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Defining Space Around Conjugated Polymers: New Vistas in Self-Amplifying Sensory Materials

This section describes general synthetic strategies developed under this grant to control interchain electronic communications within conjugated polymers (CPs). Novel chemical architectures built on iptycenes, metallorotaxanes, and canopied pyrroles restrict the dimensionality of electronic structures responsible for exciton and charge transport. Structure–property relationships emerging from studies of selected systems are discussed, focusing on their implications for the sensitivity of these materials as sensors.

π -Extended chemical architectures embedded with potential recognition sites serve as versatile platforms for developing self-amplifying sensory materials.¹ Local binding events within such constructs can modify the energy landscape that controls the mobility of energy and charge carriers. Changes in the optoelectronic properties associated with such energetic perturbations have been used to amplify recognition events with sensitivities unparalleled by their discrete molecular counterparts that lack interreceptor electronic coupling. During the past decades, a diverse array of strategies has been implemented to better understand and exploit the generation, transport, and decay of energy and charge-carrying species for useful sensing applications. In this article, we discuss synthetic strategies developed in the Swager laboratory at MIT to control the carrier mobility in conjugated polymers (CPs) by defining space around the polymer backbone. Structure–property relationships emerging from a few representative examples are highlighted. A more comprehensive coverage of this and related topics can be found elsewhere.^{1–4}

Photochemistry and Electrochemistry of Conjugated Polymers

Fluorescent Polymers

Conjugated semiconducting organic polymers efficiently generate excitons (i.e. bound electron–hole pairs) upon absorp-

tion of photons. In a simplified 1-D model, excitons diffuse along polymer backbones and thereby have a high probability of encountering energetically favorable trapping sites. These local perturbations of the exciton's transport pathways, as depicted in Scheme 1, serve as a funnel to depopulate the conduction band. The result is efficient signal amplification, as a small energy “dip” can dominate the total emission of the material. If binding events of desired analytes can induce such an energetic modification, it should be possible to use attenuation, enhancement, or wavelength shift in the emission spectra as a powerful signal transduction method. This conceptual framework can be extended to the solid state regime, in which interpolymer electronic communication is extended to 2-D or 3-D structures to overcome the inefficiency associated with analyte sampling by excitons confined to a single polymer chain. An inevitable trade-off in this case, however, is an increased self-quenching by strong interpolymer electronic coupling. This deleterious effect lowers emission quantum yield and shortens the diffusion length of excitons, significantly compromising sensory responses. Enhancing the mobility of the excitons while suppressing electronic coupling between the polymer chains, a seemingly contradictory design principle, has remained a formidable synthetic challenge in light-emitting organic materials.⁵

Scheme 1

Conducting Polymers

A partial depopulation of the valence band (p-doping) or population of the conduction band (n-doping) of semiconducting polymers generates highly conductive materi-

als. Conductivities of doped CPs are extremely sensitive to local defects, offering opportunities to develop resistivity-based sensing schemes.^{1,3} Here, deconjugation of the polymer backbone or energy mismatches between adjacent redox active centers effectively serves as resistive elements that suppress charge transport. In the absence of alternative charge-transporting pathways or tunneling effects, the result is a complete shutdown of the specific charge conduit. For an idealized 1-D CP sensor, a single barrier erected by analyte binding results in zero conductivity (Scheme 2). Signal amplification could thus be achieved by wiring electronically coupled receptors in a serial fashion. A bonus in this scenario is the substantially enhanced effective binding constant of the polyreceptor, while the intrinsic binding constant of each receptor unit can still be kept low to maintain reversibility.

Scheme 2

The 1-D model depicted in Scheme 2, however, is difficult to realize in CP-modified electrodes that need to be fabricated in mass quantities and used under ambient conditions. In addition to the defects associated with polymerization, π - π stacking interactions between adjacent CP strands provide highly networked electronic structures for charge migration. Charge-carrying quasiparticles (polarons or bipolarons) can now take alternative pathways bypassing the locally introduced energy barrier (Scheme 3), attenuating the perturbation introduced to the CP energy landscape. Although the increased dimen-

sionality of the electronic structures enhances the overall conductivity, the performance of the CP sensor is now substantially compromised. Similarly to the situations encountered with light-emitting polymers, a strategy is desired that strikes a right balance between the two seemingly incompatible design considerations: high charge mobility and limited interpolymer electronic coupling.

Scheme 3

Insulating Molecular Wires

Site-isolation is a well-known trick in biological systems. A protein matrix supports redox-active metal centers participating in electron shuttling pathways. By isolating highly reactive intermediates within buried active sites, deleterious decomposition pathways could be effectively blocked. Insulation of CPs may serve similar roles by stabilizing unusual electronic structures as well as by eliminating cofacial π -interactions responsible for their high reactivity and other undesired side effects (*vide supra*).⁶ Encapsulating organic sheaths along the polymer backbone may also direct supramolecular assembly or provide molecular recognition sites (Scheme 4). Additionally, electronically decoupled CP systems can be used as models to understand energy and charge conduction mechanisms of their fully coupled counterparts.⁷ During the past decade, the Swager research group has been exploring sterically hindered monomers to increase the dimensionality of the polymer structure. A precise control over the excitation and charge transporting pathways within such constructs afforded optoelectronic properties better suited for sensing applications, as described below.

Scheme 4

Shape-Persistent Fluorescent Polymers: Pentiptycene-Derived Porous PPE Sensors

Interpolymer electronic coupling in fluorescent polymers could be suppressed by the sheer steric bulk of the aromatic substituents placed around the rigid polymer backbone. A shape-persistent iptycene motif was integrated into poly(phenyleneethynylenes) (PPEs) to prevent π - π stacking or excimer formation (Figure 1).^{8,9} The photophysical properties of solid samples of the pentiptycene-derived PPE (**1**) are essentially identical to those of solution samples, implying minimal electronic perturbation upon assembly into a film. This postulation was further corroborated by comparison with its planar analogue **4**, which displays substantial red shifts of the 0-0 absorption and emission bands in the solid states with a significantly lowered fluorescence efficiency.

Figure 1

The electron-rich backbone of **1** displays an excellent fluorescence response to TNT and DNT, which act as electron acceptors toward photoexcited **1**^{*} (Scheme 5). The highly porous internal structure of the loosely packed polymer **1** (Figure 2) also facilitates passive diffusion of the analyte molecules, resulting in a faster signal re-

sponse than **4**. Enhanced spectroscopic stability and reproducibility of film-cast **1** were an additional bonus of preventing direct contacts between conjugated backbones of PPEs. Analogues of **1** having 2,3-dialkoxyphenylene units were also prepared, providing additional handle to modify the band gap.¹⁰ Ultra-sensitive sensing of landmine explosives by **1** is a highly rewarding example that illustrates the importance of defining space to modulate the photophysics and transport properties of CPs.

