shell molecules have demonstrated semiconductor properties.<sup>31</sup> Opportunities abound in this area, and someday (hopefully soon) a clever molecular designer will create neutral (uncharged) organic polymers that have intrinsic metallic behavior.

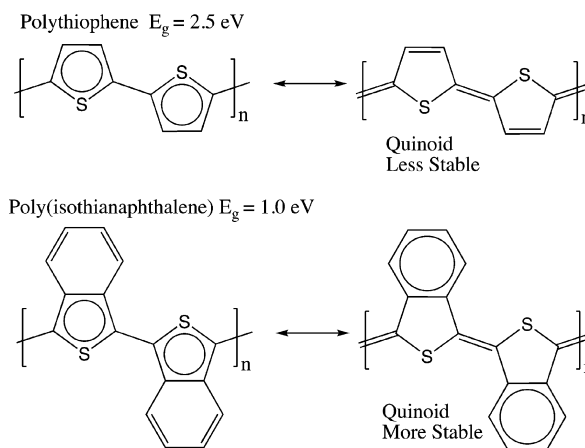
## DESIGNED ELECTRONIC STRUCTURE

To develop a slightly deeper description of the electronic structure of conducting polymers, it is instructive to begin with some basic concepts of solid-state physics that underpin conductive polymers. There is fundamental instability within all one-dimensional metallic systems, in that these materials can lower their energy by undergoing what is known as a Peierls distortion. Polyacetylene is a classic example, and if we could heat this material hot enough such that thermal vibrational excitation would cause all of the bond lengths to be equal in length, it would be a metal. However, such a state is above polyacetylene's decomposition temperature, and a ground state with bond alternation opens a band gap ( $E_g$ ) as detailed in Figure 2. Alternation in bond lengths is a powerful concept in terms of predicting band gaps of conducting polymers, and in general, greater differences in C–C lengths give larger  $E_g$ . Suppression of the Peierls distortion can be accomplished by secondary lateral (higher dimensional) interactions. For example, as mentioned in the discussion of  $(SN)_x$ , the interchain S...S interactions were key. These weak interchain interactions help to suppress a metal–semiconductor distortion in this material.

Many concepts for the design of particular band gaps and electron affinities can be distilled down to concepts taught in introductory organic courses. Aromatic rings stabilize systems by promoting electronic localization in isolated aromatic rings.<sup>32</sup> This localizing effect can be reversed by situations wherein two resonant structures both have aromatic rings competing against each other to give polymers with low gaps. Fred Wudl famously first employed this concept to produce poly(isothianaphthalene),<sup>33</sup> which displays an  $E_g$  of about 1 eV.

In this system, there is a competition between different aromatic states, as shown in Scheme 5, and this results in less

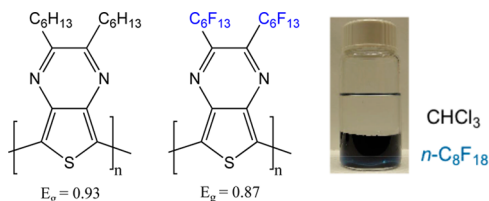
## Scheme 5. Comparison of Resonance Structures and Band Gaps of Polythiophene and Poly(isothianaphthalene)



bond-length alternation than simple polythiophene, which is shown for comparison.<sup>34</sup> Although not an analytically rigorous predictive method, comparing the relative energies of different resonance structures gives useful predictive insight into the relative magnitude of band gaps of different materials. In general, we can think of the more stable resonance structure as an indication of the valence band's energy and the higher energy resonance structure representing the relative energy of the conduction band. You will note the parallels to the description of polyacetylene, wherein the differences in bond lengths are related to bonding and antibonding interactions that define the band gap.

Another method to predictively lower the  $E_g$  of a semiconductive organic polymer is create alternating structures of electron-rich and electron-poor units. The lowering of the gap is similar to the designs of classical donor–acceptor dyes, but in the case of semiconductive polymers the physical size of the donors and acceptors can be larger than lone pairs, donor

atoms, or simple accepting groups that are typically the design elements of organic dyes. Simply put, here the donor groups raise the energy of the valence band, and the acceptor groups lower the energy of the conduction band. The donor–acceptor concept is general, and the dihexyl-substituted poly(thieno[3,4-*b*]pyrazine) shown in Figure 3<sup>35</sup> has an  $E_g = 0.93$  eV,

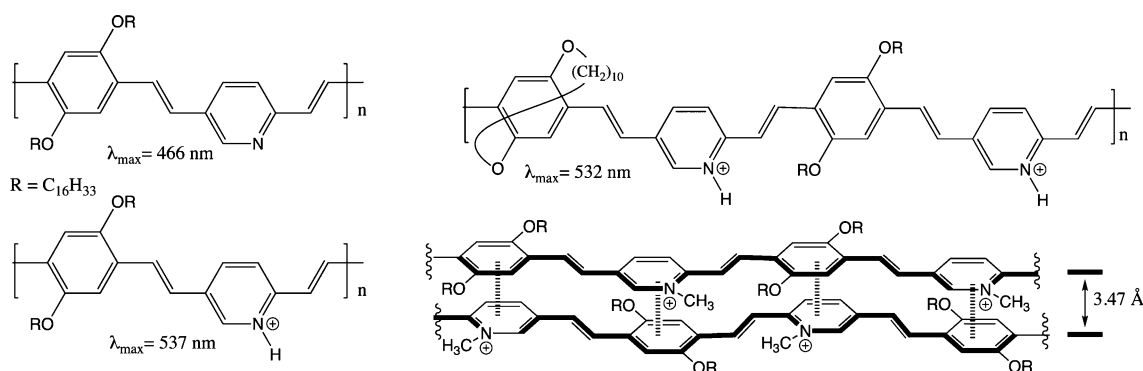


**Figure 3.** Poly(2,3-dihexylthieno[3,4-*b*]pyrazine) (left) and its perfluoroalkyl analogue (right), which displays completely orthogonal solubility as demonstrated by the photo.

which is lower than poly(isothianaphthene). In this case, the electron-rich thiophene and electron-poor pyrazine can also be considered to contribute to the lowering of the band gap. Consistent with this notion, substituting the pyrazine ring with perfluorohexane produces a further reduction in  $E_g$  to 0.87 eV.<sup>36</sup> Hence, it appears that the electron-poor substructure lowers the conduction band's energy. The high fluorine content in the latter material also provides for another new property for a conducting polymer, namely, exclusive solubility in fluorocarbon solvents with insolubility in organic solvents. These materials are n-type semiconductors, and air-stable field effect transistors were prepared from casting from fluoruous solvents.<sup>36</sup> Access to semiconductive polymers with orthogonal solubility opens the possibility for sequential solution deposition of fluoruous materials without dissolving an organic soluble base layer. Previous fabrication of electronic polymers using orthogonal solvents has required the pairing of organic- and water-soluble materials. Water can promote degradation of charged organic materials; as a result, there are advantages to working in purely nonaqueous environments. Clearly, there are other approaches to creating stratified multilayer structures, such as cross-linking a base layer, or the addition of barrier layers. The organic photovoltaic area has highlighted the importance of junctions between dissimilar materials, and new methods to tailor these interfaces are needed.

The modulation of  $E_g$  by creating alternating donor and acceptor units also has the ability to create organization

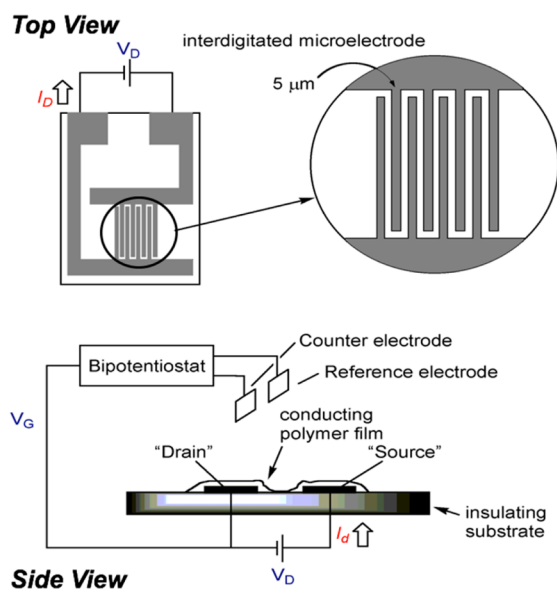
between polymer chains by preferential  $\pi$ -stacking of the charge complementary units (i.e., –D–A–D–). An early illustration of modulating the band gap and the ability of these interactions to enforce interchain order was demonstrated by the studies on the poly(arylene vinylene)s shown in Figure 4.<sup>37</sup> Rigid polymers with long alkyl side chains were known to form lamellar structures,<sup>38,39</sup> a feature that has been a hallmark of regioregular poly(3-hexylthiophene).<sup>40</sup> For the neutral polymer in Figure 4, there were no X-ray diffraction peaks from the  $\pi$ -stacking; however, with methylation a prominent diffraction with a *d*-spacing of 3.47 Å appears, indicating the presence of strong coplanar association of the polymer chains. Note that the  $\pi$ -stacking in graphite is 3.35 Å. The strapped structure in Figure 4 is incapable of organizing in the complementary –D–A–D– stacked motif and does not display the wide-angle diffractions associated with interchain correlations. The field of organic photovoltaic materials is now dominated by band structure engineering applying these general donor–acceptor concepts in largely noncrystalline or partially crystalline polymers. The extraordinary success of this approach is undeniable; however, I cannot help but think that this approach is not ideal. Specifically, an *ab initio* design of a system that optimizes charge transport would intuitively include maximizing delocalization as well as minimizing the reorganization energy for movement of charge and enhancing carrier mobility. The electronic potential that is generated by electron-poor and electron-rich groups tends to localize electrons, and disorder in these structures can create trapping sites for carriers. Most donor–acceptor polymers have varying degrees of interchain order as revealed by X-ray diffraction experiments, suggestive of D–A promoted  $\pi$ -stacking between the chains illustrated in Figure 4. As a result, it would appear that this strong interchain coupling is critical to the performance of present organic photovoltaic systems, and the associated charge transfer interactions may tend to minimize the heterogeneous nature of the electronic potential. Nevertheless, it would appear that the ultimate materials may be ones that use bond alternation derived  $E_g$ 's tailored for efficient collection of solar radiation and a highly regular structure and organized side chains that promotes interchain order (crystallinity). In addition to the use of main-chain donor–acceptor and side-chain interactions to drive organization, polymers with restricted conformations or fused ring systems can also drive crystallinity. However, many of these approaches often give rise to materials with limited solubility.



**Figure 4.** Alternating donor–acceptor poly(arylene vinylene)s that display a large red-shift in their  $E_g$  with protonation or alkylation. The strapped structure blocks  $\pi$ -stacking and reveals that the shift in  $E_g$  is intrapolymer, and the solid-state structure of the methylated structure exhibits strong interchain interactions as shown.

## ■ MAPPING CONDUCTIVITY AND THE MICROELECTROCHEMICAL TRANSISTOR

As emphasized, conducting polymers are generally intrinsically insulators, or wide band gap semiconductors, that must be oxidized or reduced (doped) to become conductive. The investigation of conductivity changes of a polymer as a function of doping is most efficiently performed electrochemically employing an experiment developed by Mark Wrighton and co-workers.<sup>41</sup> The method is best performed with interdigitated electrodes and a bipotentiostat (Figure 5), and the output from



**Figure 5.** Schematic of a microelectrochemical transistor wherein a conducting polymer is deposited on interdigitated electrodes and then placed in an electrochemical cell. Electrochemical doping by sweeping the potential ( $V_G$ ) relative to a reference electrode of the polymer causes current to flow between the source and drain electrodes with an applied potential ( $V_D$ ).

the device is appropriately described as an electrochemical transistor. In this device, when the polymer is neutral, no current will flow between the source and drain; however, with oxidative or reductive doping the material becomes conducting and current flows. It is described as a transistor because not only does it switch, but the amount of current that can flow in the circuit connecting the source and drain greatly exceeds that needed to switch the polymer. Hence, like a conventional FET, the microelectrochemical transistor is an amplifier. The performance of these devices depends upon the architecture and feature size of the electrodes; small interelectrode spacing facilitates larger currents to flow between the source and drain.

