

Insulated conducting polymers: manipulating charge transport using supramolecular complexes†

Phoebe H. Kwan and Timothy M. Swager*

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Rotaxane structures which provide functional insulation to conducting polymers can provide over a 4000-fold reduction in conductivity over non-rotaxane structures and with electrocally active copper ions in the rotaxane units the conductivity increases by more than 80 times relative to the metal-free analog.

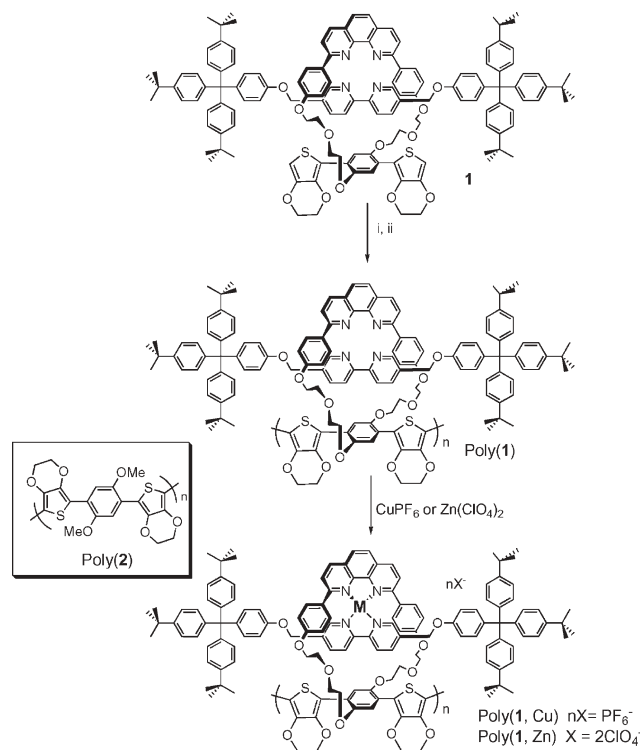
Insulation of metallic and semiconductive materials to create independent electrical conduction pathways is an indispensable element in the design of modern electronics. Effective insulation eliminates unwanted interference and can also protect conductive materials from environmental degradation, hence it plays a critical role in the performance and lifetime of a device. Concepts on how to best insulate conjugated polymer (CP) wires are in their early stages and the functionality within these structures will be key to realizing molecular electronic devices comprising only a few polymer strands. Previous reports of insulated CPs include the use of dendrons¹ and the use of the CP backbone as a thread in polyrotaxanes.² Anderson and coworkers used the latter approach to synthesize CPs with improved stability and reduced interchain interactions, such that PLEDs fabricated from these shielded polymers displayed a longer device lifetime and higher luminance.

Suppression of interchain interactions in insulated CPs impacts the charge transport properties by altering the conduction pathways. Typical CPs have inhomogeneous morphologies with coexisting regions of crystallinity and disorder.³ Within the crystalline mesostructures, efficient interchain orbital overlap gives highly delocalized electronic states that sometimes display a metallic band transport mechanism.⁴ Because of the disorder inherent in polymers, these delocalized crystalline mesostructures are separated by regions of random coils. These domains have more localized electronic states, so that charges are transported *via* an activated hopping mechanism.⁵ The bulk conductivity of a CP therefore depends on the charge transport pathways that involve the minimum distance through resistive regions.

In our continuing effort to develop CP-based sensors and devices, we are interested in controlling (restricting and/or enabling) conduction pathways at molecular length scales. Insulation *via* enshrouding a CP wire needs not lower the individual polymer's ability to transport charges and in fact it can promote a favorable rigid-rod conformation.⁶ However, the suppression of interchain interactions will severely reduce the

number of charge transporting pathways and lower their bulk conductivity compared to their unfunctionalized counterparts. To assemble functional CP wires with varying degrees of encapsulation, we continue to build on methodology pioneered by Sauvage,⁷ which has previously been employed to create conducting polyrotaxanes.⁸ The salient feature of this supramolecular approach is the ability to immobilize redox-matched metal ions (with respect to the CP backbone) in the insulation⁹ to provide facile conduction pathways.

The rotaxane monomer **1**¹⁰ 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 1. Reductive quenching of the reaction with hydrazine monohydrate, followed by cyanide treatment afforded the highly soluble, metal-free rotaxanated polymer Poly(**1**) ($M_n = 22\,000$, DPI ≈ 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) in an acetonitrile solution afforded the metal-bound polymers Poly(**1**, Cu) and Poly(**1**, Zn) in quantitative yields.



