

A Dramatic Conformational Transformation of a Regioregular Polythiophene via a Chemoselective, Metal–Ion Assisted Deconjugation

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Many have endeavored to utilize conjugated polymers for the development of materials that contain specifically mutable (i.e., tunable and/or switchable) physical properties.¹ These efforts represent attempts to harness the uncanny electronic and optical properties that are a native consequence of extended π -conjugation, the common and defining feature of all conducting polymers. The ability to dictate a fine control over the degree of conjugation is an invaluable tool for the development of such devices as polymer interconnects with singular resistance ratings, nonlinear optical devices, polymer LEDs, and conducting polymer-based molecular sensors. Studies have focused on the effect of dopant counterions² and side-chain binding of alkali metals^{1d,g,h} on the solid-state structural order and conjugation of polythiophenes. In general, cations and anions affect both conjugation and order but offer little chemoselectivity or tunability; in general, these effects are small.³ Herein we report a complete removal of conjugation in a neutral, conjugated polymer, HT-poly(3-[2,5,8-trioxanonyl]thiophene)^{1a,h} (**HT-1**), in solution by a chemoselective response to Pb^{2+} ions. Observation of this effect in the solid state is clearly seen by UV/vis spectroscopic studies, conductivity measurements, and X-ray spectroscopy studies that show that while films of **HT-1** are normally highly ordered, films of **HT-1** cast in the presence of Pb^{2+} ion are dramatically and comparatively disordered. Through this response, certain conjugational states are accessible both in solution and in the solid state.

The polymer **HT-1** is synthesized by a method developed in our lab that provides a regiochemically pure, well-defined conjugated polymer with a high molecular weight and a narrow polydispersity.^{1h,4,5} It is soluble in a number of organic solvents and, when concentration is low enough to avoid the formation of ordered aggregates, the π - π^* transition for the conjugated (“pla-

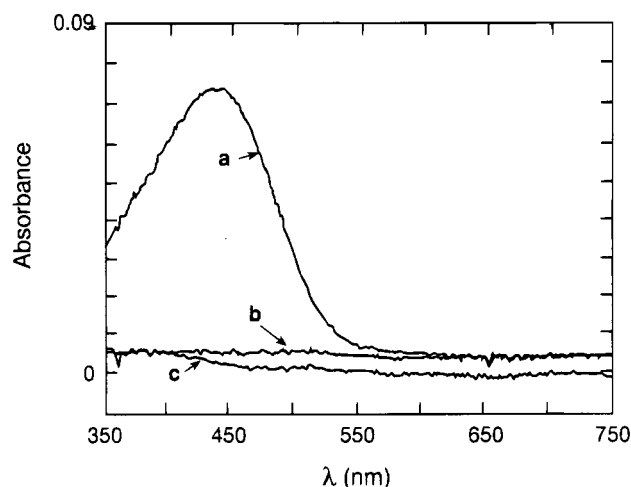


Figure 1. (a) **HT-1** in CHCl_3 , (b) PbCl_2 (saturated) in CHCl_3 , and (c) **HT-1** in CHCl_3 , with PbCl_2 (saturated).

nar”) polymer may be seen in the UV/vis spectrum as an absorbance that appears at anywhere from 440 to 470 nm (depending upon solvent system). When fully soluble Li^+ is bound podandically by **HT-1** in 1:1 $\text{CH}_3\text{-CN}:\text{CH}_2\text{Cl}_2$, there is a small decrease in the degree of polymer conjugation ($\Delta\lambda_{\text{max}} = -11 \text{ nm}$).^{1h} However, when solid PbCl_2 is shaken with a $2.5 \times 10^{-6} \text{ g/mL}$ solution of **HT-1** in CHCl_3 ,⁶ there is a chemoselective response to the Pb^{2+} ions that completely removes the polymer conjugation (Figure 1a,c). The λ_{max} for the π - π^* transition of “planar” **HT-1** in solution is 439 nm (CHCl_3 , Figure 1a), but upon the addition of PbCl_2 , this conjugation is completely and dramatically removed. The only absorption now remaining is around 260 nm and is attributed to localized thiophene states (see supporting information). This behavior represents the binding of the dissolved soft metal to the sulfur atoms in the polythiophene backbone that is accompanied by a global change in the polymer chain conformation. While the same removal of conjugation is also observed after the addition of $\text{Hg}(\text{OAc})_2$, the addition of LiOAc and $\text{Zn}(\text{OAc})_2$ has no effect on the conjugation of **HT-1** in CHCl_3 . Therefore, the response is chemoselective. Inoue et al.⁷ have reported a similar, selective coordination of Pt^{2+} by the sulfur atoms of polythiophene.