Scheme 5

Figure 2

Interlocking 3D Structures: Exciton Diffusion within Chiral Polymer Aggregates

A precise control over the relative orientation of adjacent CP strands was achieved by introducing chiral alkoxy chains into the PPE backbone.¹¹ Asymmetric environment along the rigid polymer backbone in **3** dictates positioning of the CP strands upon aggregation, affording a helical grid structure (Figure 3). Unlike its planar analogue **5**, in which strong π - π stacking interactions facilitates collinear alignment of the polymer chains, an interlocking structure is generated upon aggregation of **3**. As schematically drawn in Figure 3, arylacetylene fragments within **3** are confined within the clefts afforded by pentiptycene groups, promoting an oblique orientation of the transition dipole moments associated with neighboring polymer strands. The latter property was proposed to suppress fluorescence quenching upon

aggregation.^{6,12} Indeed, despite significant interpolymer electronic interactions as evidenced by CD and UV-vis spectra, **3** retains a significant amount of fluorescence intensity upon formation of polymer aggregates. Fully aggregated **3** in solution displayed substantially (> 15 -fold) enhanced sensitivity toward electron-poor analytes such as DNT and TNT, as compared with nonaggregated **3**. The highly-organized three dimensional chiral grid of **3** apparently extends the conjugation length of the polymer and promotes an efficient interchain exciton transport via a strong electronic coupling. The increased diffusion length of excitons within aggregated **3** was evidenced by the self-amplified sensory response in the solid state. Compared with its achiral analogue, **3** displays a steeper slope in the Stern-Volmer plots and less dependence on the film thickness upon exposure to quencher molecules. This example illustrates how a higher-order structure could be generated in the polymer aggregates by defining chiral space around the rigid CP scaffold. An oblique orientation between adjacent CP strands suppresses fluorescence quenching and the highly ordered internal structure promotes interpolymer exciton transport. A seemingly incompatible design requirement in light-emitting CP has thus been achieved by a judicious choice of building blocks.

Figure 3

Three-Strand Conducting Ladder Polymer: Redox Matching and Charge Hopping in Polymetallorotaxanes

Transition metal ions can actively participate in charge transporting pathways con-

necting insulated CP strands. Metallorotaxane-derived building blocks were designed that tightly bind redox-active metal ions. Metal coordination within the supramolecular assembly dictates the relative positioning of the ligand-appended monomers, the polymerization of which results in highly organized structures not readily accessed by conventional methods.

Multiple electroactive components were introduced in the design of the monomers **6** in order to assemble three-strand ladder polymers.¹³ Distinctively different redox windows of the bis(ethylene dioxythiophene) phenylene and bis(bithienyl) bipyridyl groups in **6** allowed stepwise electropolymerization of the macrocyclic fragments (red) and threading units (blue) (Scheme 6). Electrochemical doping of poly(**6**) afforded conductive systems in which the internal poly(bis(ethylene dioxythiophene) phenylene)s behave as isolated molecular wires while the outer poly(bis(bithienyl) bipyridyl) strands remain in an insulating state.

In situ conductivity measurements established that the $\text{Cu}^{\text{I/II}}$ redox couple in poly(**6**) assists interchain charge transport between isolated polymer chains (Scheme 7), a process facilitated by the similar redox potentials of the Cu-centered and poly(bis(ethylene dioxythiophene) phenylene)-centered electroactive sites. In addition to assisting the assembly of ladder structures by defining space around the CP backbone, an optimally positioned redox potential of the metal center gates shuttling of electrons between insulated molecular wires. As coordination of exogenous ligands affects the redox potential of this key gating unit, further elaboration of poly(**6**) for sensing applications should be a logical extension of this approach.

Scheme 7

3.4 Canopied Polymer: Reversible Protonic Doping of a Porous Polypyrrole

Canopied monomers were designed to suppress cross-communication between charge-carrying CP chains. In the prototypical monomer **7**, an insulating phenyl group was positioned directly above the pyrrole fragment to prevent interchain π - π stacking interactions in the resulting polymer (Figure 4).¹⁴ Electrochemically prepared poly(**7**) displayed a narrow potential window of high conductivity dominated by polarons (charge-delocalized cation radicals). This behavior is markedly different from the conductivity profile of the parent polypyrrole system, which continuously increases with oxidative doping. A close π - π contact between planar polypyrrole strands apparently provides 3-D electronic connectivity for charge delocalization. Limited interstrand electronic coupling in poly(**7**), on the other hand, strengthens localization of the charge carriers.

Figure 4

The mobility of the bipolarons confined within 1-D structures would be significantly lowered due to electrostatic repulsion (Scheme 8), whereas 3-D electronic conduits generated by closely stacked CPs provides energetically favorable alternative pathways for the efficient diffusion of charge carriers. Deprotonation of the iminium functional groups in oxidized poly(**7**) affords quinonoid resonance structures that impede charge transport (Scheme 8). A rapid and reversible switching between conductive and insulating states of poly(**7**) could thus be achieved by exposure to pyridine and TFA. Under similar conditions, the parent polypyrrole system displayed sluggish and irreversible responses. Densely packed polymer matrix could raise the activation barrier for the passive diffusion of the external substrate. Delocalized charge carriers in polypyrrole, on the other hand, could potentially bypass locally introduced barriers, attenuating the perturbation introduced to the energy landscape. Both properties significantly compromise the performance of this material in sensing applications. In contrast, the lowered dimensionality of the carrier transporting pathways in poly(**7**) as well as the porosity induced by mutual exclusion of sterically hindered polymer chains proved beneficial for a rapid and reversible response to the protonation states of the polymer backbone.

Scheme 8

Summary and Outlook

By adding extra dimensionality to typically planar π -conjugated materials, it has become possible to gain control over the assembly and transport properties of the CPs. In addition to minimizing undesired interstrand electronic interactions, loosely stacked polymer chains facilitate passive diffusion of analyte molecules as well as uptake and release of electrolytes through the polymer matrix. The results are fast and reversible response kinetics and minimal structural reorganization during the molecular recognition events, properties important for sensing applications. In the examples described above, key structural elements required to define space around the polymer backbones are already pre-programmed in the designer monomers. The modular approach adopted in our synthetic schemes also facilitated access to a wide range of polymers with varying degrees of electronic and steric demands, enabling detailed spectroscopic and electrochemical studies of closely related systems. Structure–property relationships emerging from such studies have provided a solid foundation, upon which further elaborations are being made to optimize the performance of CPs as sensors.

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New Reversible Resistivity-Based Sensors Based Upon Metal Containing Conducting Polymers: Demonstration of Nitric Oxide Sensor

This demonstration was performed for nitric oxide and demonstrates that similar methods can be applied to fluoride ion.