Scheme 1 Chemical polymerization of the rotaxane polymers.‡

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA. E-mail: tswager@mit.edu

† Electronic supplementary information (ESI) available: Detailed synthetic and experimental procedures, XPS spectra and computer modelling. See <http://dx.doi.org/10.1039/b508399k>

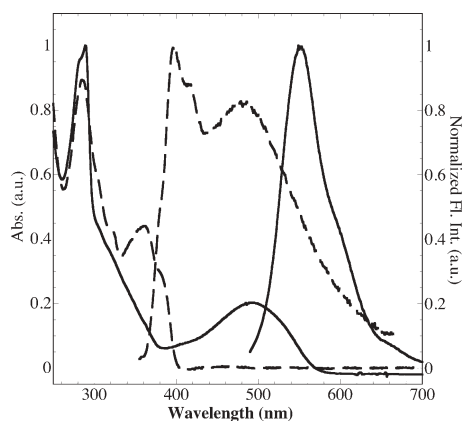


Fig. 1 Absorption and emission spectra of **1** (dashed line, $\lambda_{\text{exc}} = 325$ nm) and Poly(**1**) (solid line, $\lambda_{\text{exc}} = 465$ nm) in CH_2Cl_2 .

The solution absorption and emission spectra of Poly(**1**) are compared to its parent monomer **1** in Fig. 1. The broad and featureless absorption profile can be attributed to the poly(phenylene thienylene) structure. However, Poly(**1**) exhibits a larger bandgap ($E_g = 2.10$ eV) relative to a previously studied homolog Poly(**2**) (Scheme 1, $E_g = 1.75$ eV).¹¹ Two factors contribute to the higher bandgap observed in the rotaxanated polymer. Firstly, most planar CPs exhibit interactions between the π electron clouds of adjacent polymer chains, these interactions delocalize the orbitals and lower the energy. Poly(**1**), on the other hand, lacks the ribbon-like geometry required for lateral band delocalization. The larger bandgap in Poly(**1**) could also imply that the steric bulk of rotaxane groups favors non-planar backbone conformations and reduces the polymer's conjugation length.

In a dichloromethane solution, Poly(**1**) displays a quantum yield of 0.19 and an excited state lifetime of 0.69 ns. The polymer is photochemically doped by molecular oxygen in a facile manner and the fluorescence decreases rapidly upon irradiation in ambient atmosphere. This is strictly a redox process and Poly(**1**) can be reversibly reduced to its neutral undoped state with hydrazine. The fluorescence of both **1** and Poly(**1**) is quenched when complexed with Cu^+ and Zn^{2+} . In the case of **1**, fluorescence quenching experiments reveal a 1 : 1 rotaxane/metal ion complex. On the other hand, Poly(**1**) gives an amplified quenching response, losing >99% of its fluorescence intensity with the addition of 0.3 or 0.1 equivalents per rotaxane unit of Cu^+ and Zn^{2+} , respectively. These observations are consistent with the delocalized CP nature of Poly(**1**).¹²

To examine the degree of encapsulation of the CP backbone in Poly(**1**), we built up a computationally optimized oligomer from individual Cu^+ complexes of **1** (minimized at a PM3 level). This fixed building block was then extended to an octamer and the structure was minimized by mechanics calculations.¹³ The admittedly simplified polymer model reveals a core and shield structure wherein the conducting backbone is enshrouded by the bulky rotaxane groups. The isolation of the CP backbone prevents strong interactions with other polymers and endows Poly(**1**) with remarkable solubility. Repeated attempts to synthesize Poly(**1**) *via* electrochemical deposition using different solvents and reduced temperatures failed because polymer formed at the electrode surface readily diffused into the electrolyte solution. Polymer films for electrochemical experiments were prepared by spin-casting the

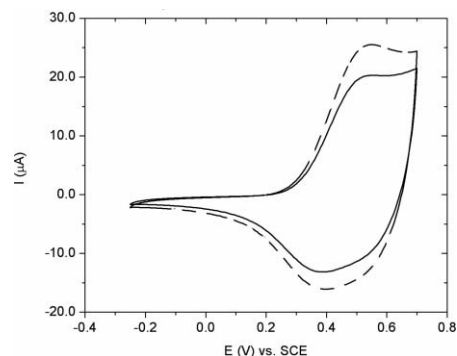


Fig. 2 CV of Poly(**1**) film on ITO electrode before (solid line) and after (dashed line) quickly dipping in a 0.1 M $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ solution in CH_3CN . Conditions: 0.1 M TBAClO₄ in 1 : 1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ at a scan rate of 100 mV s^{-1} .

chemically synthesized polymer on ITO electrodes.¹⁴ As revealed in Fig. 2, Poly(**1**) shows a pseudo-reversible redox wave at 0.4 V vs. SCE and a linear correlation between the peak current and scan rate, indicative of surface-confined redox activity.