The complete elimination of polymer conjugation is possible for dilute solutions of **HT-1**, wherein the concentration of Pb^{2+} in CHCl_3 is proportional to the concentration of sulfuric binding sites. The less polar polymer, HT-poly(3-dodecylthiophene), begins to show this effect only when the polymer concentration is extremely low,⁸ and thus the solubility of the generally insoluble Pb^{2+} ions is increased by the presence of polar heteroatoms in the side-chain substituents. The weakly binding podandic side chains must be involved in this removal of the conjugation, but this binding effect is only supplemental to the sulfur-binding interaction.

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(5) The samples used in this study had an $M_n = 32\text{K}$ and PDI = 1.7 by GPC vs polystyrene standards.

(6) A 0.2 mmol sample of PbCl_2 was added to a 17 mL aliquot of **HT-1** in distilled CHCl_3 . The mixture was shaken and then filtered through qualitative-grade filter paper in order to remove excess Pb salts.

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(8) These concentrations are very near to the detection limit of our UV/vis spectrophotometer.

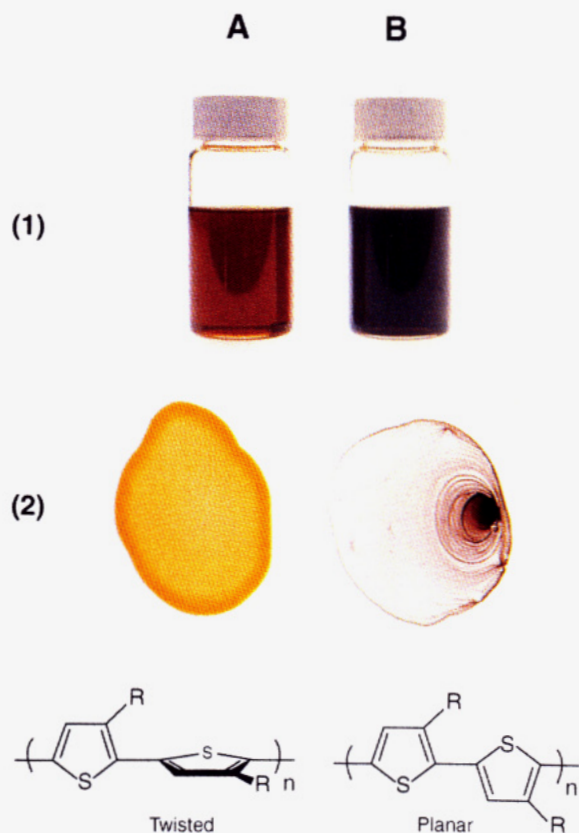


Figure 2. (1) Solution A: **HT-1** in CHCl_3 with $\text{Pb}(\text{BPh}_4)_2$ (saturated). Solution B: **HT-1** in CHCl_3 . (2) Film A is cast from solution A; Film B is cast from solution B.

Exhaustive studies have proven that the interaction is not a chemical reaction between Pb and **HT-1** nor is it an oxidation of the polymer. The NIR region of the UV/vis/NIR spectrum of **HT-1** (1.9×10^{-6} g/mL in CHCl_3) is identical to a similar sample which contained Pb^{2+} (**HT-1**, 1.9×10^{-6} g/mL in CHCl_3 ; saturated with $\text{Pb}(\text{OAc})_2$). We do not observe the development of a midgap band in the NIR region, and therefore no oxidation of the polymer has occurred. Comparative XPS measurements⁹ of films of **HT-1** cast from CHCl_3 solutions in either the presence or absence of $\text{Pb}(\text{BPh}_4)_2$ ¹⁰ indicate no change in the oxidation state of the sulfur atoms in the thiophene ring system (or of the Pb salt) as a result of the binding interaction. Furthermore, UV/vis studies of 3-(2,5,8-trioxanonyl)thiophene, **2**, 2-bromo-3-(2,5,8-trioxanonyl)thiophene, **3**, and terphenylene and ¹H NMR studies of **HT-1**, **2**, and **3** give no evidence for a chemical reaction of any these compounds upon exposure to Pb^{2+} in CHCl_3 . This would indicate that the observed effect is not the result of an oxidation of the polymer by the Pb salt or an addition of Pb to the polymer backbone.