Nitric oxide (NO) serves as an intercellular signaling agent in a diverse array of living systems.¹ This recognition has stimulated considerable interest in its detection.² In particular there has been considerable interest in developing new fluorescence methods which exhibit an irreversible spectroscopic change in response to NO.³ For many applications it is desirable to detect the concentration of nitric oxide in real time. For example, an increase in nitric oxide concentration is associated with up-regulation of the immune system⁴ and hence by continuously monitoring nitric oxide in the exhalate of an immune compromised person it may be possible to detect early stage respiratory infections.

As part of our program directed at developing sensors using conducting polymers as a gain medium⁵ we have recently turned our attention toward the detection of NO. In this effort we have focused on resistance-based detection schemes. Our choice is based in part on the fact that this type of sensor can be very simple and have low power consumption. For example, using a conducting polymer a sensor can consist simply of two electrodes (preferably microelectrodes), which are interconnected with the sensory polymer. Devices can be inexpensive enough so as to be disposable and have minimal external hardware requirements. In fact all of the necessary electronics for a high precision resistance measurements (ppm resolution) can be placed on a single chip. We further considered that the most useful devices would be those that displayed a rapid reversible response that could therefore be used to monitor a NO concentration that varies with time.

To produce a real-time nitric oxide sensor we considered that it must exhibit specifically and an easily detectable signal that responds to changes in its concentration. Coordinatively

unsaturated paramagnetic transition metal complexes are ideal candidates for recognizing (binding) nitric oxide, which has one unpaired electron in an antibonding orbital. To produce a resistance change in response to a metal-nitric oxide binding event we utilized a system where the conductivity intimately involves the transition metal center. We previously demonstrated that metal centers contribute optimally to the electronic transport in a conducting organic polymers when the redox activity of the metal center is coincident with that of an organic conducting polymer in its low resistance state.^{6, 7} When this redox-matching condition is met the metal essentially provides additional electroactive pathways for transporting charge throughout the material. Hence, ligand binding events that produce changes in its redox potential can enhance or decrease the conductivity depending upon whether this process produces a better or worse match between the transition metal and the organic conducting polymer. To test this effect for the detection of NO we made use of a redox-matched cobalt salen polymer **1**, which we have previously studied.⁷ In this system the $\text{Co}^{2+/3+}$ couple is closely, but not perfectly, matched to the redox potential of the organic polymeric backbone.

Figure 1. Cyclic voltammetry of **1** in the absence and presence of nitric oxide. Note that $\text{Co}^{2+/3+}$ wave shifts from its initial position at about -0.1 V to being indistinguishable with the organic centered activity at 0.05 V in the presence of 7mM NO.

To perform the experiments we utilized the procedure of Ford and coworkers to purify nitric oxide from a cylinder.⁸ Infrared spectroscopy (1 atm NO in a 10 cm pathlength gas cell) was used to determine that the other nitrogen oxides had been completely removed. The purified NO was collected in a acetonitrile solution ($[\text{NO}] \approx 7 \text{ mM}$) and its relative concentration was determined using cyclic voltammetry ($E^\circ = 0.867 \text{ V vs. Fc/Fc}^+$, 0.1 M TBAPF₆).

All of the electrochemical experiments were performed in acetonitrile with 0.1 M TBAPF₆ electrolyte. As shown in Figure 1 polymer **1** displays two closely spaced peaks in its cyclic voltammogram. The peak centered at approximately -0.1 V corresponds to the $\text{Co}^{2+/3+}$ couple and the peak at 0.05 V is assigned to the organic portion of the polymer. This assignment was previously confirmed by the fact that exposure to pyridine shifts the cobalt centered waves to less positive potentials while leaving the organic centered redox processes untouched.⁶ As shown in Figure 1 exposure to NO shifts the $\text{Co}^{2+/3+}$ couple to more positive potentials and effectively creates a better redox match with the organic centered electroactivity. The film rapidly returns to its original state upon placing it in fresh NO-free

electrolyte. The observed shift of the $\text{Co}^{2+/3+}$ wave to positive potential is consistent with the NO binding to the cobalt center. The highest energy electron of this nominally square planar species is in the dz^2 orbital and bonding of this unpaired electron with the NO radical thereby gives a complex with an overall higher oxidation potential. It appears that upon oxidation the complex remains intact as reduction wave assigned to NO-free cobalt center is not observed in the presence of NO. This indicates that both the Co^{2+} and the oxidized Co^{3+} centers have strong binding affinities to NO.

Consistent with our redox matching model the improved overlap between the cobalt and the organic ligand's electroactivity enhances the materials conductivity. Figure 2 shows measurements of the relative conductivity of thin films deposited on an array of interdigitated microelectrodes. These devices are effectively electrochemical transistors with the applied electrochemical potential functioning as the gate voltage and the current flowing between the source and drain electrodes is directly proportional to the conductivity.⁹ We have previously found Polymer **1** to display a peak conductivity of 40 S/cm . As can be seen in Figure 2 exposure of a microelectrochemical transistor to a 7 mM NO solution produces approximately 30% increase in conductivity. The sensor displays a highly reversible response and as shown in Figure 2b the conductivity returns to normal after 5 electrochemical cycles (100 mV/sec) in NO-free electrolyte. As a result the NO binding to the cobalt center is highly reversible.

Polymer **1** has been found to be very well behaved in aqueous systems and we previously have shown that it also functions as a highly effect catalyst for oxygen reduction at more negative potentials.¹⁰ Interesting in both aqueous and organic media we have found that the conductivity of Polymer **1** is insensitive to oxygen concentration. As a result, this material or closely related polymers have excellent prospects to function as selective reversible NO sensors in areobic aqueous environments. A resistance-based method such as shown here is not only be used for monitoring of bulk NO concentrations, but should also allow for microelectrode sensors to be produced that can be used to map out signals used in intercellular signaling.

Notes and references

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Figure 2. Drain current profile (conductivity) of a microelectrochemical transistor base upon polymer **1** in the absence and presence of NO. The potential offset between microelectrodes was 40 mV and a sweep rate of 10 mV/s was used.

A Fluorescent Self-Amplifying Wavelength Responsive Sensory Polymer for Fluoride Ion

Novel fluoride-selective sensors, utilizing fluoride-induced lactonization to highly fluorescent coumarin derivatives, are reported. The incorporation of this sensory system into a conjugated polymer amplifies the fluorescence response.

This technology for fluorescent fluoride ion detection has been licensed to Nomadics Inc.

