

Insulated Polythiophene: Self-Threaded Conjugated Polymer via Alkyl Chain Straps

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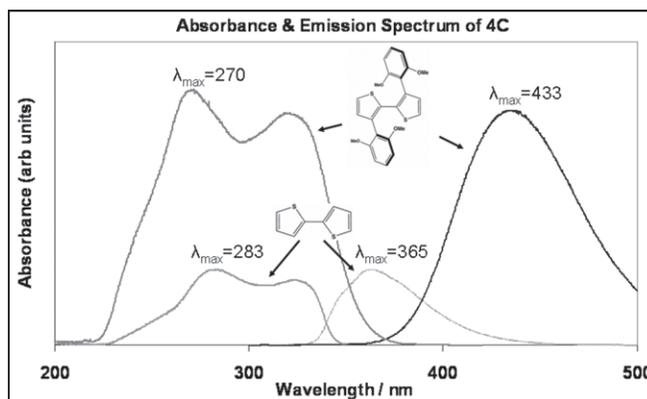
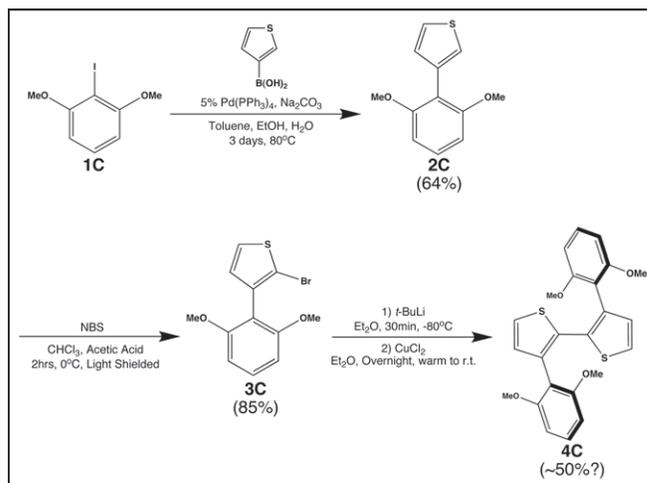
Introduction:

Polythiophenes are a popular class of organic conducting polymers, known for their environmental stability, conductivity [1], fluorescence and electroluminescent properties [2]. Conducting polymers, such as polythiophenes, have enormous potential in both static and dynamic applications, ranging from field-effect transistors and diodes to chemical sensors [3]. Many applications require the use of conducting polymers in the solid phase, which presents a painful trade off between high and low density deposition. High density deposition allows for easier charge injection as well as greater overall charge density, luminescence and conductivity. Unfortunately, inter-molecular interactions between uninsulated conducting polymers in the solid phase result in imprecise band gap control (mainly due to π - π stacking), crosstalk between threads, and quenching (lower fluorescent and electroluminescent quantum yield). While low density deposition can often alleviate these problems, it is often impractical. By inhibiting undesired inter-molecular interactions, insulated conducting polymers offer a solution; ideally, allowing for high density deposition with better band gap control and little/no loss in quantum yield [4]. In this study, we seek to develop an intramolecular bi-thiophene rotaxane with minimal degradation of the conductive, fluorescent and electroluminescent properties of bi-thiophene. The intramolecular bi-thiophene rotaxane must also be suitable for polymerization and use in the solid phase.

Results:

A bi-thiophene control compound (Scheme 1) was synthesized to both elucidate the effect of covalently attached benzene on bi-thiophene, but also to verify core components of our synthetic approach, namely Suzuki coupling [5,6] and thiophene homo-coupling. Compounds **2C** and **3C** were easily synthesized with moderate to good yield; **4C** required the optimization via multiple reaction conditions, with both a *n*-BuLi/ZnCl₂/CuCl₂ and *n*-BuLi/Fe(acac)₂ reaction resulting in 0% yield. A *t*-BuLi/CuCl₂ reaction was eventually arrived at, resulting in ~50% yield.

Optical characterization via UV-Vis spectroscopy (Figure 1) revealed that control compound **4C** had over twice the peak absorbance of bi-thiophene as well as double the Stokes shift.



