PRF Grant Number: 56002
Fundamental Studies of 4,4'-Bipyridine Aryleneethynylenes
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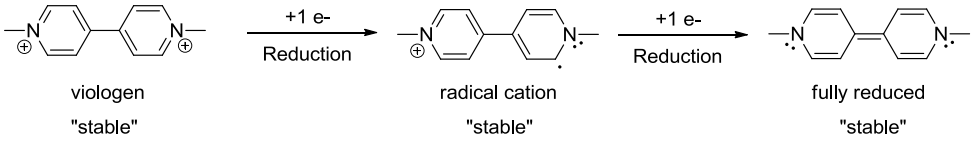
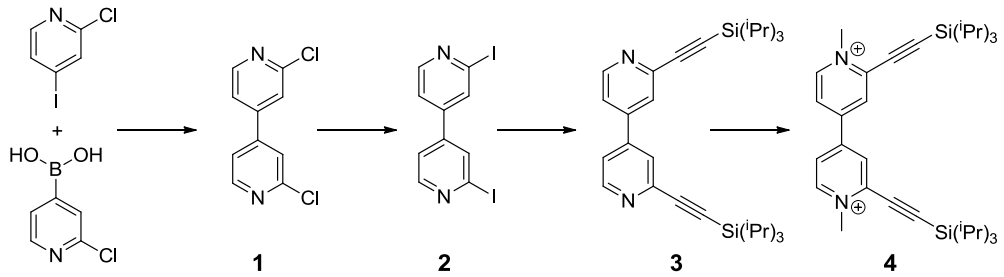
This ACS-PRF grant has allowed me to branch out from my normal research interests. The main addition to my program has been using electrochemistry as a tool in aryleneethynylene research. Undergraduate students working on this project get experience in a wet chemistry laboratory making compounds that have never before been generated or studied. In addition to the NMR, UV-vis, and fluorescence spectroscopies that students use on a fairly routine basis, they have now been introduced to cyclic voltammetry as a laboratory tool. Along with this experimental work, in order to understand the oxidation/reduction pathways of organic molecules, students have been exposed to an area of organic literature that they otherwise do not encounter in their coursework. Some students working on this project have moved onto graduate school, and others onto industry. The number one thing they have learned from this project is the resilience it sometimes takes to push a research project forward. The synthetic challenges that we have faced in this project have been non-trivial, even for a Ph.D. trained organic chemist. I am proud to state that my undergraduate students have pushed through many of these hurdles, and we can now see significant progress on the horizon.

One of the key areas of focus in this project is elaborating viologen structures with alkyne functional groups for the purpose of incorporating this structural unit into interesting supramolecular structures or devices. Viologens present interesting opportunities for molecular design as they can be reversibly reduced and oxidized into three relatively stable states. The radical cation is particularly interesting because coupling of this radical with a neighboring radical cation can be a driving force for molecular assembly.

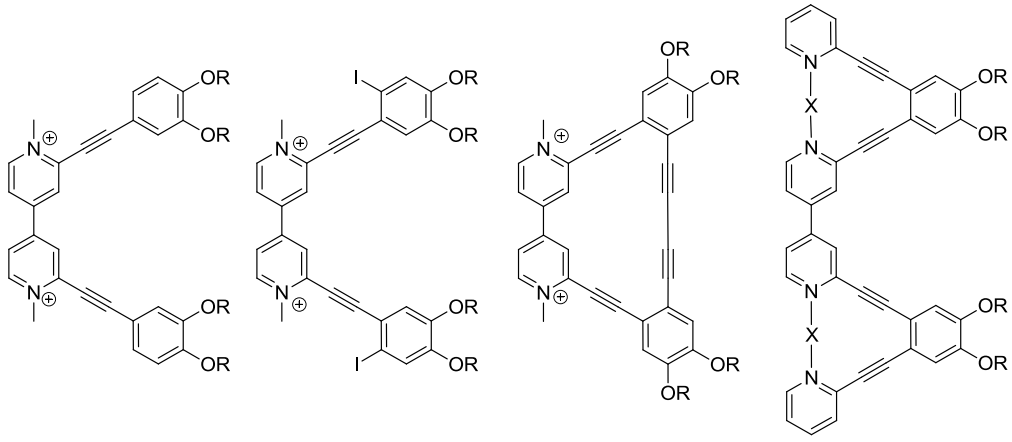


Four students over the past calendar year have been working on generating aryleneethynylene viologen compounds (e.g. **4**). So little literature exists in this area that there have been significant synthetic hurdles. Product **1**, for instance, is insoluble in almost every solvent, making conventional purification methods, such as flash chromatography, impossible. Over time, undergraduate students have developed a method for precipitating this product and selectively rinsing leftover starting materials and catalysts from the powder. Likewise, formation of product **2** should be very straightforward with conventional chemical reactions. For reasons we don't fully understand, however, almost all of these reaction conditions lead to a significant reduction of **1** to regular 4,4'-bipyridine. After many modifications, my students have found conditions that allow them to generate **2** reproducibly, with acceptable yields.



To model the compounds in which we are interested, students have been able to facilely convert compound **2** to **4** via Sonogashira coupling to TIPSacetylene, followed by methylation of **3**. Cyclic voltammetry of **4** shows the reversible double reduction/oxidation cycle that one would expect from a viologen system, which is encouraging for our attempts for further elaboration of these arylene ethynylene structures.

The first steps involved in extending our aryleneethynylene framework involved replacing the triisopropylsilyl (TIPS) groups on compound **4** with aromatic substituents. Compound **5**, for instance, can be generated easily from appropriate precursors. The importance of the solubilizing R groups on compounds such as **5** cannot be ignored. The viologen units of these compounds, with their formal charges, are quite polar, while the solubilizing groups are quite non-polar. In our hands, there are no common laboratory solvents that can dissolve **5** with dodecyloxy solubilizing groups (**5A**). We have found that branching in the solubilizing group (e.g. **5B**) can significantly increase the solubility of these viologen compounds. Students are also currently investigating triglyme solubilizing groups (e.g. **5C**) which should enhance the solubility in polar organic solvents.



5 **6** **7** **8**

A: R = $-(CH_2)_{11}CH_3$
B: R = $-CH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$
C: R = $-(CH_2CH_2O)_3CH_3$

X = Pd(II), Ag(I), or $-CH_2CH_2-$

Compound **6** represents an important synthetic intermediate in the development of more complex structures. A student has generated this compound and its non-methylated precursor and is currently exploring its solubility profile and electrochemical behavior. A different student is one synthetic step away from generating the non-methylated version of macrocycle **7**. This molecule should have interesting electrochemical behavior. The macrocyclic framework might also help with supramolecular assembly via π-π stacking interactions. Compounds such as **8** are also important for the completion of this project. In these compounds, students are focusing on the transition metal binding behavior of these 4,4'-bipyridine compounds rather than the electrochemistry of methylated derivatives. Students have learned about the solution binding behavior of **8** to Pd(II) and Ag(I) through NMR titration studies. We are waiting to publish these results until we have acceptable crystal structures of theses complexes. In addition to metal binding behavior, once the electrochemical details are known for simpler compounds, such as **5**-**7**, students will investigate the possibility of bridged viologens in compounds such as **8**.