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

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Abstract: Synthetic strategies to control interchain electronic communications within conjugated polymers (CPs) are described. 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.

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Key words: conjugated polymer, sensor, transport, exciton, fluorescence, resistivity, iptycene, poly(phenyleneethynylene), π - π stacking, metallorotaxane, pyrrole

1 Introduction

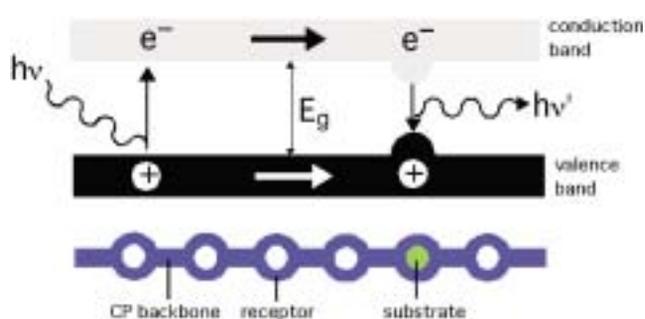
π -Extended chemical architectures embedded with potential recognition sites serve as versatile platforms for developing self-amplifying sensory materials.¹ Local binding events within such constructs can modify the energy landscape that controls the mobility of energy and charge carriers. Changes in 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

2 Photochemistry and Electrochemistry of Conjugated Polymers

2.1 Fluorescent Polymers

Conjugated semiconducting organic polymers efficiently generate excitons (i.e. bound electron-hole pairs) upon absorption 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 tradeoff 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,



Scheme 1

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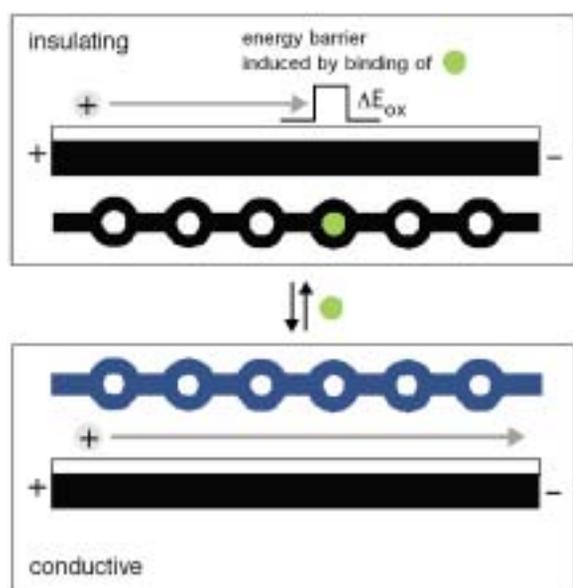
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significantly compromising sensory responses. Enhancing the mobility of the excitons while suppressing electronic coupling between the polymer chains, a seemingly contradictory design principle, has remained a formidable synthetic challenge in light-emitting organic materials.⁵

2.2 Conducting Polymers

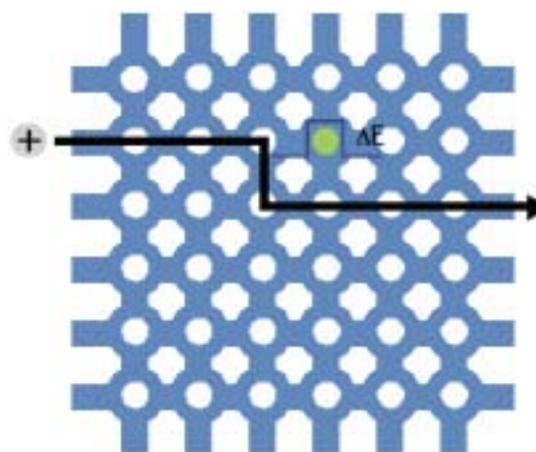
A partial depopulation of the valence band (p-doping) or population of the conduction band (n-doping) of semi-conducting polymers generates highly conductive materials. Conductivities of doped CPs are extremely sensitive to local defects, offering opportunities to develop resistivity-based sensing schemes.^{1,3} 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