The utility of the microelectrochemical transistor is demonstrated by mapping the conductivity for different polymers.<sup>42</sup> These studies revealed that with very high doping levels the polymers have dramatic reductions in their conductivity, as shown for poly(3-methylthiophene) in Figure 6. This effect is the result of depleting the bands that are formed with carrier injection. For oxidative doping at low doping levels radical cations (polarons) dominate, and dications (bipolarons) are the prevalent species at higher doping levels. At the extreme high levels of oxidation the carriers are densely packed in the material. We can invoke that the band is now empty and not capable of conducting, but an equally intuitive

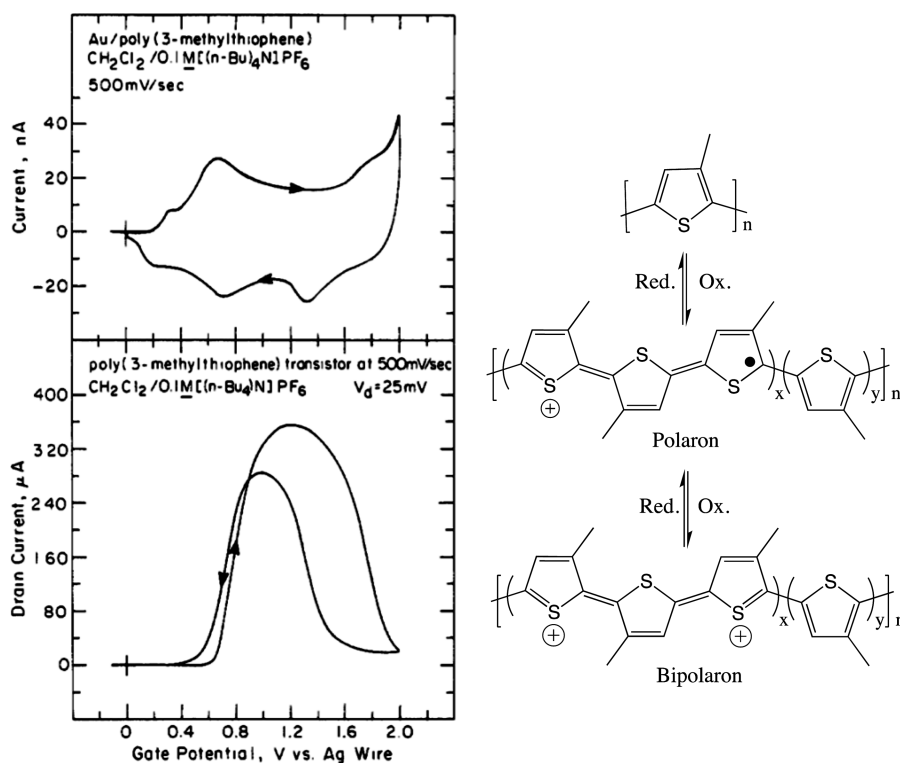
explanation is that the electrostatic repulsions associated with charge movement are sufficiently high that the system transitions to a state that is reminiscent of, but not equivalent to, a Mott insulator.<sup>43</sup>

The windows of conductivity become narrower in materials having localization of their electronic structures caused by cross-conjugation, heterogeneous electronic potentials, or  $\pi$ -systems interrupted by saturated centers or nonconjugating groups. As I will illustrate, these localized systems can still be highly conductive through hopping conduction mechanisms with conductivities competitive with many  $\pi$ -extended networks. At one extreme, we can ignore the fact that there is a band structure and consider hopping conduction to simply be an electron exchange reaction between a neutral and oxidized (or reduced) molecular species. A special behavior is expected in this case, and you can easily prove that for a degenerate reaction  $A + A^+ \rightleftharpoons A^+ + A$  with a fixed amount of redoxophore, A, the electron transfer rate =  $k_{\text{exchange}}[A][A^+]$  is maximal when exactly half of the material is oxidized (reduced). Note that this is a localized molecular version of the half-filled band discussed earlier, and a physics view is that we have weakly interacting states and hence a very narrow energy band. Narrow bands created with little or no delocalization can, however, have a high density of states at a particular energy. As a result, if the localized units are close enough for efficient electron tunneling and there are low reorganization energies associated with the electron transfer (redox) events, then a highly conductive state is possible.

Placing discrete (confined) redoxophores in polymer backbones can create a situation wherein the conductivity follows this self-exchange model. For example, the planarized pyridinium ion shown in Figure 7 displays a narrow window of conductivity, which appears to be centered at the half-wave potential for the reduction of the radical cation to the neutral state.<sup>44</sup> I consider the pyridinium, as synthesized, state of this material to be the ground state, and hence reduction of n-doping causes conductivity. The fully reduced antiaromatic state could alternatively be considered the ground state, and in this case with oxidation the polymer induces conductivity thereby qualifying it as a p-type conductor. The cyclic voltammogram features are sharper than those of more electronically delocalized polymers, and the resonance structures in Figure 7 illustrate this. Further delocalization across multiple repeat units would be at the expense of trading aromatic rings for quinoidal resonance structures. The dicationic polymer with chloride counterions is exclusively soluble in water, and with a  $\sigma_{\text{max}} = 30 \text{ S/cm}$ , this material is one of the most conductive n-type materials ever produced. Correspondingly, the polypyridinium shown also displays very high FET electron mobilities of up to  $3.4 \text{ cm}^2/(\text{V s})$  in air. However, as is often the case, there is a problem, and the FET on/off ratio is only 20. Hence, with transistor switching the mobile ions appear get stuck somewhere and create persistent carriers in the polymer. This latter result suggests that ionic structures with mobile ions may not be good for fast switching FETs. We are not in a position to make broad generalizations; however, mobile ions that are connected with the redox state of the polymer can be used to create persistent switches, sensors and nonvolatile memory devices nonvolatile memory devices.

Polymers that lack extended  $\pi$ -conjugation based on their topology can also be highly conductive. To demonstrate this fact, we created highly conductive materials wherein the redox active thienyl groups are linked by *meta*- and *para*-phenylene





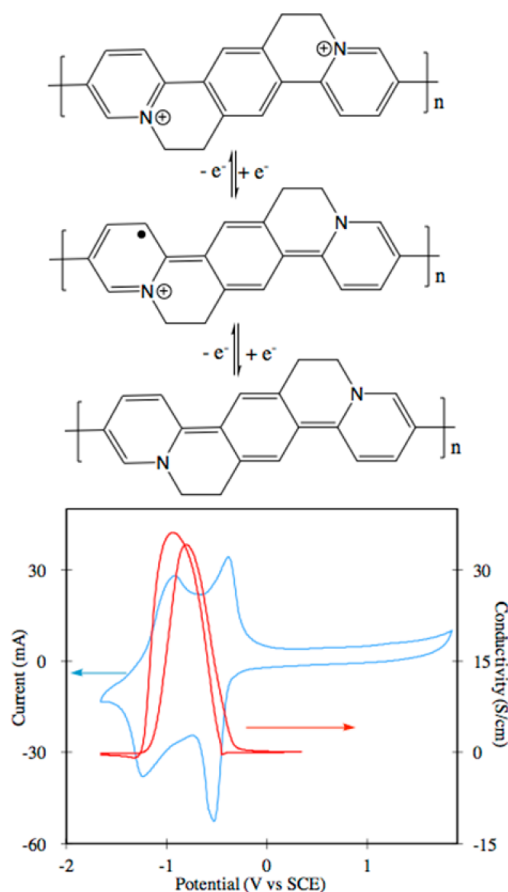
**Figure 6.** Data from a microelectrochemical transistor showing the behavior of poly(3-methylthiophene). The top plot is the cyclic voltammogram from the interdigitated electrode array wherein the source and drain are maintained at the same potential. In the bottom, the same device is observed in “transistor mode” wherein the current that flows between the source and drain is plotted while cycling over the same potential range. This current is directly proportional to the conductivity of the polymer. Note that the transistor current is more than  $10^3$  larger than the Faradaic (switching) current associated with the cyclic voltammogram. Reproduced with permission from ref 38. Copyright 1989 Wiley-VCH Verlag GmbH & Co. KGaA.

groups, PMPT-OAc and PPPT-OAc (Figure 8).<sup>45</sup> In accord with simple organic chemistry resonance structures, *meta*-phenylenes have generally been long considered to be poor candidates as conductors.<sup>46</sup> Contrary to this conventional wisdom, PMPT-OAc and PPPT-OAc exhibit very similar maximum conductivities of  $\sim 200$  S/cm. The lack of extended delocalization in the *meta*-analogue results in a relatively narrow energy band, and when we consider conduction through rapid redox (electron-transfer) reactions between different redoxophores, the situation is optimal with the different groups all having similar energies. Curiously, after removal of the acetyl groups, the polymers maintain their conductivity. The electroactivity and the conductivity profile of the *meta*-isomer shift  $\approx 300$  mV negative in potential, whereas the *para*-isomer's profile is largely unchanged. The resonance structures suggested in Scheme 6 for a bipolaron state give insight into this observation and highlight the important role of the phenolic oxygens.

As mentioned, having all redox potentials equal is optimal for self-exchange; however, in reality there will be energetic dispersion because of the local electrostatic potentials associated with fluctuations and diffusion of electrolyte. An example of how this sensitivity can be used to create a useful property is illustrated by the pH and ion dependence of calixarene-based conducting polymers such shown in Figure 9. For the base polymer (Figure 9, top) oxidation in acetonitrile, some of the protons from the phenols are lost, the redoxophores become mismatched, and the conductivity plummets.<sup>47</sup> This sensitivity to charge inspired the design of a crown ether structure, and this material displays similar binding constants for  $K^+$  and  $M^{2+}$  but has radically different

conductivity responses to these ions.<sup>48</sup> With oxidation in acetonitrile, the phenolic protons are lost and replaced with monovalent ( $K^+$ ) or divalent ( $M^{2+}$ ) ions bound to the crown ether receptor. The disordered in  $K^+$  complexes creates energetic dispersion in the redox states, and the materials are not conductive. In contrast, the  $M^{2+}$ -bound materials enjoy a highly regular structure, ensuring that all of the segments have the same redox potentials (i.e., same environments) to produce a conductive state.

When looking for structures with redox activity, one is quickly drawn to transition metal coordination chemistry. The area of redox conductivity between transition metal complexes was studied decades ago by the group of Royce Murray in thin films created by the electrodeposition and polymerization of vinyl-substituted octahedral ruthenium and osmium pyridyl, bipyridyl, and terpyridyl compounds. In a seminal paper in 1986, they demonstrated the correlation in conductivity maxima and  $E_{1/2}$  that I mentioned earlier. Specifically, in experiments that are largely equivalent to those of Wrighton,<sup>41</sup> they mapped out conductivity peaks ( $10^{-6}$ – $10^{-4}$  S/cm) for  $[\text{Os}(\text{bpy})_2(\text{vpy})_2](\text{ClO}_4)_x$  (bpy = bipyridyl, vpy = 4-vinylpyridine) (Scheme 7) that coincide with the  $E_{1/2}$  potentials of the  $\text{Os}^{\text{III/II}}$ ,  $\text{Os}^{\text{II/I}}$ , and  $\text{Os}^{\text{I/0}}$  waves.<sup>49</sup> It is important to note that in the more reduced forms of these complexes the electrons actually reside on the ligands. Hence, the bpy groups are best considered radical anions that are stabilized by coordination to cationic metals. Even earlier work on redox conduction of transition metal complexes demonstrated implications for bioelectronics wherein ferrocene was found to be well matched for charge transport between glucose oxidase and carbon electrodes to create glucose sensors.<sup>50</sup> Another notable



**Figure 7.** Water-soluble n-type conducting polymer ( $M_n \approx 15\text{K Da}$ ), the resonance structures illustrating its reduction, and its conductivity and cyclic voltammogram as determined using the microelectrochemical transistor method. By determining the thickness of the polymer between the electrodes, the absolute conductivity can be determined.

application of self-exchange electrical conduction is the use of osmium bipyridyl complexes to “wire” enzymes to electrodes.<sup>51</sup> These transition metal materials represent some of the best redox conductors with pendant redox groups with completely saturated backbones. There has been more recent interest in saturated polymers having pendant redox active nitroxides for organic battery applications.<sup>52,53</sup> These materials are also conductive with  $\sigma \approx 10^{-5}$  S/cm,<sup>54</sup> and empirically it would seem that conductivities for highly disordered redox self-exchange systems that lack direct  $\pi$ - $\pi$  orbital contact are limited to around  $\sigma \approx 10^{-4}$  S/cm.