Fluoride, the smallest anion, has unique chemical properties and its recognition and detection are of growing interest because it is associated with nerve gas and the refinement of uranium used in nuclear weapons manufacture. As a result, there is a need to develop new selective and sensitive methods for fluoride detection in environments that are not easily served by conventional ion selective electrodes. Most of the emerging detection methods have focused on receptors that differentiate fluoride from other anions, such as chloride, phosphate or nitrate and convert the binding into an electrochemical or optical response.^[1] These efforts have enjoyed success and in some cases have resulted in the ability to visually detect fluoride ions.^[2,3,4]

An approach to greater sensitivity in fluorescence detection schemes is to use the exciton-transporting properties of semiconducting polymers to amplify perturbations (transduction events) produced by analyte binding. These methods were originally demonstrated using electron-transfer quenching^[5a] and variations on this scheme have been used to create a number of chemical and biological sensory schemes, most of which involve changes in the emission intensities.^[5] In spite of these successes, it is generally preferred for a fluores-

cence sensory signal to involve a new emission at a different wavelength rather than a modulation of an existing signal. The advantage of the latter approach lies in the fact that a new signal is inherently easier to detect than an intensity change. Furthermore nonspecific chemical interactions are more likely to produce intensity changes than new signals, hence we can also expect specificity gains in properly designed sensors that create new emissions. Fluorescence resonance energy transfer (FRET) is broadly used to produce new emissive signals and the amplification of these processes due to intramolecular energy transfer from conjugated polymers has been demonstrated.^[6] New analyte-triggered emissions, if optimally deployed, offer high specificity and low background. In consideration of how to best construct such a system for the selective detection of fluoride we have decided to explore schemes using fluoride's unique chemical reactivity with silicon,^[7] rather than elaborate receptors. In a fusion of these different elements, we report herein a fluoride sensory system in which a fluoride triggered Si-O cleavage results in the formation of a highly fluorescent coumarin [Eq. (1)] and show how the interconnection of this transduction element to a conjugated polymer produces a 100-fold sensitivity enhancement.

Equation 1

Our decision to focus on the fluoride ion triggered formation of coumarins, was predicated upon the fact that they are well-known class of laser dyes with high radiative quantum yields.^[8] To this end we synthesized a series of coumarin derivatives with varying electron donating groups in the 7-position of the coumarin to tune the absorption and emission wavelengths as shown (compounds **1a** to **3a** in

Table 1). The synthesis of the indicators involved a two-step sequence, namely silylation of the corresponding 2-hydroxy benzaldehyde, followed by a condensation reaction under the modified Knoevenagel conditions.^[9] The TBS group was chosen as the protecting group for the phenols to promote selectivity to fluoride by rendering indicator **2** stable (unreactive) to likely interferents. Indeed **2** is stable in THF solutions containing an excess of chloride ions (tetrabutylammonium salt). To avoid a possible problematic *trans-cis* isomerization of the double bond, we used diethyl malonate to introduce symmetrically substituted double bonds in **1**, **2**, and **3**.

Table 1. Photophysical data in dichloromethane

Compound	Abs. Max. ^[a] (log ϵ)	Emission Max. ^[a]	Φ ^[b] (%)
1	322 (3.66)	-	<0.01
2	386 (4.31)	450	0.2
3	384 (4.43)	489	0.8
4	(4.76) ^[c]	482	12
1a	334 (3.71)	415	12
2a	417 (4.39)	450	81
3a	412 (4.64)	529	37
4a	(4.80) ^[c]	517	30

[a] Given in nanometers. [b] Determined with quinine sulfate as a standard. [c] Per monomer unit.

The cyclization reaction is irreversible and produces a time-dependent dosimetric response that is controlled by the reaction kinetics. The rate of the cyclization of **2** to **2a** in THF solution was monitored by fluorescence and found to be first order in **2**, independent of fluoride (tetrabutylammonium salt, TBAF), and relatively slow with a rate constant of $k = 2 \times 10^{-4} \text{ s}^{-1}$. The rate constants do not change for the ranges from 0.5 to 3 molar ratio of fluoride ion relative to **2**. Hence it appears that the silyl cleavage (or fluoride association with the silyl)

is fast and that the cyclization is the slow step. A 10-fold excess of fluoride ion provides an enhancement in the rate and a saturation of the emission intensity is observed in approximately 2 hours (Figure 1a). The rate acceleration at high fluoride concentrations suggests additional ionic associations with the TBAF salt. The non-innocence of excess fluoride is further revealed by additional peaks in **2a**'s absorbance spectra (Figure 1a inset) that are present at high TBAF concentration but absent after an aqueous extraction.

To impart greater sensitivity to our fluoride-induced lactonization detection scheme, we decided to design semiconductor polymer-indicator conjugates that could amplify the response. Amplification of a turn-on sensor can in principle be performed by bringing a chromophore of the proper spectral characteristics proximate to the polymer to achieve fluorescence resonant energy transfer (FRET).

Figure 1. Emission changes of indicator **2** (a) and sensory polymer **4** (b) upon addition of TBAF. The insets show the respective absorption spectra of the initial solution (0 min, dashed line) and after exposure to TBAF (2 h, solid line). The second inset at the top right is absorption spectrum of **2a** after aqueous extraction, which removes absorptions that appear to be the result of interactions with fluoride ion. Experimental conditions: THF at 298 K in all cases. (a) **2**, $3.2 \times 10^{-6} \text{ M}$ and TBAF, $33 \times 10^{-6} \text{ M}$; (b) **4**, $1.5 \times 10^{-6} \text{ M}$ (repeating group concentration) and TBAF, $1.6 \times 10^{-7} \text{ M}$.

Indeed our purpose in synthesizing **3a** with a longer wavelength emission was to enable this type of detection scheme. However in spite of our chromophore engineering, the cyclized coumarins lacked the proper energy matching with poly(phenylene ethynylene)s (PPEs), which are the most widely used semiconducting sensory polymers.

To overcome the constraints of FRET we decided to pursue a potentially more powerful approach wherein the electronic character of the indicator is strongly electronically coupled to the band structure of the polymer. This approach enables an additional energy transfer mechanism (known as Dexter energy transfer for small molecules) wherein activation of an indicator locally perturbs the polymer's band gap. This approach is further attractive because detailed fluorescence depolarization

studies have shown that the strong electronic coupling (band structure) in PPEs contributes more to energy transfer than Förster energy transfer, the basis of FRET schemes.^[10] Hence in strongly electronically coupled conjugation schemes a few cyclization events triggered by fluoride ions will produce local minima in the bandgap that trap mobile excitons to give a new emission^[11] (Figure 2). The facile transport of excitons in semiconductive organic polymers allow them to sample many potential transduction sites and thereby dramatically

increase the probability of emission from a lower energy trapping (cyclized) site. The result is an amplified turn-on sensory scheme.

In designing PPE-conjugates we sought to develop a general scheme that could be exploited for future indicator chemistries. We were further motivated by the fact that band-gap engineering by the interconnection of pendant chromophores to semiconducting polymers is applicable to other electrooptical technologies. Our semiconductive sensory polymer designs have focused on **4**, a PPE-based material (Scheme 1), which makes use of a thiophene-bridge to connect the sensory *o*-silyloxybenzylidene malonate moiety with the polymer backbone.^[12] Thiophene is the linkage of choice because it's strong π -electron delocalizing nature will relay electronic perturbations in the side-chains to the conjugated backbone and it is synthetically versatile.