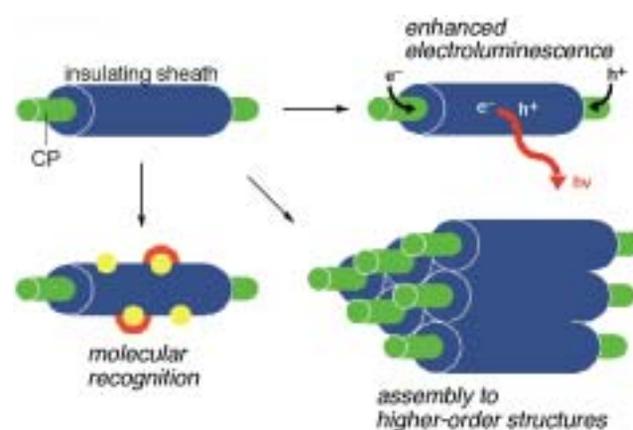
(Scheme 3), attenuating the perturbation introduced to the CP energy landscape. Although the increased dimensionality of the electronic structures enhances the overall conductivity, the performance of the CP sensor is now substantially compromised. Similarly to the situations encountered with light-emitting 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

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



Scheme 4

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 exciton and charge transporting pathways within such constructs afforded optoelectronic properties better suited for sensing applications, as described below.

3.1 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(phenyleneethylenes) (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.

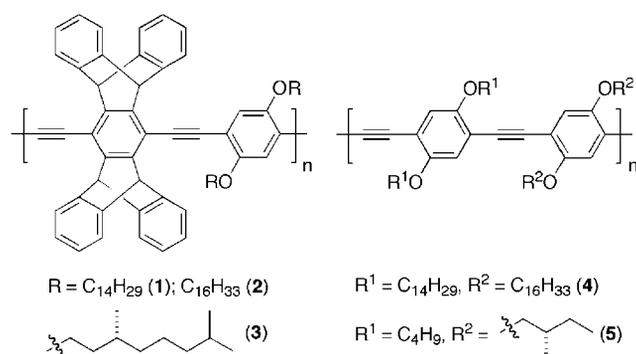
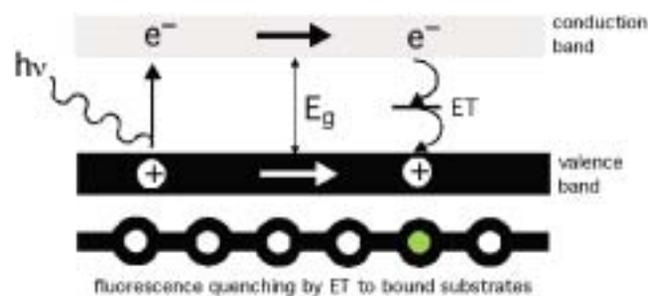


Figure 1

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 response 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 photo-physics and transport properties of CPs.



Scheme 5

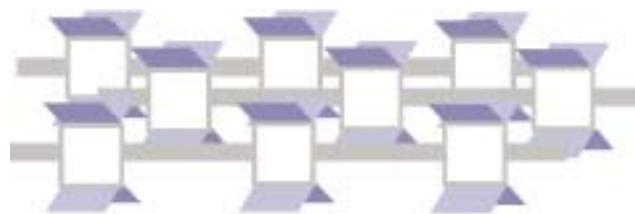


Figure 2

3.2 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 facilitate 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 non-aggregated **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.