Considering the facile conduction in vinyl polymers containing pendant redox-active metal complexes, it was only natural to create completely conjugated systems integrating redox-active transition metals. The trick is to get the metals to be actively involved in the conduction processes. You will note that conductive transition metal polymers just discussed all have a full coordination sphere about the metal. This was not an arbitrary selection and is central to produce the observed conductivities. The issue is that coordination compounds have charge largely localized about the metal, and strong associations with ions and polar/coordinating solvents will occur if given the chance. The octahedral (saturated) coordination ensures that all ion and solvent interactions are strictly outer sphere in nature. The result is a relatively uniform electrochemical potential of the metal complexes that is insensitive to the local

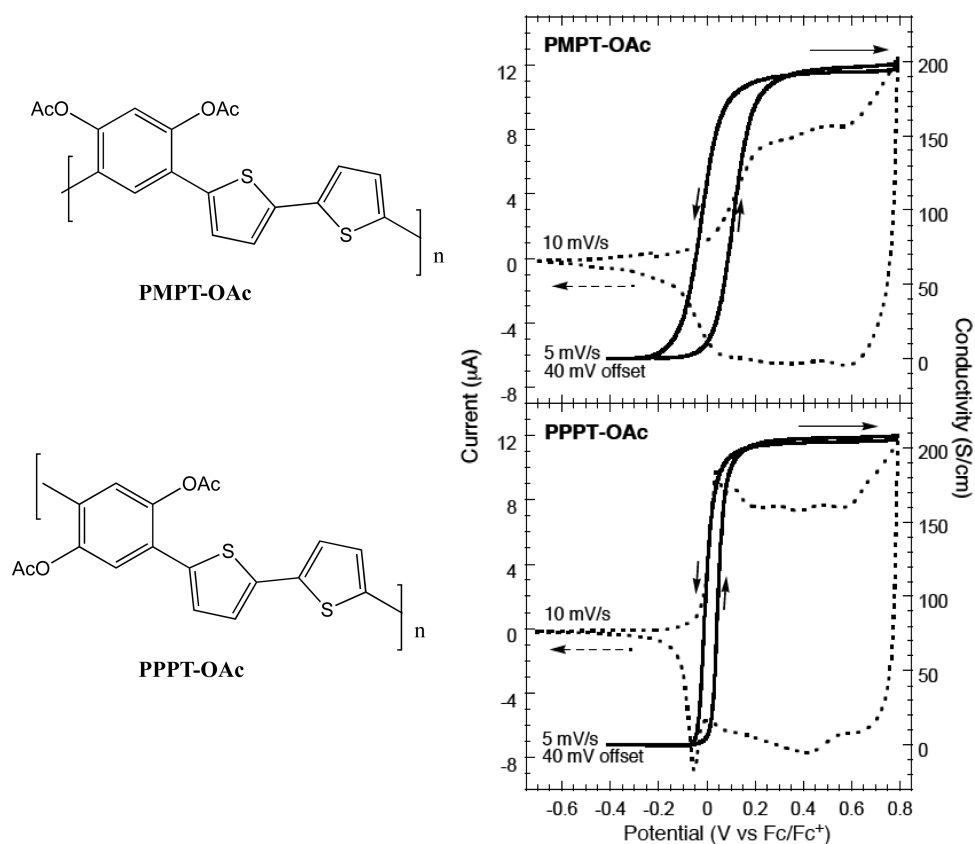
environment. Such insensitivity does limit function, and I am always on the lookout for responsive materials; hence, coordinately unsaturated metal complexes are attractive. However, disordered polymeric films of a redox-active square planar complexes suffer from redox potential variations, a result of strong electrostatic interactions and coordination of the metal centers with ions and solvent, that give only  $\sigma = 10^{-3}$  S/cm.<sup>55</sup> Delocalization of charge in  $\pi$ -conjugated materials minimizes these electrostatic effects by diffusing the injected charge to minimize the electrostatic interactions. You will recall that weaker electrostatic interactions with large and diffuse counterions is the same principle we invoke to understand why HI is a much stronger acid than HF.

The first highly conductive conducting oligomers were based on transition metal thiolates (degree of polymerization  $\approx 3$ ), and John Reynolds demonstrated in his PhD research that these materials could have conductivities up to 20 S/cm.<sup>56</sup> The most conductive are the  $(\text{Ni}(\text{S}_4\text{C}_2))_n$  oligomers shown in Scheme 8. The lack of solubility limits the polymerization to short oligomers ( $n = 3$ ). Hence, these materials resemble molecular charge transfer compounds, wherein we can think of the metal ions as providing partial oxidation of the thiolate ligands to provide radical character. Indeed, they are characterized as intrinsically conductive materials and oxidation by exposure to  $\text{I}_2$  vapor led to a decrease in conductivity. The metal thiolates remain as one of the few conducting polymer/oligomer materials to have intrinsic conductivity.

The preceding examples represented the state of the art in the early 1990s for metal-containing conducting polymers, and we set out to examine the design landscape. In particular, we wanted sensory materials wherein the metal's local electroactivity contributed to the conductivity such that binding of ligands would give large changes in the material's resistivity. By considering the self-exchange conductivity designs articulated here, we went on to show that if the organic- and metal-centered redox potentials could be designed to have the same potential, then highly conductive materials are generated. In this effort, we used electroactive cobalt salen complexes that are linked into electroactive polymers by thiophene groups (Figure 10).<sup>57</sup> In accord with Scheme 6, we expected the oxygens, which in this case are bond to the metal ions, to bear some positive charge when oxidized. In materials wherein the salen ligands are linked through bithiophene linkages the  $\text{Co}^{\text{II/III}}$  redox couple is at a lower potential than the organic centered oxidations. As a result of this mismatch (Figure 10), there is no conductivity associated with the  $\text{Co}^{\text{II/III}}$  couple. However, with di(ethylenedioxythiophene) (EDOT) linkages between the salens, the organic-centered electroactivity now overlaps with that of the  $\text{Co}^{\text{II/III}}$ , and the total conductivity is enhanced by about 6 times. The EDOT complexes displayed conductivities that are  $10^6$  times greater than those of the localized poly(vinyl osmium) materials.

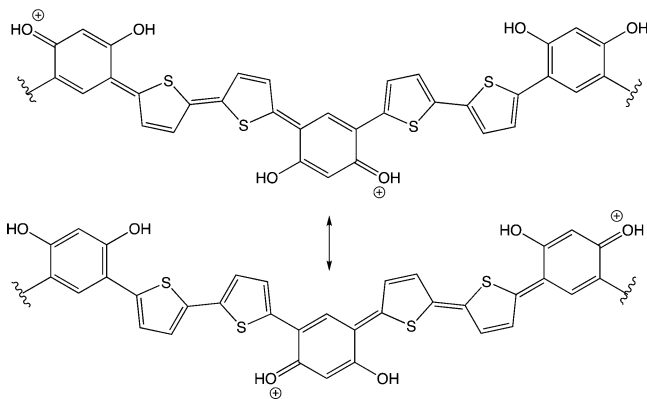
As predicted, perturbing the  $\text{Co}^{\text{II/III}}$  by the binding of a ligand results in a conductivity change. This is shown for the binding of lutidine to the cobalt center in Figure 11, which shifts the electroactivity to lower potential and dramatically lowers the conductivity. In the  $\text{Co}^{\text{II}}$  state the metal center is paramagnetic and binds to nitric oxide (NO) radicals. We went on to use this effect to create highly selective chemiresistive sensors for NO gas under realistic conditions.<sup>58</sup>

Supramolecular transition polymers based upon the pioneering designs of Jean Pierre Sauvage offered rich opportunities for the development of electronic materials.<sup>59</sup> In particular, he



**Figure 8.** Cyclic voltammograms and conductivity profiles of *meta*- and *para*-isomers. Note that their conductivities are nearly equivalent.

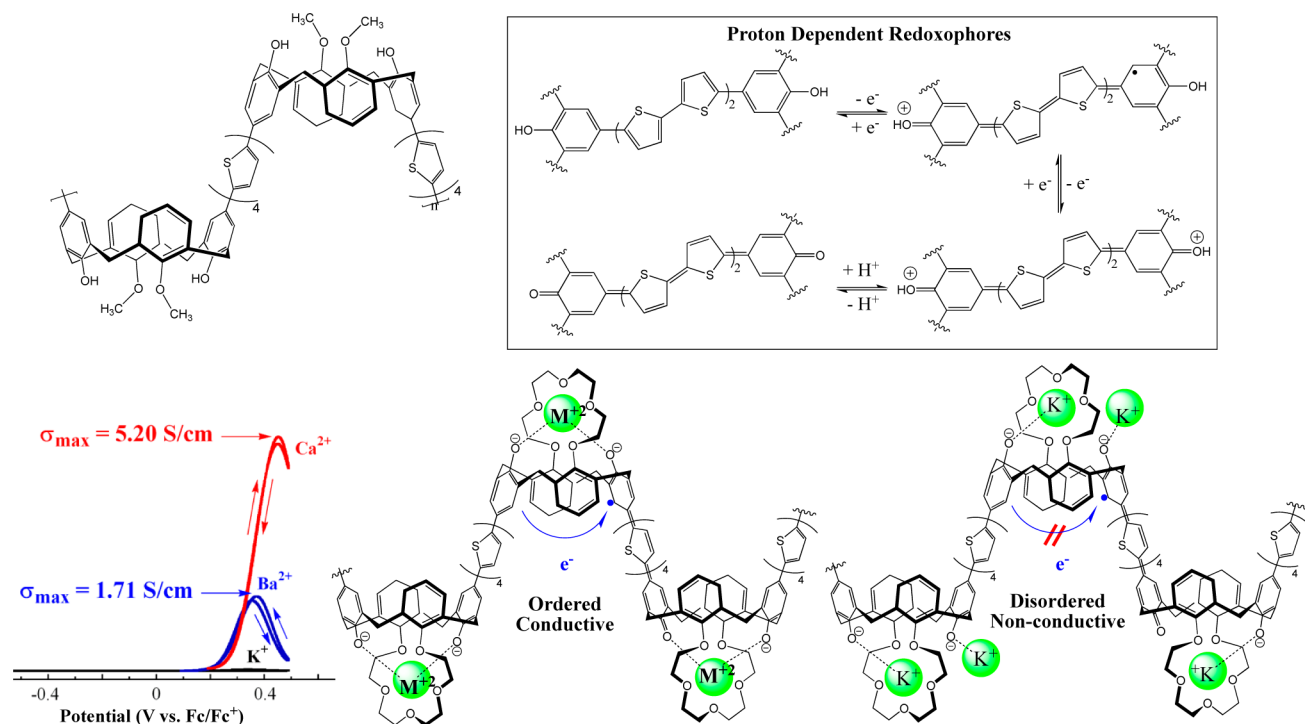
**Scheme 6. Resonance Structures That Show Displacement of Charge in Hydrolyzed and Oxidized PMPT-OAc**



demonstrated how ligand-restricted metal coordination geometries (tetrahedral and octahedral) will rapidly spontaneously assemble into elaborate structures with near perfection. An early example of applying these methods for the assembly of a rotaxane-conjugated oligomer came from Jean-Marie Lehn and co-workers.<sup>60</sup> They demonstrated the assembly of extended metallorotaxane structures using Sauvage's signature macrocycle and set the stage for the formation of new electronic materials. This platform represented an ideal venue to test the role of metal-centered electroactivity. Specifically, tetrahedral rotaxane systems were known to assemble with nearly equal ease around electrochemically inactive  $Zn^{II}$  centers as well as redox-active  $Cu^I$  ions. An illustration of this is shown in Figure 12 wherein to the electroactivity and conductivity of two metallorotaxanes, PolyRot( $Zn$ ) and PolyRot( $Cu$ ), are com-

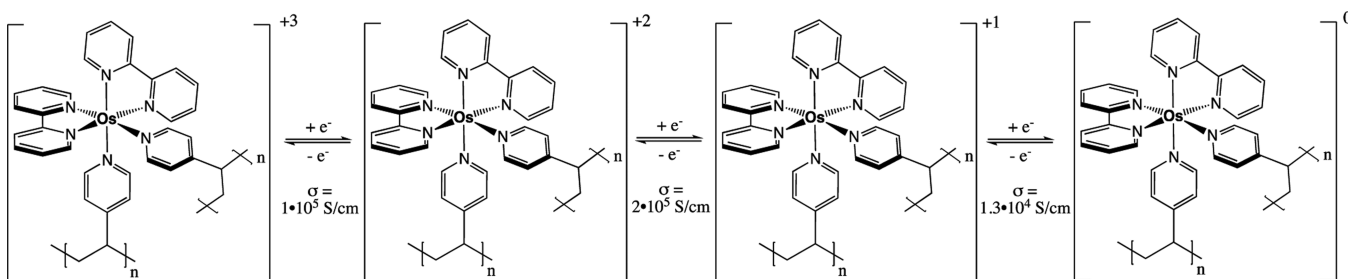
pared. These materials differ only in the identity of the metal ion. A striking feature is the degree to which the polymer backbone, which is completely conjugated, behaves as an isolated redox unit with two completely isolated one-electron redox waves. In accord with our previous discussion, the conductivity maxima coincide with the potential at which half of the species are oxidized (i.e., the  $E_{1/2}$ ), and it behaves as an efficient redox conductor with  $\sigma_{max} = 7 \times 10^{-4}$  S/cm for PolyRot( $Zn$ ). The  $Cu^{II}$  couple overlaps the first one-electron ligand-centered wave, and in PolyRot( $Cu$ ) this results in the highest conductivity being associated with the first wave rather than the second, as is the case for the  $Zn$  analogue ( $\sigma_{max} = 1 \times 10^{-3}$  S/cm).<sup>61</sup> It was also found that you could use this same overlapping conductivity to dope polymers, and demetalated polymers underwent conductivity enhancements of more than  $10^6$  when they are metalated with  $Cu^{II}$  ions. The modest conductivities in these materials relative to the previously discussed Co-salen polymers are likely the result of reduced interpolymer interactions as a result of the rigid metallorotaxane structure.