The synthesis of sensory polymer **4** is shown in Scheme 1.^[13] Bis(trimethylsilyl)ethynylphenyl thiophene **7**, obtained from **5** by selective Stille cross-coupling and subsequent Sonogashira cross-coupling reactions, was derivatized to the corresponding dioxaborolane **8**. A further cross-coupling reaction with the appropriate triflate **9**^[14] produced the thiophene-bridged diaryl compound **10**. Desilylation of diethynylenes using TBAF, fol-

Scheme 1. Reagents and conditions: a) 2-tributylstannylthiophene, $\text{PdCl}_2(\text{PPh}_3)_2$, DMF, 80 °C, 12 h, 76%; b) TMSA, $\text{Pd}(\text{PPh}_3)_4$, CuI, Toluene/DIPA 4:1, 80 °C, 20 h, 76%; c) $t\text{BuLi}$, THF, -70 °C, 90 min, then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, RT, 4 h, 59%; d) $\text{Pd}(\text{PPh}_3)_4$, triethylamine, DMF, 100 °C, 24 h, 64%; e) TBAF, THF, RT, 1 h; f) TIPSCl, imidazole, DMF, RT, 2 h, 75% over two steps; g) $\text{Pd}(\text{PPh}_3)_4$, CuI, Toluene/DIPA 4:1, 65 °C, 24 h, 43%; h) TiCl_4 in CCl_4 to THF, 0 °C, then **14** and diethylmalonate in THF, then pyridine in THF, 0 °C, 1 h and RT, 2 h, 88%; i) TBAF, THF, RT, 3 h, 98%. TMSA = trimethylsilylacetylene, DIPA = diisopropylamine.

lowed by silylation of phenol with TIPSCl, gave the monomer **12**.^[15] A Sonogashira cross-coupling polymerization provided polymer **14**.^[16] As a final step we modified polymer **14** using a titanium-mediated Knoevenagel reaction with diethyl malonate to produce the desired sensory polymer **4**.

The effect of coumarin formation on polymer **4**'s bandgap is readily apparent by inspection of the absorption and emission spectra before and after quantitative conversion to **4a** by treatment with an excess of TBAF. As expected, both absorbance and emission spectra of the coumarin-containing form **4a** in dichloromethane solution were red-shifted compared to those of its precursor **4** (Figure 3). Moreover, the emission change from blue to blue-green is readily detected visually. Cyclization also caused a significant increase in the fluorescence quantum yield of the conjugated polymer (**4**: $\Phi = 0.12$; **4a**: $\Phi = 0.30$). These results indicate that we can trigger a strong

change in photophysical properties of PPEs using an electronic perturbation from the appended indicator. The GPC analysis of the polymer **4** and **4a** revealed molecular weights of $M_n = 1.06 \times 10^4$ and $M_n = 1.05 \times 10^4$, respectively.

Fluorescence studies reveal that our amplification scheme is highly effective. Kinetic studies for the polymer **4** were not possible in the same way as for the small molecule **2**, because the polymer's fluorescence quantum yield varies as a function of conversion and at low conversion we observe less efficient emission. Nevertheless it is clear that the polymer **4** has a faster response to fluoride ion (Figure 1b). The enhanced fluoride sensitivity of **4** relative to **2** is clearly evident when one considers that exposure of **4** (1.5×10^{-6} M based upon the repeating group) to fluoride (1.6×10^{-7} M, TBAF in THF) results in a complete transformation of **4**'s fluorescence intensity maximum in 2 hours. Alternatively **2** required a 100-fold higher fluoride concentration to achieve a complete fluo-

rescence transformation over the same time period with all other conditions the same (Fig-

Figure 3. Absorption (a) and emission (b) spectra of polymer **4** (dashed line: $\lambda_{\text{max}} = 378$ nm, $\epsilon = 57600$ M⁻¹cm⁻¹; emission $\lambda_{\text{max}} = 482$ nm) and **4a** (solid line: $\lambda_{\text{max}} = 396$ nm, $\epsilon = 63400$ M⁻¹cm⁻¹; emission $\lambda_{\text{max}} = 517$ nm) in dichloromethane showing changes upon coumarin-formation.

ure 1). Hence we conclude that **4** is approximately 100 times more sensitive than its small molecule-based counterpart **2**. This amplification factor is in accord with our previous determination of exciton diffusion in isolated polymers.^[5a] It should be noted that energy migration within isolated polymers (i.e. dilute solutions) is inherently inefficient due to the one-dimensional exciton diffusion.^[17] Thin films that display two- and three-dimensional transport characteristics exhibit more favorable transport statistics and also benefit from improved Förster energy transfer process between polymer chains. Unfortunately **4** is strongly quenched in thin films, however it should be possible to generate related indicator materials

with desirable solid-state properties and much larger amplification factors in the future.

In summary, we have introduced a new system for the detection of fluoride ion and successfully amplified the response using exciton migration in a semiconducting organic polymer. In contrast to most semiconductive polymer sensor schemes that rely on changes in emission intensity, this sensory system utilizes a new fluorescence signal. The approach of directly interconnecting the indicator electronically with the polymer's band structure is a promising alternative to FRET schemes and we intend to apply this approach to other analytes of interest.

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Insulated Conducting Polymers: Manipulating Charge Transport Using Supramolecular Complexes

We report the synthesis of conducting polymers in which bulky rotaxane groups wrap around a poly{1,4-bis[2-(3,4-ethylenedioxy)thienyl]-2,5-dialkoxybenzene} backbone to produce varying degrees of insulation. Chemical oxidative polymerization of the monomer with Cu(OTf)₂ afforded the polyrotaxane. Molecular modeling reveals that polyrotaxane structure gives an insulated wire. Optical studies suggest that the rotaxane groups introduce steric strain to the backbone and perturb the polymer's electronics, as illustrated by the increased bandgap compared to the unadorned poly{1,4-bis[2-(3,4-ethylenedioxy)thienyl]-2,5-dimethoxybenzene}. We also investigated the optical, electrochemical and conducting properties of rotaxanated polymer and its corresponding metal-bound polyrotaxanes. We observed amplified polymer fluorescence quenching upon complexation of transition metal ions, while alkali metal ions elicit unusual fluorescence response. Encapsulation of the conducting polymer backbone narrows the redox window of the polymer and causes more than 10³-fold conductivity decrease. On the other hand, the overlapping redox activity of the polymer backbone and copper centers allows the metal centers to mediate charge conduction between neighboring wires and results in a 10²-fold conductivity increase compared to the metal-free polymer.