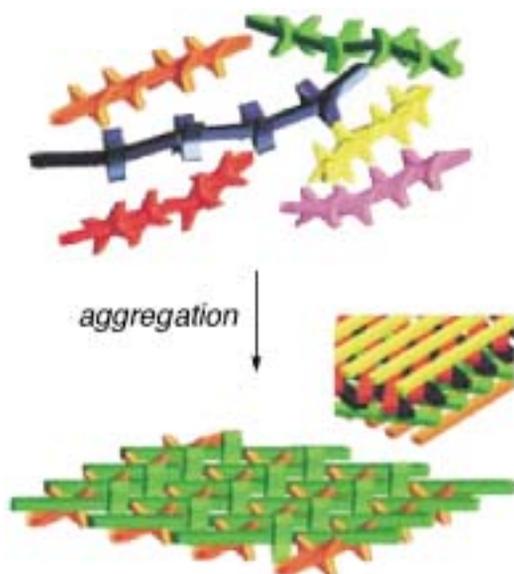


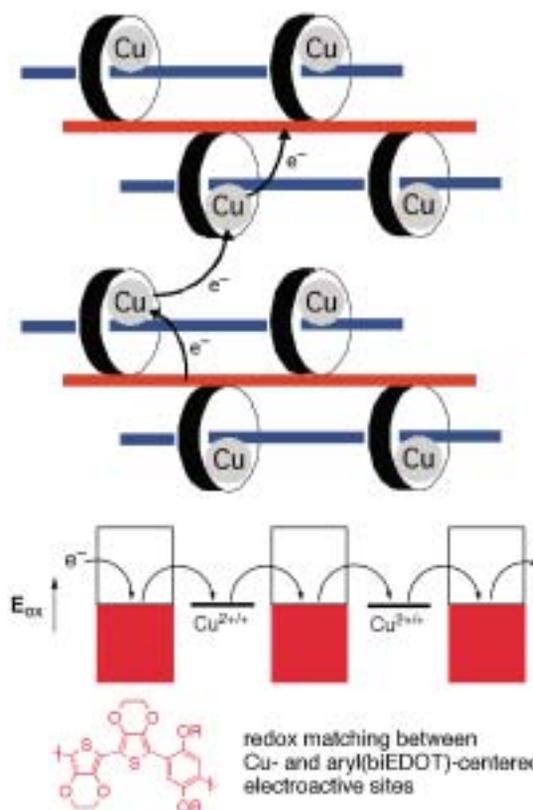
Figure 3

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

Transition metal ions can actively participate in charge transporting pathways connecting 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.

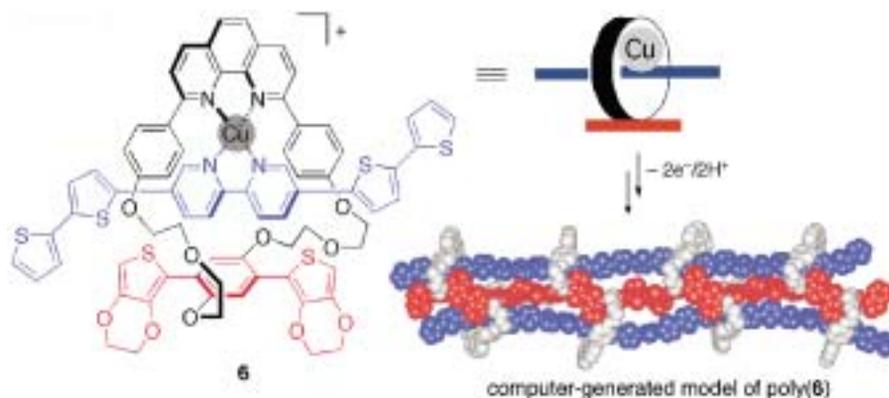
Multiple electroactive components were introduced in the design of the monomers **6** in order to assemble three-

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.



Scheme 7

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



Scheme 6

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.

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.

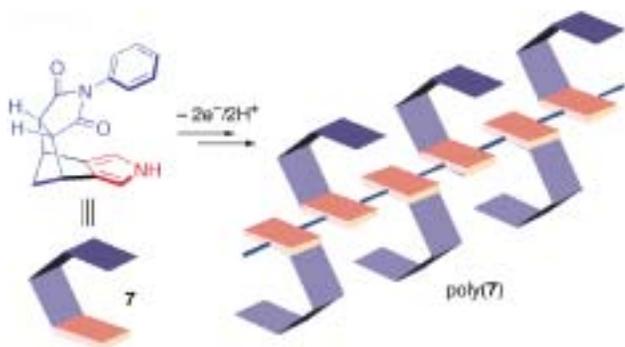
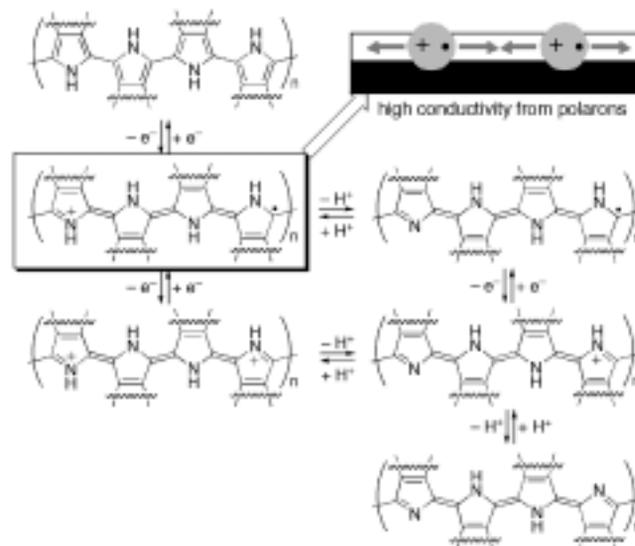


Figure 4

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 provide 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 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

4 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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