The role of copper-centered redox activity in promoting conductivity is dramatically exemplified in the three-strand polymer ladder shown in Figure 13.<sup>62</sup> This material is complex and was assembled by a sequential and templated two-stage polymerization. In effect, we create a molecular wire, and at low applied potentials the core (red polymer) is made to be conductive (oxidized) while the outer blue layer remains insulating (neutral). At higher applied potentials, the insulating blue polymer is switched to a conductive state, and high bulk conductivity is achieved. This is strictly the case when the polymer contains redox-inactive zinc ions. However, with the addition of copper ions, the situation changes. Copper centers

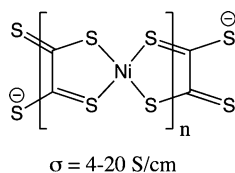


**Figure 9.** (top) A segmented conducting polymer incorporating a calix[4]arene in the main chain. This material displays a pH-sensitive conductivity and is conductive when protonated as shown in the drawings of the redoxophore substructure. (bottom) Conductivity traces as a function of applied electrochemical potential to the segmented ionophore conducting polymer shown. The charge balance provided by the M<sup>2+</sup> ions for the fully reduced case (phenolates) creates a homogeneous potential. In the case of K<sup>+</sup>, the conductivity is >10<sup>3</sup>-fold lower due to charge irregularity caused by disorder from the multiple cations and their direct interaction with the phenolates.

**Scheme 7.** Osmium Polymers That Display the Conductivities Shown at the Half-Wave Potentials ( $E_{1/2}$ ) between the Different States Shown



**Scheme 8.** A Metal Thiolate Oligomer with Intrinsic Conductivity



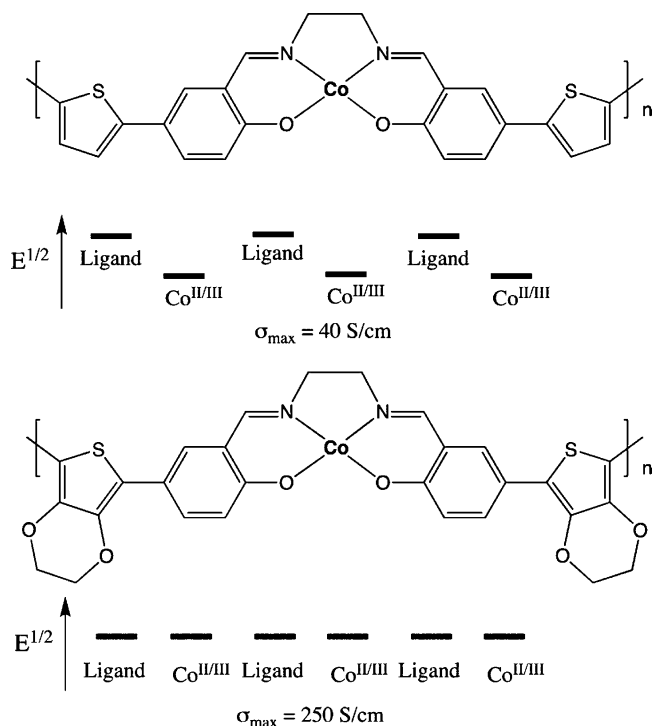
mediate conduction between the red cores on neighboring polymers even with the blue polymer in its insulating state.

There are several teachings from coordination chemistry with redox-active ligands that may offer other new opportunities to the adventurous researcher. Molecules that have matched redox states between the metal and the ligand can undergo a process known as valence tautomerization. This has been studied extensively in cobalt compounds having catecholate/*o*-semi-quinonate/*o*-quinone ligands (Scheme 9) wherein changes between Co<sup>II</sup>/Co<sup>III</sup> oxidation states can be switched with

mechanical stress, optical excitation, or temperature.<sup>63</sup> Similar transitions in conducting materials could be excellent candidates for switches, and one could imagine creating transistors or sensors that switch based upon electrically or chemically stimulating this transition to give large changes in conductivity.

In looking forward at this area, we have extensive proof that when a ligand and metal are properly matched in their redox potentials, an intrinsically conductive material is produced. The original studies revealing the high conductivity of (Ni(S<sub>4</sub>C<sub>2</sub>)<sub>n</sub>) oligomers stand out as a system wherein the amalgamation of the metal and organic states are particularly strong. The recognition of the importance of redox-active ligands is important, and there are many potential variations that have properties similar to the catecholate family just discussed. As a highlight to this point, Mircea Dincă has recently taken conductive metal organic polymers to new heights with integrated designs of metal organic frameworks.<sup>64</sup> His solution to create conducting materials ( $\sigma_{\max} = 40$  S/cm) employed





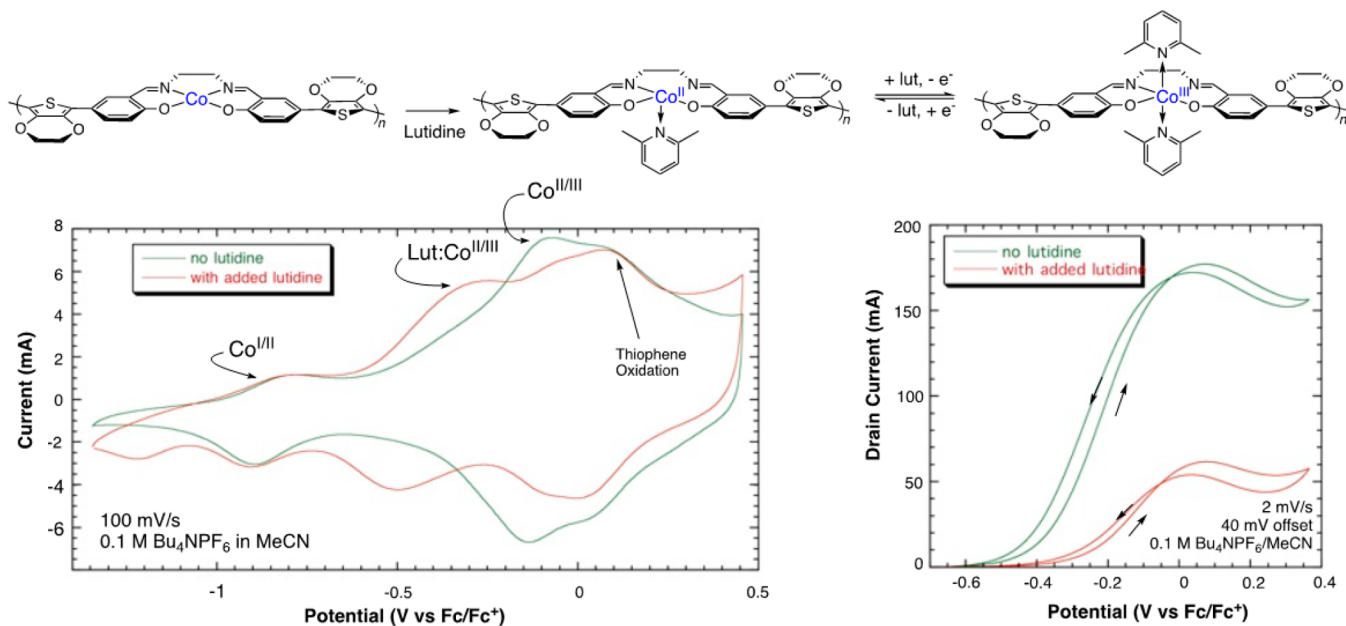
**Figure 10.** Structures of Co-salen-based conducting polymers. In the top structure the ligand-based electroactivity is at a higher oxidation potential than the  $\text{Co}^{\text{II/III}}$  couple, and there is conductivity associated with the partial oxidation of the ligand but no conductivity associated with the metal. In the bottom structure the EDOT groups result in a redox matching of the ligand and the  $\text{Co}^{\text{II/III}}$ , and the metal-centered redox activity contributes to the conductance.

extended triphenylene hexaamine groups that also give a matched redox state, and although in Figure 14 it is drawn as a closed-shell structure, it is likely that electronic configurations similar to the metal-semiquinonates contribute to the electronic structure. The 3-fold junctions create two-dimen-

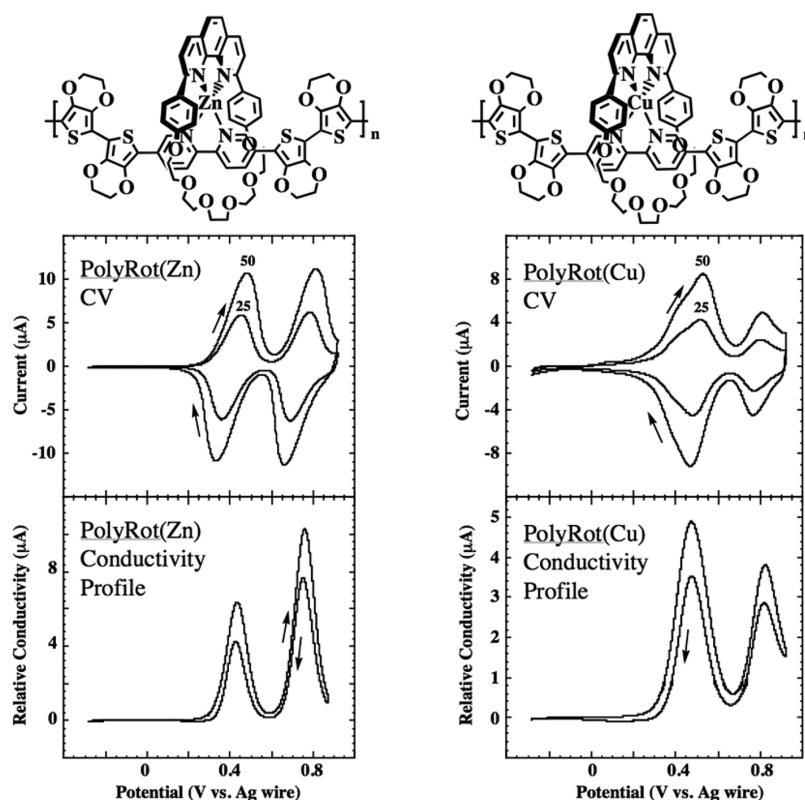
sional polymers that assemble in an eclipsed crystalline lattice to form honeycomb structures with molecularly defined precise porosity. These innovations have opened up avenues for the creation of new generations of size-selective, chemiresistive sensors, and indeed, these materials have shown great promise.<sup>65,66</sup>

Throughout our discussion, we have been talking about localized vs delocalized electronic structures. It should come as no surprise that the nature of the carriers may also be effected. From the very beginning of the conducting polymer field, with the study of neutral solitons in polyacetylene, it has been recognized that conjugated polymers often have mobile radicals. In aromatic polymers, the carriers in lightly doped structures are polarons. As originally formulated, these radical species were thought of as, or at least drawn as, intrachain species. However, in condensed form wherein the planes of the  $\pi$ -electronic states are packed face-to-face, it is not surprising that there are electronic interactions between the polymer chains. This coupling can take the form of very weak bonds and are dependent upon the degree of delocalization. This bonding to produce what are known as  $\pi$ -dimers came to light in a series of experiments by Larry Miller and Kent Mann on model oligothiophene compounds wherein they found that mixtures of radical cations displayed a reduced EPR signal at high concentrations.<sup>67</sup> The implication is that a multicentered cofacial  $\pi$ -bond between two radical cations leads to spin pairing. These interactions can also be present in conducting polymers, and a “dimerized polaron” is the same as an interchain bipolaron. Hence, these studies teach us that simply defining carriers using intrachain Lewis dot structures is likely an oversimplification. Figure 15 summarizes the different possibilities and the spin pairing that results from interchain bonding.

Polymers with more localized redox states (more localized polarons) are best suited to produce  $\pi$ -dimers (the more diffuse the orbitals, the weaker the interchain bonding). This is nicely illustrated with salen-based conducting polymers that tend to



**Figure 11.**  $\text{Co}^{\text{II/III}}$  couple is shifted to lower potential by the coordination of the donating lutidine ligand. The separation in potential between the ligand- and metal-centered electroactivities causes the observed decrease in conductivity.