Insulation of electroactive materials to create independent electrical conduction pathways is an indispensable element in the design of modern electronics. Effective insulation eliminates unwanted interference and can also protect conductive materials from environmental degradation, hence it plays a critical role in the performance and lifetime of a device. The concept of insulation becomes more strenuous as scientists and engineers strive to create con-

jugated polymer (CP) wires and molecule-based electronic devices whose functions are comparable to, if not surpass their inorganic counterpart. In an ideal CP-based device, the electroactive element might comprise only a few polymer strands. An effective insulating layer must sequester the individual addressable components without compromising the minuscule dimensions of the device. On the macroscopic level, encapsulation of CPs can be achieved using host-guest materials such as mesoporous silica. In polymer/silicate composites, prepared by template synthesis, the polymer chains occupy the microporous channels in the zeolite.¹²³⁴ By controlling the pore diameter and the alignment of the channels, scientists can dictate the degree of interchain electronic interactions between polymer strands. The key advantage of this approach is the ability to effectively isolate the polymer wire with the silicate layer and pattern the charge conduction pathways by aligning the channels.

Encapsulation of CPs can also occur on the molecular level, namely, by attaching the insulating groups directly onto the repeat units of the polymer. Insulation of individual polymer chains can be achieved via this approach. A wide range of insulating groups has been studied in the literature. Schenning and coworkers demonstrated the encapsulation of end-capped poly(triacetylene) (PTA) and poly(pentaacetylene) (PPA) oligomers with laterally appended *Frechet*-type dendrons..⁵ Alternatively, encapsulation can be achieved via the formation of inclusion complexes in the form of polyrotaxanes. Cacialli et al. have demonstrated that PPPs and PPVs threaded through cyclodextrin rings exhibit improved stability and reduced intermolecular interactions and solid-state packing effects. Consequently, PLEDs fabricated from these shielded polymers display longer device lifetime and

higher luminance than those made from the unthreaded polymers.⁶ Suppression of inter-chain interactions in insulated CPs has significant impact on the charge transport properties of the polymers. These changes can be reflected in both the photophysical and electrochemical properties of the polymers. As mentioned above, isolating fluorescent polymers prevents polymer aggregation, which can lead to red-shifted emission and fluorescence quenching via nonradiative energy transfer. In conducting polymers, encapsulation alters the conduction percolation pathways through which charges migrate. The bulk conductivity of a CP is related to the charge transport properties, which, in turns, depends on a myriad of factors. Among these factors, the morphology of the polymer plays a pivotal role. Traditional unfunctionalized CPs, such as polythiophene or polyacetylene, adopt an inhomogeneous “spaghetti” morphology, in which regions of crystallinity and disorder coexist.⁷ In these crystalline mesostructures, efficient packing of the rigid rod polymer chains allows orbital overlap between polymer chains, hence the electronic states within these regions are highly delocalized. These regions often exhibit high local conductivity, since charge carriers can migrate via a metallic band transport mechanism.⁸ Separating these metallic islands are regions of random coils. In these disordered regions, the electronic states of individual polymers (or bundles) become localized. As a result, inter-chain charge transport in these regions occurs predominantly via a hopping mechanism at interchain junctions.⁹ Occasionally, charges can also hop across grain boundary between metallic islands.⁹ The bulk conductivity depends on the charge percolation pathways created by these different morphologies within the sample. Let us now consider the morphology of insulated CP wires. Attaching insulating groups to the repeat units of the polymer causes the polymer chains to adopt a shape-persistent rigid rod morphology.¹⁰ As discussed above, suppression of interchain interactions and polymer packing can severely reduce the number of charge percolation pathways. As a result, insulated conducting polymers should exhibit significant lower bulk conductivity compared to its unfunctionalized counterparts.

In our continual effort to develop CP-based sensors and devices, we became interested in the idea of the directed charge conduction provided by the insulated molecular wire approach. Using the methodology developed by Sauvage to develop supramolecular complexes with a phenanthroline core¹¹, our group has designed conducting polyrotaxanes with varying degrees of encapsulation.¹² This work is an extension of our endeavor to create a truly insulated molecular wire by incorporating bulky rotaxanes to the polymer backbone. The salient feature of these supramolecular elements is their ability to immobilize metal ions in the polymer periphery, such that the metal ions can participate in the conduction. Metal-mediated macroscopic conduction in these organic-metal hybrid systems provides a platform for the development of ultrasensitive chemosensors.

The synthesis of the rotaxane monomer **1** has been described previously. The monomer features a 1,4-bis[2-(3,4-ethylenedioxy)thienyl]-2,5-dialkoxybenzene moiety that undergoes facile oxidative polymerization in the presence of mild oxidants such as copper (II) triflate, as depicted in Scheme 4.1. Reductive quenching of the reaction with hydrazine monohydrate, followed by cyanide treatment afforded the highly soluble, metal-free rotaxanated polymer Poly(**1**). Attempts to determine M_w of Poly(**1**) using GPC failed as the polymer was trapped in the guard column, the same problem we encountered with the previously reported rotaxanated PPEs.¹³ Using a modified HPLC method, as described in the supporting information section, the average molecular weight of Poly(**1**) was determined to be *ca.* 22100, which corresponds to an estimated DPI of 10. Simple stirring of a solution of Poly(**1**) with one equivalence of $\text{Cu}(\text{CH}_3\text{CN})\text{PF}_6$ or $\text{Zn}(\text{ClO}_4)_2$ (relative to the repeat unit) afforded the metal-bound polymers Poly(**1**, Cu) and Poly(**1**, Zn), respectively. To elucidate the influence of encapsulation by the rotaxane groups on the electronics and the bulk charge transport of the CP backbone, we prepared the model polymer without the rotaxane groups, Poly(**2**) in accord with literature procedures (Scheme 2).¹⁴ Poly(**2**) features the unadorned

1,4-bis[2-(3,4-ethylenedioxy)thienyl]-2,5-dimethoxybenzene repeat unit. The solubilizing effect of the rotaxane groups is apparent as Poly(**2**) displays negligible solubility in most organic solvents.

Scheme 1. Chemical Polymerization of the Rotaxane Polymers.^a

^a (i) 2.7 equiv. Cu(OTf)₂, CAN. (ii) KCN, CAN/H₂O.

Scheme 2. Electropolymerization of Monomer **2** to Model Polymer Poly(**2**).