Scheme 1, top: Synthetic pathway for bi-thiophene control compound.

Figure 1, bottom: UV-Vis spectra for bi-thiophene control compound **4C** and bi-thiophene. Bi-thiophene absorbance/emission spectra in orange and aqua respectively; **4C** absorbance/emission spectra in red and blue respectively. Note the increased absorbance and Stokes shift of **4C** versus bi-thiophene.

The increased absorbance could be attributed to a change in thiophene's electron density due to the attached benzene. The increase in Stokes shift was likely due to the increase in the number of degrees of freedom between **4C** and bi-thiophene (more rotation/vibration states in which to dissipate energy).

Synthesis of the intramolecular bi-thiophene rotaxane followed the same basic approach as the bi-thiophene control compound (Scheme 2), with reactions proceeding with similar yields. The cyclization reaction was particularly challenging, requiring optimization across a variety of reactors; the highest yield being 20% via discrete feed semi-batch reactor (portion wise). For comparison, a batch reactor under the same reaction conditions achieved a 6.5% yield. The bromination reaction (**6R/3C**) for the intramolecular rotaxane was unsuccessful (Figure 2). Noting that deuterium was not visible on H^1 -NMR, we elucidated lithiation site specificity via *t*-BuLi lithiation and deuterated methanol quenching. This test revealed no selectivity between the two α -positions on the thiophene group, ruling out the possibility of selective coupling via direct lithiation. The final coupling reaction remains elusive.

Conclusions and Future Directions:

This study reveals that the synthesis of a bi-thiophene intramolecular rotaxane (**7R**) is plausible; however, without the complete synthesis of the intramolecular bi-thiophene rotaxane, comparison to bi-thiophene and the synthetically successful bi-thiophene control compound **4C** is impossible. We will continue working on completing the coupling of **7R**, and then proceed to optical characterization. If favorable (minimal degradation of the fluorescent and electroluminescent

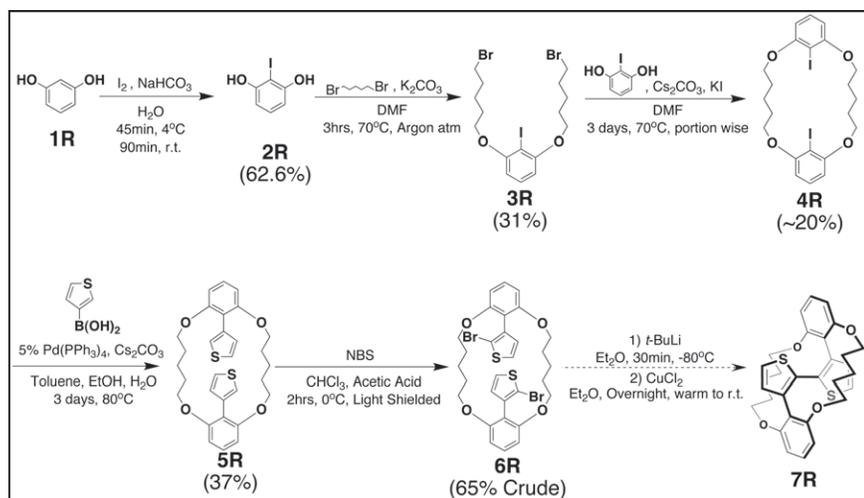
properties of bi-thiophene) polymerization, bulk property and solid-state studies will ensue.

Acknowledgements:

I would like to thank the Macromolecules Group and NIMS for their generous hosting. On both a personal and professional level, living and working in Japan was an amazing experience. Research funded by the National Nanotechnology Infrastructure Network Research Experience for Undergraduates Program and National Science Foundation.

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Scheme 2, left: Synthetic pathway for intramolecular bi-thiophene rotaxane.

Figure 2, below: H^1 -NMR spectra of **5R** and **6R** using the same brominating reaction and workup as $2C \rightarrow 3C$. Note that **5R/6R** and **2C/3C** are identical on TLC.