**Figure 12.** Cyclic voltammograms (top plots) of supramolecular polymers PolyRot(Zn) and PolyRot(Cu) taken with interdigitated electrodes at scan rates of 50 and 25 mV/s in  $\text{CH}_2\text{Cl}_2/\text{N}(\text{Bu})_4\text{PF}_6$  electrolyte and conductivity profiles (bottom plots) of the same electrodes. For PolyRot(Zn) the tetra-EDOT sequence behaves as an isolated redox unit that is interrupted by nonoxidizable bipyridyl groups. This gives rise to two one-electron oxidation waves, and the conductivity maxima coincide with the  $E_{1/2}$  for each. In the case of the PolyRot(Cu), the  $\text{Cu}^{\text{I/II}}$  redox couple is coincident with the first ligand-based oxidation, and the conductivity is increased relative to the second organic-centered wave, indicating the metal centers' redox activity enhances the polymer's conductivity.

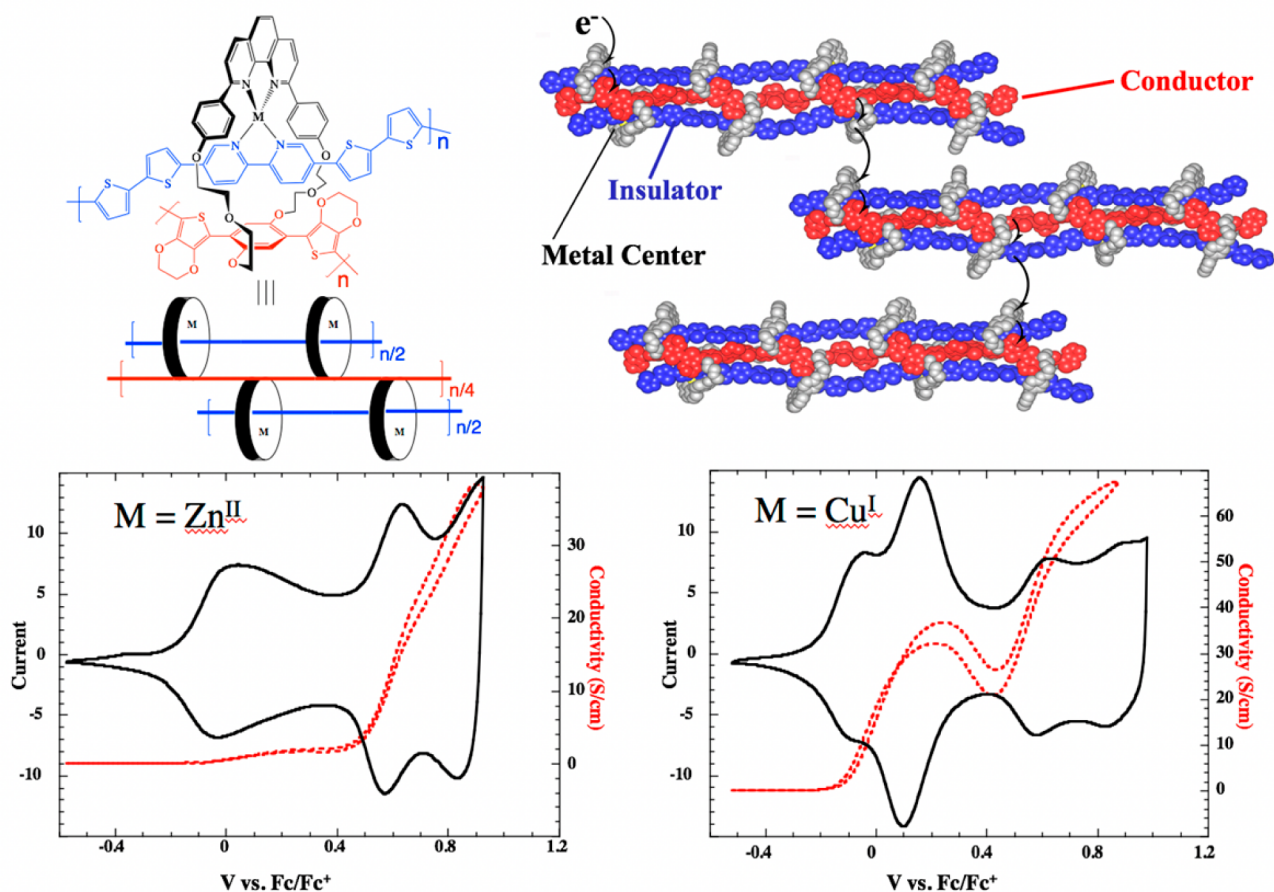
produce  $\pi$ -dimers, and the ability to produce a  $\pi$ -dimer was probed as a function of added steric bulk. The signatures of the different dimerized states shown in Figure 15 are revealed by comparing cyclic voltammograms and *in situ* measured spin densities as a function of applied electrochemical potential. For example, comparing the two nickel polymers in Figure 16, the sterically unencumbered polymer displays strong intermolecular interactions with four redox waves in its voltammogram and two clear windows with increased spin density. In contrast, the addition of two pendant phenyl groups limits interchain associations, and simplified electrochemical behavior is observed with two redox waves. The spin density peaks with the first oxidation and that drops quickly with further oxidation.

This notion of  $\pi$ -dimers and the implications that at low doping levels carriers may very well be best described as interchain polarons have particular relevance to the present intense, worldwide focus on donor–acceptor polymers for photovoltaic applications. In these cases, injected polarons will localize on the donor unit and could be subject to interchain interactions. Dimerized polarons (or interchain bipolarons) can be shallow traps that slow down carrier diffusion. However, if the structures assemble promoting donor–acceptor interchain stacking (Figure 4), then this effect can be mitigated because the organization prevents two intrachain polarons being proximate to each other. The photovoltaic field has determined that processing and promoting of high cofacial organization, as well as lateral dipoles, all have influence on the performance. The literature is too vast here to summarize, however, but the

forgotten  $\pi$ -dimer concepts have relevance, and perhaps new thinking along these lines will inspire new innovations.

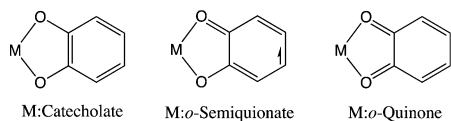
## ■ MAGNETIC AND MAGNETO-OPTICAL PROPERTIES

I have devoted a considerable amount of discussion in this Perspective to the use of metals to enhance and modulate conductivity. A remaining grand challenge for the area of metal–organic polymers is to create air-stable polymeric materials with a conductive ferromagnetic state at room temperature. One approach to this goal can be found in what is called the double exchange mechanism, which is responsible for magnetism in  $\text{Fe}_3\text{O}_4$ , magnetite.<sup>68</sup> In magnetite, all of the iron atoms are in octahedral geometries with high spin states. There are formally two  $\text{Fe}^{\text{III}}$  ions and one  $\text{Fe}^{\text{II}}$  in the structure, and the conductivity of this material is connected directly to the magnetism. In particular, delocalization (hopping conduction) of the extra electron associated with the  $\text{Fe}^{\text{II}}$  is only allowed according to the Pauli principle when all of the unpaired electrons are aligned as shown in Figure 17. The quest for magnetic ordering in synthetic molecular constructions is beyond the scope of this Perspective, and interested parties will benefit from reading a recent review by Joel Miller, one of the pioneers of that area.<sup>69</sup> You will find that many of the concepts on the designs of molecular magnets involve redox reactions between metals and ligands, similar to those that I have been discussing. However, Miller emphasizes that using open-shell ligands is key to create magnetic ordering. The more concentrated the spin, the better, and for magnetic molecular



**Figure 13.** A three-strand supramolecular ladder polymer assembled by sequential polymerization of the inner (red) group followed by the blue group. The red polymer oxidizes at about 0 V, and the other blue polymer oxidizes at potentials of 0.55 V or higher. Note that the blue polymer has two clear waves because the electronic structure is interrupted by the bipyridyl group. When the blue polymer is in its neutral insulating state and the metal ion is  $\text{Zn}^{\text{II}}$ , the material has minimal conductivity. Oxidation of the blue polymer renders the system conductive. However, for the copper complexes the metal-centered redox activity mediates electron transport between the polymers (top right). In this case, the conductivity profile has a peak that is coincident with the  $\text{Cu}^{\text{I/II}}$  electroactivity.

### Scheme 9. Different States of Catecholate Ligand–Metal Complexes



materials one of the favorite bridging ions between the metal ions is the radical anion of tetracyanoethylene ( $\text{TCNE}^{\bullet-}$ ).

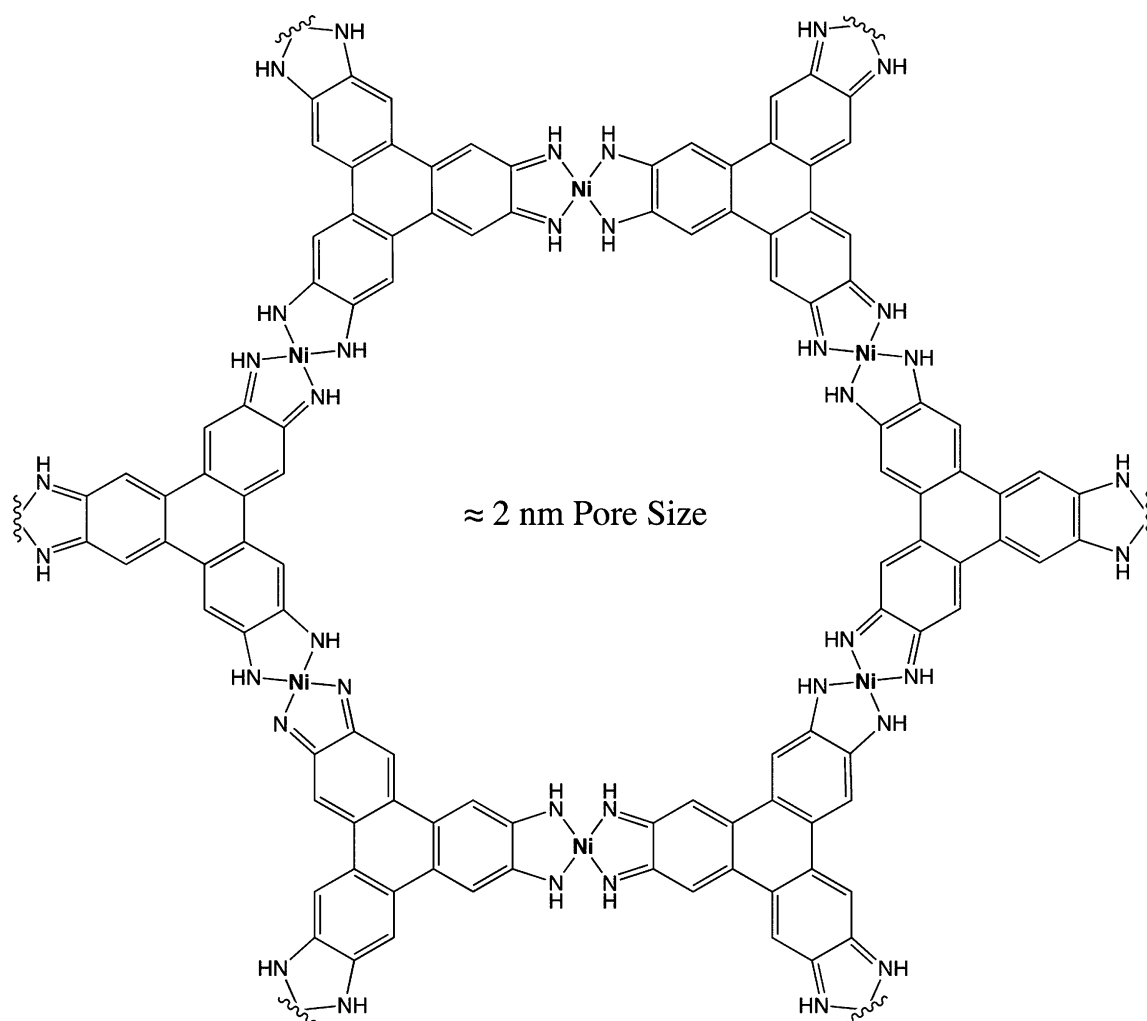
Recent discoveries have shown conjugated polymers to display extraordinary and unpredicted magneto-optical properties. The effect is related to the classical studies of Michael Faraday more than 170 years ago when he demonstrated the dual electrical and magnetic properties of light by measuring what is now known as the Faraday rotation. In the Faraday experiment, plane-polarized light transmitted along the direction of a magnetic field through a solution or solid containing magnetic ions experiences a rotation in its polarization (Figure 18).

Plane-polarized light can be considered as being composed of equal contributions of two opposite-handed circularly polarized beams, and the rotation of the polarization plane indicates that one of these chiral components is slowed as a result of a magnetic interaction. The physics is obviously more complex,

but this provides a base intuition on the phenomena. The quantification of the ability of a material to rotate light is described as a Verdet constant that has the units of  $\text{deg}/(\text{T m})$  (degrees/(tesla meter)). The Faraday rotation has a number of important applications including the ability to create optical isolators in laser systems and to measure magnetic fields. Indeed, the most sensitive noncryogenic magnetometers make use of optical measurements of Faraday rotations.