Figure 1 illustrates the solution absorption and emission spectra of monomer **1** and Poly(**1**). Upon polymerization, the increased delocalization of the electroactive backbone lowers the bandgap of the system, as reflected in the red-shift in the absorption and emission bands of Poly(**1**) compared to its parent monomer **1**. Although the broad and featureless absorption profile of Poly(**1**) is in agreement with that of Poly(**2**) previously reported by Reynolds, Poly(**1**) exhibits a higher absorption onset at 2.10 eV than the reported value of 1.75 eV for Poly(**2**).¹⁷ Two factors might contribute to the higher bandgap observed in the rotaxanated polymer. Firstly, because of its planar repeat unit, the shape of Poly(**2**) resembles a ribbon. This allows interactions between the π electron clouds of adjacent polymer chains, which delocalizes the orbitals and lowers the energy. Poly(**1**), on the other hand, lacks the planar geometry required for lateral band delocalization. As a result, Poly(**1**) displays a higher bandgap than the model polymer. Alternatively, the larger bandgap in Poly(**1**) could indicate that the incorporation of rotaxane groups perturbs the electronics of individual polymer chains. It is well known that bulky side groups can introduce steric strain between repeat units along the polymer backbone, thereby twisting the backbone out of local planarity. As the π orbital delocalization between repeat units is decreased, the bandgap is shifted to higher energies.

The metal-free Poly(**1**) emits at 550 nm, with weak but noticeable vibronic features. In a dichloromethane solution, Poly(**1**) displays a relative quantum yield of 0.19 and an excited state lifetime of 0.69 ns. Measures to exclude oxygen and trace amount of acids from the solution sample were necessary to prevent depletion of the polymer's fluorescence. We have previously shown that the rotaxane monomer **1** forms a 1:1 complex with transition metal ions, and the resulting complex quenches exciplex emission via an electron or energy transfer mechanism.¹² In the molecular wire approach, linking the rotaxane units together in a conjugated polymer is analogous to wiring the receptors in series. The conjugated backbone allows electronic communication between the repeat units, such that a local perturbation in a receptor can affect the global transport proper-

ties of the polymer.¹⁵ As the tetrahedral metal complex quenches the mobile exciton at a rate faster than the radiative recombination, it results in an amplification in the quenching response, as illustrated in Figure 2. The Stern-volmer plots for Cu^+ and Zn^{2+} display positive deviation from linearity, indicative of static quenching. Furthermore, quenching of more than 99% was observed with the addition of 0.3 equivalents of Cu^+ or 0.1 equivalents of Zn^{2+} relative to the repeat units. Binding of alkali metal ions elicits a different emission response, as illustrated in Figure 2. With initial addition of Na^+ , the polymer fluorescence diminishes. However, when 0.5 equivalents or more of Na^+ is added, the polymer emission returns with concomitant red shift and eventually reaches a plateau at about 70% of the original intensity ($F_0/F \approx 1.4$). We have previously demonstrated that alkali metal ions bind to the lower rim of the rotaxane monomer **1**.¹⁶ As the metal ion is stabilized by the oxygen atoms in the threading unit and the EDOT groups, the resulting complex displays a new emissive exciplex. Consequently, we attribute the interesting observations in the Na^+ -bound polymer to the complexation of group 1 metal ions in the lower pocket of the rotaxane groups.

We constructed a model of the Cu^+ monomer **1** using a PM3 level geometry optimization. Using the computationally optimized conformer as a fixed building block, we then conducted molecular mechanics calculations on an octamer.¹⁶ Simple inspection of the admittedly

simplified polymer model reveals a core and shield structure with the conducting backbone enshrouded by the bulky rotaxane groups. Such a structure has profound implications on the transport properties of the polymer. The phenanthroline portion of the macrocycle and the threading unit provide a rigid insulating shield that limits the rate of interchain charge hopping and impedes conduction. Compared to the ribbon-like planarity of Poly(2), the core and shield structure of Poly(1) leads to an augmented diameter and more complex packing. As the density of the electroactive elements, i.e. the CP backbone, decreases, the possible charge transport pathways present per volume unit in the rotaxanated polymer is also diluted. We therefore anticipate significantly lower conductivity in Poly(1) relative to its unadorned parent Poly(2).

Poor solubility and processibility present major hurdles in the utilization of simple unfunctionalized CPs in devices. Organic chemists have generally ameliorated the problems by adding flexible or ionic side chains to the polymer backbone. Ironically, we encountered numerous challenges in the handling and investigation of Poly(1) because of its remarkable solubility. Repeated attempts to synthesize Poly(1) via electrochemical deposition using different solvents and reduced temperatures failed because the polymer formed at the electrode surface readily diffused into the electrolyte solution. As a result, we performed all electrochemical experiments from spin-cast films of the chemically synthesized polymer on ITO electrodes. Even so, in conventional organic electrolyte systems, the high solubility attributed to electroactivity loss in the reduction sweeps of the polymer CV, since the oxidized species readily dissolve from the electrode surface. However, we eventually discovered that using 0.1 M tetrabutylammonium perchlorate in a 1:1 mixture of acetonitrile and water afforded the most stable and reproducible CVs. As revealed in Figure 3, Poly(1) shows a pseudo-reversible redox wave at 0.4 V vs. SCE with linear correlation between the peak current and scan rate, indicative of surface-confined redox activity. To elucidate the effect of the rotaxane groups on the electrochemical

behavior of the polymer, we prepared Poly(2) via electrochemical deposition on ITO electrode and investigated its electrochemical properties. As demonstrated in Figure 4, Poly(2) remains electroactive between -0.5 and 0.5 V vs. SCE. Reynolds and coworkers documented the remarkably broad redox activity of Poly(2) and attributed it to the low bandgap and delocalized electronic states.¹⁷ Encapsulating the polymer backbone with bulky rotaxane groups impedes the interchain π - π interactions. Consequently, the localization of the electronic states of the polymer chains results in the narrowing of the electroactivity window.

Figure 3. CV of Poly(1) thin film on an ITO electrode in 0.1 TBAClO₄ in 1:1 CH₃CN/H₂O at 100 mV/s. (Inset) Current at E_{pa} as a function of scan rate.

Figure 4. Top: Film growth of Poly(2) on ITO electrode in 0.1M TBAPF₆ in DCM at 100 mV/s. Shown here are scans 1, 5, 10, 15 and 20. Bottom: Scan rate dependence of the Poly(2) thin film at 25, 50, 100 and 200 mV/s on ITO electrode in 0.1M TBAClO₄ in 1:1 CH₃CN/H₂O.

Our group and others have previously observed enhancement of electroactivity in other CP systems bearing the CP backbone of Poly(1) by the isopotential copper ions.^{12,17} The tetrahedral binding pocket of the rotaxane unit displays a high affinity to copper ions and places the ions in an optimal situation to interact with the polymer backbone. At first glance, the CV of Poly(1, Cu) exhibits no discernible difference from that of the metal-free Poly(1), even though XPS of the polymer film confirms the presence of copper ions. As revealed in Figure 5, simple dipping of a Poly(1) film in a CuPF₆/CH₃CN solution increases the current density in both oxidation and reduction sweeps by 30%, while the general shape of the CV is retained.¹⁸ Treatment of the Poly(1) with aqueous Cu(SO₄)₂ yields similar response. These observations confirm the excellent

overlap between the copper-centered and polymer electrochemistry.