In concentrated solutions of **HT-1**, we are able to tune the conjugation length. Figure 2 contains photographs which demonstrate the effect of Pb^{2+} ions on a concentrated solution of **HT-1** and the resulting films cast from each solution. Vial **A** contains a concentrated (1×10^{-3} g/mL in CHCl_3) solution of **HT-1** that has been satu-

rated with $\text{Pb}(\text{BPh}_4)_2$. Vial **B** contains a deep magenta solution of **HT-1** (1×10^{-3} g/mL in CHCl_3) without added Pb salts. The polymer in this solution (vial **B**) is highly conjugated ($\lambda_{\text{max}} = 575\text{--}600$ nm; band edge at 700 nm). In concentrated solution an aggregative, supramolecular ordering of the polymer occurs (the typical dilute solution $\lambda_{\text{max}} = 439$ nm in CHCl_3 ; band edge at 550 nm). We have recently used light scattering in order to verify this self-ordering behavior.¹¹ A striking transformation occurs upon the introduction of the Pb^{2+} ion that is accompanied by a 50–100 nm blue shift in the λ_{max} and a 50 nm blue shift in the band edge ($\lambda_{\text{max}} = 480\text{--}550$ nm; band edge at 650 nm). This is seen in the photograph of the orange-red solution in vial **A**. Films cast from the solution in vial **A** (with Pb^{2+}) are less conjugated and more disordered in the solid state than in the solution from which they were cast (film **A**). A film cast from vial **A** (film **A**) is yellow in color ($\lambda_{\text{max}} = 440$ nm; band edge at 550 nm). In contrast, films cast from the salt-free solution in vial **B** (Film **B**) are deep crimson in color ($\lambda_{\text{max}} = 520$ nm; band edge at 720 nm). There is a large (170 nm) difference in the band edge between films cast in the presence and the absence of Pb^{2+} . Since films of pure $\text{Pb}(\text{BPh}_4)_2$ are colorless, the Pb^{2+} ions induced a large disordering of the polymer. While it has been reported that the incorporation of Cu^{2+} ions into an electrochemically prepared poly(3-substituted thiophene) has an ordering effect on the polymer chains,¹² the evidence presented here clearly indicates that the chains of **HT-1** become twisted out of conjugation in the solid state as a consequence of a recognition/binding phenomenon (Figure 2). Comparison, by X-ray analysis, of a film of **HT-1** to a similar film that had been cast in the presence of $\text{Pb}(\text{OAc})_2$ indicates that the Pb^{2+} ions cause a significant amount of disorder in the film. X-ray diffraction shows that the very strong, wide-angle reflection, which represents interchain stacking of thiophene rings, has a half-width of 0.23 Å for a film that contained Pb^{2+} . In contrast, the corresponding half-width for the uncontaminated film is 0.11 Å. In addition, iodine-doped films of **HT-1** that had been cast from a solution (in CHCl_3) that was saturated with $\text{Pb}(\text{OAc})_2$ showed a ≈ 10 000-fold decrease in electrical conductivity when compared to similar samples that contained no Pb salts ($\sigma \approx 0.001\text{--}0.01$ vs $\sigma \approx 100\text{--}1000$ for samples without Pb). It is clear that the incorporation of Pb^{2+} decreases the amount of order in the resulting film.

In conclusion, we have observed that all conjugational order in a solution of a conjugated polymer may be instantly and selectively eliminated through the addition of a Pb^{2+} . Furthermore, we have shown that films of **HT-1** can be fabricated in a manner that allows for the selection between ordered and a disordered states. However, we have yet to find a method by which we may reverse this effect. This work also emphasizes how the development of a reliable method for the preparation of well-defined and fully characterized self-ordering, conjugated polymers allows for the realistic development of sensitive molecular probes. This is critical to efforts to understand the salient features of conformational

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(10) $\text{Pb}(\text{BPh}_4)_2$, which has a relatively high solubility in CHCl_3 , was used for this experiment in order to increase in the concentration of Pb^{2+} relative to that of **HT-1**. While the removal of the conjugation in dilute solutions can be observed with $\text{Pb}(\text{BPh}_4)_2$, the very large absorption of the phenyl groups obscure the effect spectroscopically.

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control and to the realization of genuine tunability of properties.

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Supporting Information Available: Listings include ^1H NMR spectra, GPC data, UV/vis spectra and XPS data (18 pages). Ordering information is given on any current masthead page.

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