Select pedagogical conjugated organic polymers exhibiting Faraday rotation are shown in Figure 19. The breakthrough in this area began with the measurement of an unexpectedly high Verdet constant ( $V$ ) of  $6.25 \times 10^4 \text{ deg}/(\text{T m})$  in films of regioregular poly(3-hexylthiophene).<sup>70</sup> This value is considerably larger than conventional iron garnet films that have  $V \approx 10^3 \text{ deg}/(\text{T m})$  and comparable to state-of-the-art commercial terbium gallium garnet ( $V = 7.68 \times 10^4 \text{ deg}/(\text{T m})$ ), materials developed specifically for their magneto-optical properties. Faraday rotations are enhanced by strong spin–orbit coupling, free carriers, and/or unpaired electrons. Hence, it is perplexing that a polymer lacking heavy atoms that is nominally undoped with very dilute paramagnetic species would have such a large  $V$ . The physics explaining the electromagnetic couplings that are responsible for this effect are still evolving, and it would appear that longer range electronic interactions (coherence) are likely necessary to facilitate coupling to these nonresonant





**Figure 14.** A two-dimensional coordination polymer that assembles in an eclipsed structure to generate a porous, hexagonal (honeycomb) structure.

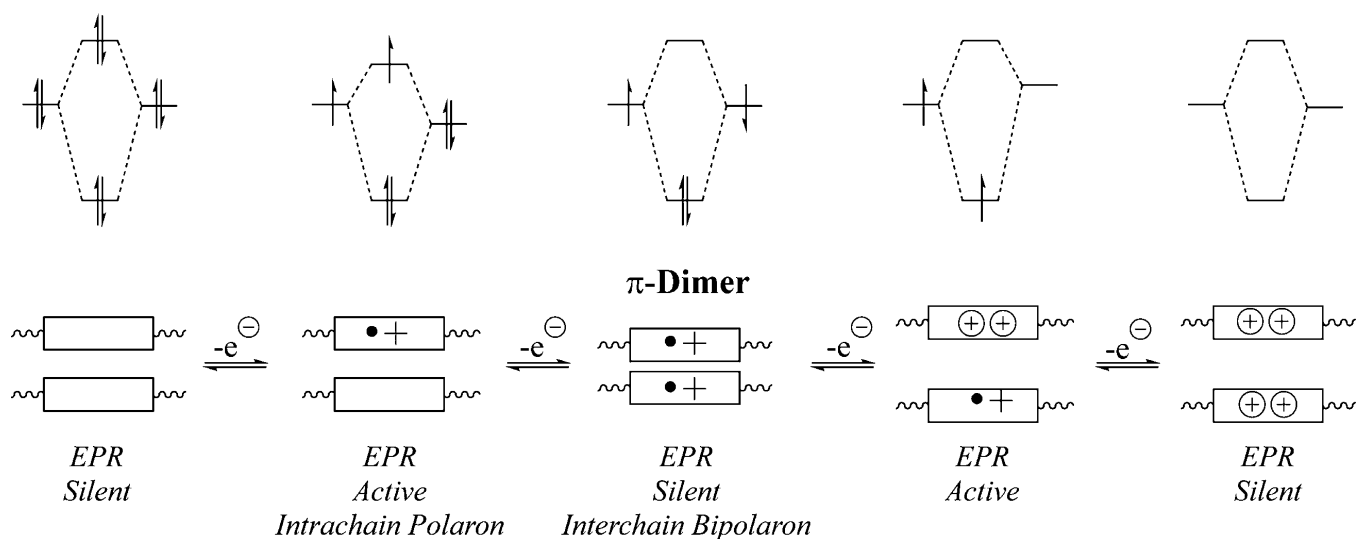
optical excitations. The organization of the polymers afforded by regioregularity as originally proposed by Rich McCullough<sup>71</sup> appears to be critical to achieve large Verdet constants. A key study revealed dramatic reductions in the Faraday rotation with only small reductions in regioregularity, and regiorandom poly(3-hexylthiophene) exhibits rotations that are below detection limits.<sup>72</sup> The lamellar structure of regioregular poly(3-alkylthiophene)s promotes both intrapolymer and interpolymer electronic delocalization. The effect is not limited to polythiophenes, and a donor–acceptor poly(arylene ethynylene) has also been reported to have  $V = 25 \times 10^4$  deg/(T m).<sup>73</sup> These authors also investigated regioregular poly(3-hexylthiophene) and poly(3-dodecylthiophene) and confirmed their high Verdet constants with values of  $V = 20 \times 10^4$  deg/(T m) and  $V = 11 \times 10^4$  deg/(T m), respectively. The rigid rod character and large persistence lengths of these types of poly(arylene ethynylene)s<sup>74</sup> may underpin their magneto-optical performance, and these materials, when substituted with long alkyl chains, have been shown to organize into highly regular lamellar structures.<sup>75</sup> However, based upon my knowledge of these materials, only short oligomers of the structure shown will be soluble. Hence, there is a conspicuous absence of any chemical characterization in the publication, which is probably the result of the limited solubility. Nevertheless, based upon the prospects for interoligomer donor–acceptor interactions that were discussed previously,

and the tendency of these donor–acceptor poly(arylene ethynylene)s to assemble into lamellar organizations, it is reasonable to assume that they indeed have extended solid-state order. As a result of the higher bond length alternation and associated electron affinity, poly(arylene ethynylene)s are not particularly good at stabilizing polarons. This suggests that the large  $V$  values are likely not coming exclusively from dilute radical species. This is not to say that magnetic interactions should be discounted, and a recent publication has revealed that doping a chiral poly(fluorene) with nitroxide diradicals (Figure 19, bottom) generates an even higher value of  $V = -38 \times 10^4$  deg/(T m).<sup>76</sup> Hence, integrated systems containing paramagnetic ions would appear to hold promise as the next generation of magneto-optical materials.

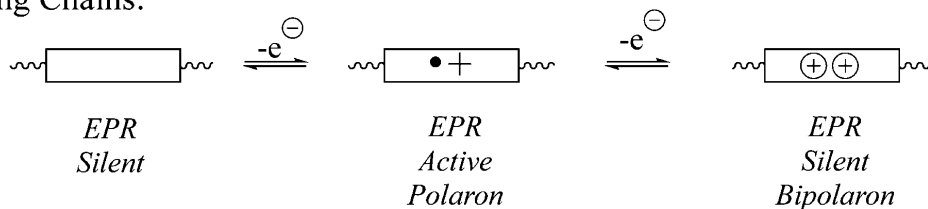
The last study reveals a number of other important features. The fact that chirality is important should not be a surprise as we are rotating plane polarized light. Enhancing the “chirality” of the electrons to enhance the magneto-optical response makes intuitive sense, even without understanding the physics. An additional issue is that the morphology of poly(fluorene)s having branched bulky side chains is not lamellar. Hence, although interchain couplings may still be important, it does not appear that a lamellar structure is required as was originally assumed based upon the studies on regioregular poly(3-alkylthiophene)s.<sup>72</sup> In fact, the authors argue that the conformation is that of a helical polymer with the radicals,



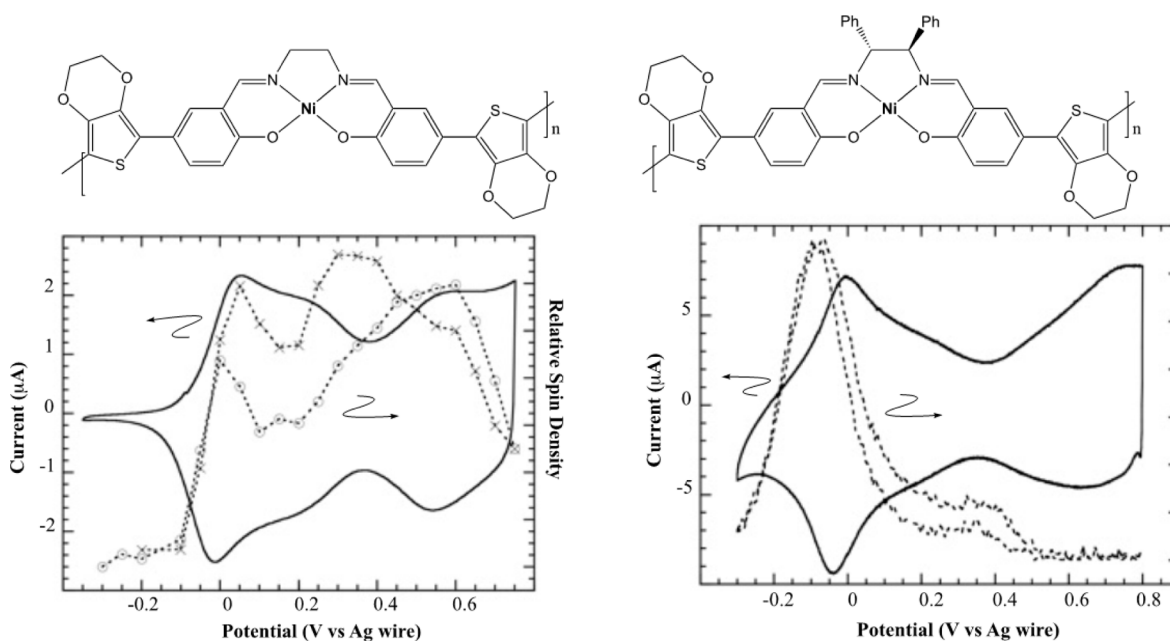
## Interacting Chains:



## Noninteracting Chains:



**Figure 15.** Schematic diagrams illustrating the cases of a confined  $\pi$ -system (shown as a box) where carriers can interact to give strong interchain interactions (top) and the case wherein a system is isolated so as to be properly described as an intrachain carrier (bottom).



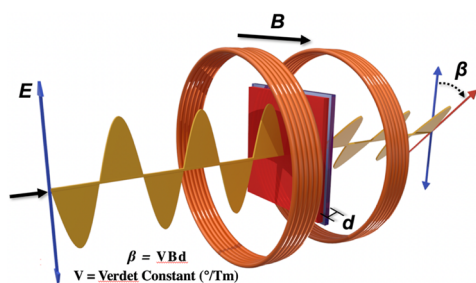
**Figure 16.** Cyclic voltammograms of two closely related metallo-organic polymers that differ only in the steric bulk about the polymer chain. The polymer at the left has minimal steric impediments and displays electroactivity and spin densities that are consistent with the formation of  $\pi$ -dimers. The material shown at the right has pendant phenyl groups that prevent interchain interactions and display a voltammetry and spin density that is best described by the intrachain model.

that have a cylindrical shape, nestled between the polymer chains.

New materials with very large magneto-optical coefficients will have some very significant technological implications. Magnetic sensors are widely used to detect the relative



**Figure 17.** Simplified diagram illustrating how the extra electron associated with the Fe<sup>II</sup> center in magnetite can delocalize when all of the unpaired spins are aligned. If neighboring Fe<sup>III</sup> centers were aligned antiparallel, the transfer would violate the Pauli principle.



**Figure 18.** Illustration of a plane polarized light wave propagating down the axis of an applied magnetic field,  $B$ , and being rotated by an angle,  $\beta$ , by a magneto-optical material of thickness,  $d$ .

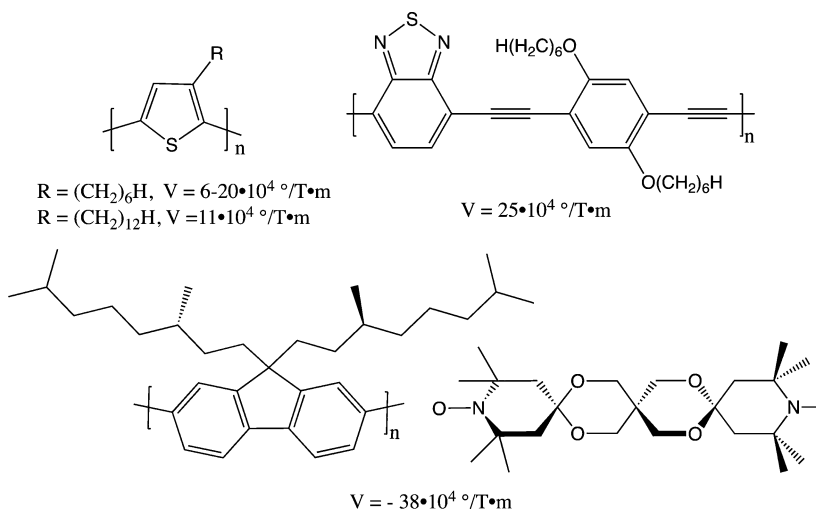
positions of objects and can be used for applications both trivial (e.g., telling you that your door is ajar in an automobile) and boundary-pushing (e.g., for precise positioning in nanofabrication). Optical methods that do not require electrical contact with the sensors are certain to spawn new applications that are not easily addressed by conventional sensors. The ultrahigh sensitivity that is possible using these emerging magneto-optical methods also has many implications for detection, which range from detecting physical movement/position of dynamic objects or even in detecting the magnetic signals associated with brain activity. The latter is called magnetoencephalography, and to monitor these small magnetic signals presently requires superconducting detectors and a large cryogenic device to be placed around the subject's stationary head.<sup>77</sup> The prospects for a fiber optical system that operates at

ambient temperatures is exciting and could enable new generations of control systems that couple brain activity to mechanical or electronic systems.