Figure 5. CV of Poly(1) film on ITO electrode before (solid line) and after (dashed line) quickly dipping in a 0.1 M Cu(CH₃CN)₄PF₆ solution in CH₃CN. Conditions: 0.1 M TBAClO₄ in 1:1 CH₃CN/H₂O at a scan rate of 100 mV/s.

We performed *in-situ* UV-vis spectroscopy of the polymers as a function of applied electrochemical potential using ITO as a working electrode. To ensure that the polymer had come to equilibrium at each potential, we held the polymer film at each potential for 30 seconds before taking the measurements. In its pristine state, the metal-free Poly(1) shows an absorption with λ_{max} at 487 nm (Figure 6). Dipping the metal-free polymer film in the LiClO₄ supporting electrolyte gradually shifts the absorption maximum to 513 nm with a weak shoulder at 711 nm (Figure 6). Previously, our group has reported that protonation of a structurally related conducting polyrotaxane shifts the polymer absorption to lower energies, and that holding the polymer film at reducing potentials can achieve deprotonation.¹⁹ For Poly(1), however, holding the potential at -0.40 V for 20 min. induced no change in the UV-vis spectra of the polymer film, indicating that lithium binding, not protonation, is responsible for the emergence of the new absorption features. We shall call this partially-chelated polymer Poly(1, Li) for a more accurate description. On the other hand, Poly(1, Cu) displays two absorption features with λ_{max} at 487 and 749 nm, which correspond to the polymer absorption and the charge transfer band, respectively. The red shift in the polymer ab-

sorption of Poly(**1**, Li) suggests the Lewis acidic Li^+ perturbs the electronic states of the polymer backbone via geometry change and/or electrostatic interactions. This observation supports our earlier assertion that alkali metal ions prefer binding to the lower rim of the rotaxane unit, where the oxygen atoms stabilize the cations.²⁷ On the other hand, because Cu^+ chelates to the phenanthroline portion of the macrocycle, the absorption band assigned to the conjugated polymer backbone remains unchanged. With increasing doping levels, the intensity of the interband absorption bands decreases and a low-energy absorption band at 751 nm emerges for both Poly(**1**, Li) and Poly(**1**, Cu). In the heavily doped state (≥ 0.6 V vs. Ag/AgCl), the absorption band at 751 nm is depleted and the spectra show increasing intensity at long wavelengths that extend into the near-IR. This feature is characteristic of free carriers in the metallic state and is referred to as a free carrier tail.²⁰ In addition, the metal-ligand charge transfer band in Poly(**1**, Cu) remains throughout the majority of the sweep cycle, showing only minor depletion at the highly doped state.

Comparisons of the conductivity of iodine-doped Poly(**1**) and Poly(**2**) pressed pellets support our assertion that the rotaxane groups provide insulation around the polymer chains. To ensure homogeneous and complete doping, we exposed the pressed pellets in a chamber of I_2 under reduced pressure at an elevated temperature for at least 2 hours. As shown in Table 1, Poly(**1**) displays a bulk conductivity that is three orders of magnitude lower than that of Poly(**2**). The experimental data demonstrate that encapsulation of the polymer backbone by rotaxane units impedes the formation of highly delocalized mesostructures and suppresses interwire charge hopping. Random copolymerization of **1** and **2** in the presence of a Cu^{2+} oxidant afforded Poly(**1**, **2**) (Scheme 3). As expected, varying the concentration of the rotaxane groups along the polymer alters the degree of insulation. Decreasing the concentration of the rotaxane units creates “holes” in the insulation layer, such that interchain charge hopping can occur at these sites. Because the number of

charge percolation pathways increases, Poly(**1**, **2**) displays a moderate increase in the conductivity compared to Poly(**1**). For systems with immobilized Zn^{2+} , a redox inactive ion, the polymer chains behave as insulated wires and we observed only minor changes in the conductivity. For Poly(**1**, Cu), however, the overlapping electroactivity between the metal centers and the conjugated polymer creates an optimal situation for the Copper ions to participate in the conduction. Compared to the metal-free polymer, Poly(**1**, Cu) shows a 90 times increase in the conductivity.

Figure 6. Spectroelectrochemistry of Poly(**1**, Li) (left) and Poly(**1**, Cu) (right) on ITO electrodes in 0.1M LiClO_4 in 1:1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$. Measurements were made after holding the electrode at the given potential for 30 sec. to ensure equilibrium. Potential was measured against Ag/AgCl reference electrode.

Scheme 3. Random copolymerization of **1** and **2** to yield Poly(**1**, **2**). **Table 1.** Conductivity Comparison of Various Rotaxanated Polymers and the Model Polymer.^a

	σ (S/cm)	STDEV
Poly(1)	0.00107	0.00003
Poly(2)	4.52	1.03
Poly(1 , Cu)	0.0902	0.0133
Poly(1 , Zn)	0.00393	0.00081
Poly(1 , 2)	0.00777	0.00086

^a Measurements were taken with pressed pellets of the polymers doped with iodine vapor

Summary

We have described the chemical synthesis, UV-vis spectroscopy, fluorescence spectroscopy, electrochemistry, and conducting properties of conducting polymers bearing solubilizing rotaxane groups. Physical studies (UV-Vis, electrochemistry) of Poly(**1**) suggest that the bulky rotaxane groups encapsulate the conjugated polymer chains, resulting in a higher bandgap and more localized electrochemistry compared to the unfunctionalized Poly(**2**). Chelation of transition metal ions to the phenanthroline-bipyridine core creates exciton traps along the polymer backbone and results in amplified fluorescence quenching. Alkali metal ions, however, bind to a different cavity of the rotaxane and generate different fluorescence response. Electrochemical data suggest that the bulky rotaxane groups insulate the CP wires and dramatically hinder bulk charge transport. As a result, Poly(**1**) exhibits a three orders of magnitude decrease in conductivity relative to Poly(**2**). Binding of redox inactive metal ions

such as Zn²⁺ produces no significant change in conductivity. However, in the case of copper ions, we observed excellent overlap in the copper centers and the polymer's electrochemistry. The immobilization of copper ions in the polymer periphery provides interconnects for charge hopping and consequently produces a nearly 10²-fold increase in the polymer's conductivity.

This study explores the feasibility of encapsulating conjugated polymers by attaching pendant supramolecular groups. As discussed in the beginning, the continual effort to create CP- and molecule-based devices requires effective insulation of their conducting elements. The bulky rotaxane groups wrap around the center polymer wire and severely hinder interchain charge hopping. In addition, immobilization of isopotential transition metal ions in the rotaxane repeat units can modulate the charge transport of the polymer and increase the bulk conductivity. While these results demonstrate the versatility of our approach to insulated molecular wires, further fundamental studies are required before practical applications can emerge.

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