Binding of Cu^+ ions to Poly(**1**) to produce Poly(**1**, Cu) enhances the electroactivity by approximately 30% (Fig. 2). Since the copper ions are isopotential with the CP backbone,¹⁵ the CV of Poly(**1**, Cu) exhibits no discernible new peaks from the CV of the metal-free Poly(**1**). The presence of copper ions was confirmed after electrochemical analysis by XPS of the polymer films. For these comparative electrochemical studies, dipping a Poly(**1**) film in a $\text{CuPF}_6/\text{CH}_3\text{CN}$ ¹⁶ solution or in aqueous $\text{Cu}(\text{SO}_4)_2$ yields similar electrochemical enhancements on the respective CVs.

The delocalized nature of doped Poly(**1**) and Poly(**1**, Cu) was further confirmed by UV-vis spectroscopy as a function of applied electrochemical potential. In its pristine state, the metal-free Poly(**1**) shows an absorption band with λ_{max} at 487 nm (Fig. 3). Dipping the polymer film in a LiClO_4 supporting electrolyte shifts the λ_{max} to 513 nm with a weak shoulder at 711 nm. In contrast, 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. 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

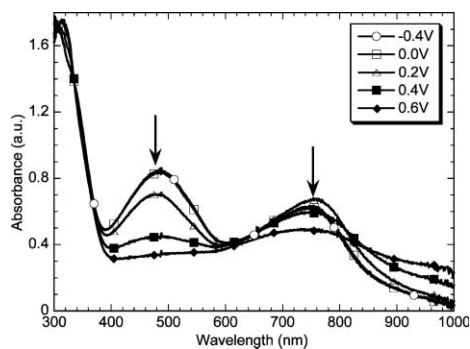
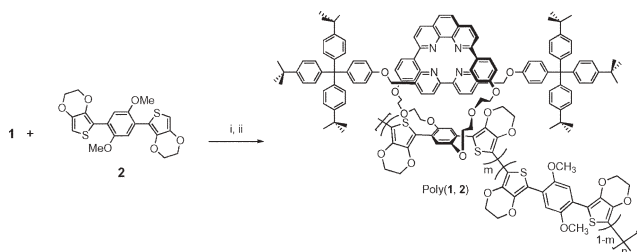


Fig. 3 Spectroelectrochemistry of Poly(**1**, Cu) on ITO electrodes in 0.1 M LiClO_4 in 1 : 1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$. Measurements were made after holding the electrode at the given potential vs. Ag/AgCl for 30 s to ensure equilibrium.

Table 1 Conductivity comparison of various rotaxanated polymers and the model polymer^a

	$\sigma/S \text{ cm}^{-1}$	STD
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



Scheme 2 Random copolymerization to yield Poly(1, 2).§

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.¹⁷

Comparisons of the pressed pellet conductivity of iodine-doped Poly(1) and Poly(2) 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 I₂ under reduced pressure at an elevated temperature for at least 2 h. 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 the encapsulation provided by the rotaxane units impedes the formation of highly delocalized mesostructures and suppresses interwire charge hopping. Random copolymerization of an equimolar mixture of 1 and 2 in the presence of a Cu²⁺ oxidant afforded Poly(1, 2) (Scheme 2). Decreasing the concentration of the rotaxane units on the polymer backbone creates “holes” in the insulation layer, such that interchain charge hopping can occur at these sites. As the number of charge percolation pathways increases, Poly(1, 2) displays a moderate increase in the conductivity compared to Poly(1) (Table 1). For systems with immobilized Zn²⁺, a redox inactive species within the potential window of our interest, the polymer chains behave as insulated wires and we observed only minor changes in the conductivity of Poly(1, Zn) compared to Poly(1). 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 mediate interchain charge transport. Compared to the metal-free polymer, Poly(1, Cu) shows a 90 times increase in the conductivity.

In summary, we have demonstrated that Poly(1) exhibits optical and electrochemical properties consistent with a highly delocalized CP structure that is partially insulated by bulky rotaxane groups. Poly(1) exhibits a three orders of magnitude decrease in the bulk conductivity relative to Poly(2) and binding of redox inactive metal

ions such as Zn²⁺ produces no significant change in conductivity. However, chelation of the electrochemically isoenergetic copper ions (Cu⁺/Cu²⁺) into the rotaxane units introduces charge hopping pathways between the delocalized charge transporting CP backbone, hence we observed a 10²-fold increase in conductivity.

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Notes and references

‡ (i) 2.7 equiv. Cu(OTf)₂, ACN. (ii) KCN, ACN/H₂O.

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