## FINAL THOUGHTS

I continue to marvel at the complexity and hidden treasures that exist in electronic polymers. Synthetic chemists, as molecular architects, are in the position to create endless variations of these materials with real-world consequences. One lesson from the field of conjugated polymer is that precision in synthesis is critical and electronic polymers are not as defect tolerant as other polymeric materials. Generating defect-free high molecular weight materials is an important goal, and new chain growth methods are needed. Science is probably trendy to a fault. The field of conducting polymers began with conductivity and electroactivity as ruling the day, with dreams of low-loss, inexpensive powerlines. Electroactivity and bandgap engineering have given rise to impressive advances in electrochromic materials based on conducting polymers.<sup>78</sup> FET demonstrations suggested the prospects for fully integrated organic electronics. The optimization of transport (carrier mobility) at low doping levels in FETs is also highly relevant for organic photovoltaic applications. Other areas such as chemical sensors, biosensors, and electrochemical storage also remain of interest.

In this Perspective, I have picked some different topics and tried to present things in a simplistic way. Much of the physics underpinning the materials we aspire to make will be beyond the typical chemists' comprehension. Hence, we need to follow our intuition and know enough to understand to recognize when we have hit on something that will push the boundaries of current science and technology. Creating robust polymers with metallic ground states should be a continuing goal, in spite of heavy focus on semiconductors in recent years. Recognize that the physicists do not completely understand high-temperature superconductivity, and perhaps an intrinsically conductive polymer could open up a new window into this magical state. Electronic delocalization/coherence is highly variable in conducting polymers. Disordered electrostatic potentials, the largest of which come from dopant counterions, tend to localize electrons. Intrinsic organic metals that do not



**Figure 19.** Two polymers (top) and a polymer diradical composite (bottom) investigated for their magneto-optical properties and their associated Verdet constants.

suffer from this issue are certain to have some nice surprises. Hybrid materials incorporating transition metal centers generated the first intrinsic conductors, and the mixing and matching of electroactive organics with metal centers has seen limited attention. We have barely scratched the surface of the possibilities of creating new metal–organic conducting polymers.

I also emphasized the role of interchain interactions and  $\pi$ -dimerization. Switchable attractive interactions between segments of polymers could be used to dynamically change a material's mechanical properties. Conducting polymer actuating materials can be produced that dynamically stiffen or contract/expand and thereby emulate mammalian muscle.<sup>79</sup> We have all seen many wiggling filament videos that make use of bending interactions in organic polymers or carbon nanotubes. However, these effects are usually caused by only a couple of percent strain in the material, and studies are seldom done that involve demonstrating physical work by moving loads. Additional advances in polymer actuators (artificial muscles) will come from applying a number of different forces and effects. Forming and dissociating molecular bonds between polymer chains can provide the needed driving forces to make actuators that rival mammalian muscle. Molecular mechanical linkages can play a role, and the  $\pi$ -dimers in molecular hinges<sup>80,81</sup> can create a latch state that can be activated and hold a load without continuing to expend energy, something our muscles do not enjoy. One of the major problems in organic actuators is to make a material that can undergo >10% dimension changes and not change its resistance (fatigue) over thousands to millions of cycles. Soft materials are likely the key to emulating muscles, and energy-efficient soft actuators are needed to enable new generations of versatile robotic systems.

The incorporation of heavy elements into organic conductors is also an area that is ripe to generate quantum jumps in different materials properties. There has been an enduring large interest in the substitutions creating main-group materials including materials containing Si, Ge, P, Se, and Te. These studies have all largely focused on band gaps, electron affinities, and/or carrier transport with some efforts to create photovoltaic devices. Continued emphases of materials containing heavy atoms and expanding investigations of their utility would seem to be in order. In the area of photovoltaics, the now-record-holding efficient lead perovskites teach us that creating a high internal dielectric constant, which allows excitons to dissociate at room temperature, is a key consideration. Perhaps materials having a large content of heavy main-group elements can generate high enough polarizability; however, it also seems that integrating diamagnetic metals could help to create new lead-free solar cells that similarly do not require a bulk heterojunction. Heavy atoms and paramagnetism are also likely to produce new generations of magneto-optical materials. My guess is that many of the organic materials designed for photovoltaic systems will also have outstanding magneto-optical performance, and we only need to start looking more broadly to break this area wide open.

One of my favorite sayings is "Ideas are cheap, and making things work is the real challenge." Hence, the ownership of the next new best materials for X, Y, Z... application belongs to the researchers who do the hard work of translating ideas to reality. We are in a materials-limited world, and likewise the scientists who develop new materials can change the world.

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### Notes

The author declares no competing financial interest.

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Timothy M. Swager is the John D. MacArthur Professor of Chemistry and the Director, Deshpande Center for Technological Innovation at the Massachusetts Institute of Technology. A native of Montana, he received a BS from Montana State University in 1983 and a Ph.D. from the California Institute of Technology in 1988. After a postdoctoral appointment at MIT, he was on the chemistry faculty at the University of Pennsylvania (1990–1996) and returned to MIT in 1996 as a Professor of Chemistry and served as the Head of Chemistry from 2005–2010.

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## REFERENCES

- (1) Lee, K.; Cho, S.; Park, S. H.; Heeger, A. J.; Lee, C.-W.; Lee, S.-H. Metallic Transport in Polyaniline. *Nature* **2006**, *441*, 65–68.
- (2) Wang, Z. H.; Scherr, E. M.; MacDiarmid, A. G.; Epstein, A. J. Transport and EPR Studies of Polyaniline: A Quasi-One-Dimensional Conductor with Three-Dimensional "Metallic" States. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *45*, 4190–4202.
- (3) Walatka, V. V. J.; Labes, M. M.; Perlstein, J. H. Polysulfur Nitride-A One Dimensional Chain with a Metallic Ground State. *Phys. Rev. Lett.* **1973**, *31*, 1139.
- (4) An amusing story that Alan MacDiarmid often told his friends is that when Mort Labes first told him about (SN)<sub>x</sub>, he had thought it was (Sn)<sub>x</sub>. Alan and his colleagues at the University of Pennsylvania went on to spend some time thinking about how how this new allotrope of tin metal could possibly be stable.
- (5) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. Synthesis of Electrically Conducting Organic Polymers-Halogen Derivatives of Polyacetylene, (CH)<sub>x</sub>. *J. Chem. Soc., Chem. Commun.* **1977**, 578–580.

- (6) Greene, R. L.; Street, G. B.; Suter, L. J. Superconductivity in Polysulfur Nitride (SN)<sub>x</sub>. *Phys. Rev. Lett.* **1975**, *34*, 577–579.
- (7) Little, W. A. Possibility of Synthesizing an Organic Superconductor. *Phys. Rev.* **1964**, *134*, A1416–A1424.
- (8) Williams, J. M.; Schultz, A. J.; Geiser, U.; Carlson, K. D.; Kini, A. M.; Wang, H. H.; Kwok, W. K.; Whangbo, M. H.; Schirber, J. E. Organic Superconductors- New Benchmarks. *Science* **1991**, *252*, 1501–1508.
- (9) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. Superconductivity at 18K in Potassium-Doped C<sub>60</sub>. *Nature* **1991**, *350*, 600–601.
- (10) BCS refers to Bardeen–Cooper–Schrieffer, who received the Nobel Prize in Physics in 1972 for their microscopic theory of superconductivity.
- (11) Monthoux, P.; Pines, D.; Lonzarich, G. G. Superconductivity without Phonons.
- (12) As is typical, trendy names often rebrand areas, and types of ladder polymers were previously referred to as graphite ribbons. For example: Goldfinger, M. B.; Swager, T. M. Fused Polycyclic Aromatics via Electrophile-Induced Cyclization Reactions: Application to the Synthesis of Graphite Ribbons. *J. Am. Chem. Soc.* **1994**, *116*, 7895–6.
- (13) Ezawa, M. Peculiar Width Dependence of the Electronic Properties of Carbon Nanoribbons. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, *73*, 045432.
- (14) Cohen, M. J.; Garito, A. F.; Heeger, A. J.; MacDiarmid, A. G.; Mikulski, C. M.; Saran, M. S.; Kleppinger, J. Solid State Polymerization of S<sub>2</sub>N<sub>2</sub> to (SN)<sub>x</sub>. *J. Am. Chem. Soc.* **1976**, *98*, 3844–3848.
- (15) [https://en.wikipedia.org/wiki/E.T.\\_the\\_Extra-Terrestrial](https://en.wikipedia.org/wiki/E.T._the_Extra-Terrestrial).
- (16) Chen, D.; Winokur, M. J.; Cao, Y.; Heeger, A. J.; Karasz, F. E. Stage-1 Phases of Alkali-Metal-Doped Conducting Polymers. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *45*, 2035–2045.
- (17) Marsella, M. J.; Fu, D.; Swager, T. M. Synthesis of Regioregular Poly(Methyl Pyridinium Vinylene): An Isoelectronic Analog to Poly(Phenylene Vinylene). *Adv. Mater.* **1995**, *7*, 145–147.
- (18) Willis-Fox, N.; Belger, C.; Fennell, J. F.; Evans, R. C.; Swager, T. M. Threading the Needle: Poly-*pseudo*-rotaxanes with Enhanced Fluorescence and Size-Exclusion based Sensing. *Chem. Mater.* **2016**, *28*, 2685–2691.
- (19) Kivelson, S.; Chapman, O. L. Polyacene and a New Class of Quasi-One-Dimensional Conductors. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1983**, *28*, 7236–7243.
- (20) Chun, D.; Cheng, Y.; Wudl, F. The Most Stable and Fully Characterized Functionalized Heptacene. *Angew. Chem., Int. Ed.* **2008**, *47*, 8380–8385.
- (21) Mondal, R.; Shah, B. K.; Neckers, D. C. Photogeneration of Heptacene in a Polymer Matrix. *J. Am. Chem. Soc.* **2006**, *128*, 9612–9613.
- (22) Anthony, J. E. The Larger Acenes: Versatile Organic Semiconductors. *Angew. Chem., Int. Ed.* **2008**, *47*, 452–483.
- (23) Bendikov, M.; Duong, H. M.; Starkey, K.; Houk, K. N.; Carter, E. A.; Wudl, F. Oligoacenes: Theoretical Prediction of Open-Shell Singlet Diradical Ground States. *J. Am. Chem. Soc.* **2004**, *126*, 7416–7417.
- (24) Winkler, M.; Houk, K. N. Nitrogen-Rich Oligoacenes: Candidates for n-Channel Organic Semiconductors. *J. Am. Chem. Soc.* **2007**, *129*, 1805–1815.
- (25) Bunz, U. H. F.; Engelhart, J. U.; Lindner, B. D.; Schaffroth, M. Large N-Heteroacenes: New Tricks for Very Old Dogs? *Angew. Chem., Int. Ed.* **2013**, *52*, 3810–3821.
- (26) Matsumi, N.; Chujo, Y.  $\pi$ -Conjugated Organoboron Polymers via the Vacant p-Orbital of the Boron Atom Poly. *Polym. J.* **2008**, *40*, 77–89.
- (27) Kawai, S.; Saito, S.; Osumi, S.; Yamaguchi, S.; Foster, A. S.; Spijker, P.; Meyer, E. Atomically Controlled Substitutional Boron-doping of Graphene Nanoribbons. *Nat. Commun.* **2015**, *6*, 8098.
- (28) Messersmith, R. E.; Siegler, M. A.; Tovar, J. D. Aromaticity Competition in Differentially Fused Borepin-Containing Polycyclic Aromatics. *J. Org. Chem.* **2016**, *81*, 5595–5605.
- (29) Abe, M. Diradicals. *Chem. Rev.* **2013**, *113*, 7011–7088.
- (30) Dane, E. L.; Swager, T. M. Carbanionic Route to Electroactive Carbon-Centered Anion and Radical Oligomers. *Org. Lett.* **2010**, *12*, 4324–4327.
- (31) Kubo, T.; Shimizu, A.; Sakamoto, M.; Uruichi, M.; Yakushi, K.; Nakano, M.; Shiomi, D.; Sato, K.; Takui, T.; Morita, Y.; Nakasujii, K. Synthesis, Intermolecular Interaction, and Semiconductive Behavior of a Delocalized Singlet Biradical Hydrocarbon. *Angew. Chem., Int. Ed.* **2005**, *44*, 6564–6568.
- (32) Kertesz, M.; Choi, C. H.; Yang, S. Conjugated Polymers and Aromaticity. *Chem. Rev.* **2005**, *105*, 3448–3481.
- (33) Wudl, F.; Kobayashi, M.; Heeger, A. J. Poly(isothianaphthene). *J. Org. Chem.* **1984**, *49*, 3382–3384.
- (34) Hoogmartens, I.; Adriaensens, P.; Vanderzande, D.; Gelan, J.; Quattrocchi, C.; Lazzaroni, R.; Bredas, J. L. Low-bandgap Conjugated Polymers. A Joint Experimental and Theoretical Study of the Structure of Polyisothianaphthene. *Macromolecules* **1992**, *25*, 7347–7356.
- (35) Wen, L.; Duck, B. C.; Dastoor, P. C.; Rasmussen, S. C. Poly(2,3-dihexylthieno[3,4-b]pyrazine) via GRIM Polymerization: Simple Preparation of a Solution processable, Low-Band-Gap Conjugated Polymer. *Macromolecules* **2008**, *41*, 4576–4578.
- (36) Takeda, Y.; Andrew, T. L.; Lobez, J. M.; Mork, A. J.; Swager, T. M. An Air-stable Low Bandgap n-Type Organic Polymer Semiconductor Exhibiting Selective Solubility in Fluorous Solvents. *Angew. Chem., Int. Ed.* **2012**, *51*, 9042–9046.
- (37) Fu, D.-K.; Xu, B.; Swager, T. M. Alternating Poly(Pyridyl Vinylene Phenylene Vinylene)s: Synthesis and Solid State Organizations. *Tetrahedron* **1997**, *53*, 15487–15494.
- (38) Ballauff, M. Stiff-Chain Polymers-Structure, Phase Behavior, and Properties. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 253–396.
- (39) Ofer, D.; Swager, T. M.; Wrighton, M. S. Solid State Ordering and Potential Dependence of Conductivity of Poly(2,5-dialkoxy-p-Phenyleneethynylene). *Chem. Mater.* **1995**, *7*, 418–25.
- (40) Osaka, I.; McCullough, R. D. Advances in Molecular Design and Synthesis of Regioregular Polythiophenes. *Acc. Chem. Res.* **2008**, *41*, 1202–1214.
- (41) White, H. S.; Kittleson, G. P.; Wrighton, M. S. Chemical Derivatization of an Array of Three Gold Microelectrodes with Polypyrrole: Fabrication of a Molecule-Based Transistor. *J. Am. Chem. Soc.* **1984**, *106*, 5375–5377.
- (42) Ofer, D.; Crooks, R. M.; Wrighton, M. S. Potential Dependence of the Conductivity of Highly Oxidized Polythiophenes, Polypyrroles, and Polyaniline – Finite Windows of High Conductivity. *J. Am. Chem. Soc.* **1990**, *112*, 7869–7879.
- (43) Mott insulators are discussed in most introductory solid state physics textbooks and are materials that should be conductive when you only consider simple band theory. However, electron–electron (charge) repulsions in materials that have lower polarizability can result in localized electronic states that prevent electronic conduction.
- (44) Izuhara, D.; Swager, T. M. Poly(Pyridinium Phenylene)s: Water Soluble N-Type Polymers. *J. Am. Chem. Soc.* **2009**, *131*, 17724–17725.
- (45) Song, C.; Swager, T. M. Highly Conductive Poly(Phenylene Thienylene)s: Meta-Phenylene Linkages Aren't Always Bad. *Macromolecules* **2005**, *38*, 4569–4576.
- (46) Brédas, J. L.; Chance, R. R.; Baughman, R. H.; Silbey, R. *Ab initio* Effective Hamiltonian Study of the Electronic Properties of Conjugated Polymers. *J. Chem. Phys.* **1982**, *76*, 3673–3678.
- (47) Yu, H.; Xu, B.; Swager, T. M. A Proton-Doped Calix[4]arene-Based Conducting Polymer. *J. Am. Chem. Soc.* **2003**, *125*, 1142–1143.
- (48) Yu, H.-h.; Pullen, A. E.; Büschel, M. G.; Swager, T. M. Charge Specific Interactions in Segmented Conducting Polymers: A New Approach to Selective Ionoresistive Responses. *Angew. Chem., Int. Ed.* **2004**, *43*, 3700–3703.
- (49) Chidsey, C. E. D.; Murray, R. W. Electroactive Polymers and Macromolecular Electronics. *Science* **1986**, *231*, 25–31.
- (50) Cass, A. E. G.; Davis, G.; Francis, G. D.; Hill, H. A. O.; Aston, W. J.; Higgins, I. J.; Plotkin, E. V.; Scott, L. D. L.; Turner, A. P. F. Ferrocene-Mediated Enzyme Electrode for Amperometric Determination of Glucose. *Anal. Chem.* **1984**, *56*, 667–671.



- (51) Heller, A. Electrical Wiring of Redox Enzymes. *Acc. Chem. Res.* **1990**, *23*, 128–134.
- (52) Nishide, H.; Koshika, K.; Oyaizu, K. Environmentally Benign Batteries Based on Organic Radical Polymers. *Pure Appl. Chem.* **2009**, *81*, 1961–1970.
- (53) Janoschka, T.; Hager, M. D.; Schubert, U. S. Powering up the Future: Radical Polymers for Battery Applications. *Adv. Mater.* **2012**, *24*, 6397–6409.
- (54) Rostro, L.; Wong, S. H.; Boudouris, B. W. Solid State Electrical Conductivity of Radical Polymers as a Function of Pendant Group Oxidation State. *Macromolecules* **2014**, *47*, 3713–3719.
- (55) Audebert, P.; Capdevielle, P.; Maumy, M. Redox and Conducting Polymers Based on Salen-Type Metal Units- Electrochemical Study and Some Characteristics. *New J. Chem.* **1992**, *16*, 697–703.
- (56) Reynolds, J. R.; Lillya, C. P.; Chien, J. C. W. Intrinsically Electrically Conducting Poly(metal tetrathiooxalates). *Macromolecules* **1987**, *20*, 1184–1191.
- (57) Kingsborough, K. P.; Swager, T. M. Electroactivity Enhancement by Redox Matching in Cobalt Salen-Based Conducting Polymers. *Adv. Mater.* **1998**, *10*, 1100–1104.
- (58) Holliday, B. J.; Stanford, T. B.; Swager, T. M. Chemoresistive Gas-Phase Nitric Oxide Sensing with Cobalt-Containing Conducting Metallopolymers. *Chem. Mater.* **2006**, *18*, 5649–5651.
- (59) Sauvage, J.-P. Transition Metal-Containing Rotaxanes and Catenanes in Motion: Toward Molecular Machines and Motors. *Acc. Chem. Res.* **1998**, *31*, 611–619.
- (60) Sleiman, H.; Baxter, P. N. W.; Lehn, J.-M.; Airola, K.; Rissanen, K. Multicomponent Self-Assembly: Generation of Rigid-Rack Multimetallic Pseudorotaxanes. *Inorg. Chem.* **1997**, *36*, 4734–4742.
- (61) Zhu, S. S.; Carroll, P. J.; Swager, T. M. Conducting Polymetalloporotaxanes: A Supramolecular Approach to Transition Metal Ion Sensors. *J. Am. Chem. Soc.* **1996**, *118*, 8713–4.
- (62) Buey, J.; Swager, T. M. Three-Strand Conducting Ladder Polymers: Two-Step Electropolymerization of Metalloporotaxanes. *Angew. Chem., Int. Ed.* **2000**, *39*, 608–612.
- (63) Hendrickson, D. N.; Pierpont, C. G. Valence Tautomeric Transition Metal Complexes. *Top. Curr. Chem.* **2004**, *234*, 63–95.
- (64) Sheberla, D.; Sun, L.; Blood-Forsythe, M. A.; Er, S.; Wade, C. R.; Brozek, C. K.; Aspuru-Guzik, A.; Dincă, M. High Electrical Conductivity in Ni<sub>3</sub>(2,3,6,7,10,11 hexaiminotriphenylene)<sub>2</sub>, a Semiconducting Metal–Organic Graphene Analogue. *J. Am. Chem. Soc.* **2014**, *136*, 8859–8862.
- (65) Campbell, M. G.; Sheberla, D.; Liu, S. F.; Swager, T. M.; Dincă, M. Chemiresistive Sensing with Cu<sub>3</sub>(hexaiminotriphenylene)<sub>2</sub>, an Electrically Conductive 2D Metal–Organic Framework. *Angew. Chem., Int. Ed.* **2015**, *54*, 4349–4352.
- (66) Campbell, M. G.; Liu, S. F.; Swager, T. M.; Dincă, M. Chemiresistive Sensor Arrays from Conductive 2D Metal–Organic Frameworks. *J. Am. Chem. Soc.* **2015**, *137*, 13780–13783.
- (67) Miller, L. L.; Mann, K. R.  $\pi$ -Dimers and  $\pi$ -Stacks in Solution and in Conducting Polymers. *Acc. Chem. Res.* **1996**, *29*, 417–423.
- (68) Rosencwaig, A. Double Exchange and the Metal-Nonmetal Transition in Magnetite. *Phys. Rev.* **1969**, *181*, 946–948.
- (69) Miller, J. S. Magnetically Ordered Molecule-Based Materials. *Chem. Soc. Rev.* **2011**, *40*, 3266–3296.
- (70) Gangopadhyay, P.; Voorakaranam, R.; Lopez-Santiago, A.; Foerier, S.; Thomas, J.; Norwood, R. A.; Persoons, A.; Peyghambarian, N. Faraday Rotation Measurements on Thin Films of Regioregular Alkyl-Substituted Polythiophene Derivatives. *J. Phys. Chem. C* **2008**, *112*, 8032–8037.
- (71) Prosa, T. J.; Winokur, M. J.; McCullough, R. D. Evidence of a Novel Side Chain Structure in Regioregular Poly(3-alkylthiophenes). *Macromolecules* **1996**, *29*, 3654–3656.
- (72) Gangopadhyay, P.; Koeckelberghs, G.; Persoons, A. Magneto-optic Properties of Regioregular Polyalkylthiophenes. *Chem. Mater.* **2011**, *23*, 516–521.
- (73) Araoka, F.; Abe, M.; Yamamoto, T.; Takezoe, H. Large Faraday Rotation in a  $\pi$ -Conjugated Poly(arylene ethynylene) Thin Film. *Appl. Phys. Express* **2009**, *2*, 011501.
- (74) Cotts, P. M.; Swager, T. M.; Zhou, Q. Equilibrium Flexibility of a Rigid Linear Conjugated Polymer. *Macromolecules* **1996**, *29*, 7323–7328.
- (75) Ofer, D.; Swager, T. M.; Wrighton, M. S. Solid State Ordering and Potential Dependence of Conductivity of Poly(2,5-dialkoxy-p-Phenyleneethynylene). *Chem. Mater.* **1995**, *7*, 418–25.
- (76) Lim, C.-K.; Cho, M. J.; Singh, A.; Li, Q.; Kim, W. J.; Jee, H. S.; Fillman, K. L.; Carpenter, S. H.; Neidig, M. L.; Baev, A.; Swihart, M. T.; Prasad, P. N. Manipulating Magneto-Optic Properties of a Chiral Polymer by Doping with Stable Organic Biradicals. *Nano Lett.* **2016**, *16*, 5451–5455.
- (77) Hämäläinen, M.; Hari, R.; Ilmoniemi, R. J.; Knuutila, J.; Lounasmaa, O. V. Magnetoencephalography—Theory, Instrumentation, and Applications to Noninvasive Studies of the Working Human Brain. *Rev. Mod. Phys.* **1993**, *65*, 413–497.
- (78) Beaujuge, P. M.; Reynolds, J. R. Color Control in  $\pi$ -Conjugated Organic Polymers for Use in Electrochromic Devices. *Chem. Rev.* **2010**, *110*, 268–320.
- (79) Smela, E. Conjugated Polymer Actuators for Biomedical Applications. *Adv. Mater.* **2003**, *15*, 481–494.
- (80) Song, C.; Swager, T. M.  $\pi$ -Dimer Formation as the Driving Force for Calix[4]arene-based Molecular Actuators. *Org. Lett.* **2008**, *10*, 3575–3578.
- (81) Takita, R.; Song, C.; Swager, T. M.  $\pi$ -Dimer Formation in an Oligothiophene Tweezer Molecule. *Org. Lett.* **2008**, *10*, 5003–5005.