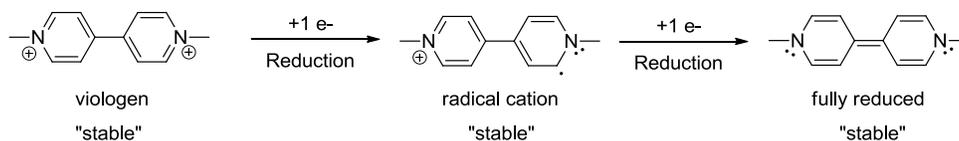


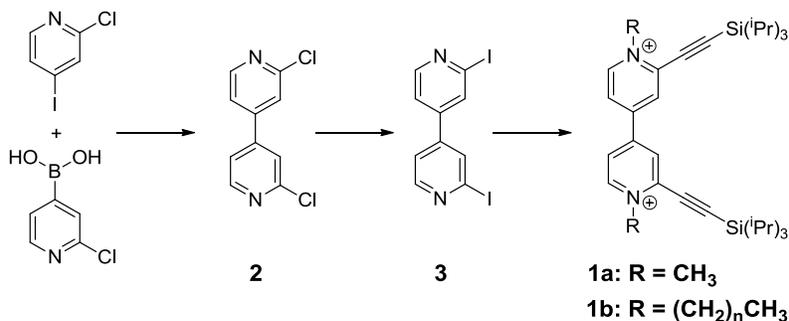
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Fundamental Studies of 4,4'-Bipyridine Aryleneethynylenes  
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To date, six undergraduate students at the University of Wisconsin-Stevens Point have synthesized and studied the properties of novel 4,4'-bipyridine aryleneethynylenes. Of the four that have graduated, three are pursuing graduate degrees in chemistry (Nevada; Minnesota; Ruhr-University Bochum, Germany) and the other is working in a genetics laboratory in a nearby community. The two continuing students, who both plan to pursue graduate degrees in biochemistry upon graduation, will work on these projects over the next calendar year. Students who have worked on these projects have gained significant experience synthesizing and purifying organic molecules. Additionally, in their efforts to characterize novel molecules, students have developed expertise with NMR spectroscopy, mass spectrometry, and cyclic voltammetry.

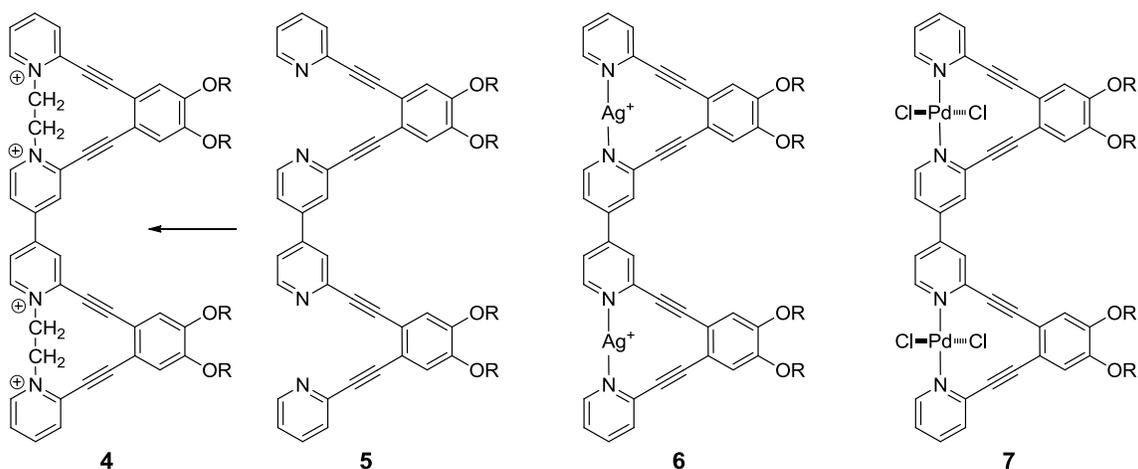
Our research group has a history of synthesizing novel aryleneethynylene structures that can be strategically manipulated via external stimuli including transition metal coordination or halogen bonding. Careful application of these strategies allows us to control the structure and therefore properties of organic molecules. The work we are performing through the ACS-PRF grant has expanded my group's work to include organic species that can be addressed via electrochemical stimuli. The centerpiece of this effort is viologen systems that can be reversibly oxidized and reduced via electrochemical means. This venture into electrochemistry, partially supported via a potentiostat purchase with internal funds, is a new direction for the Bowling group.



The electrochemistry of viologens is well known and has been a focus of study for decades. Our intent is to use the interactions of viologen subunits to control the conformations and properties of elaborate aryleneethynylene structures. However, because there is very little in the literature regarding ethynyl-substituted viologens, we had to first explore the synthesis and electrochemistry of simple model systems, such as **1a**. What we found is that the synthesis of even simple ethynyl-substituted bipyridines is non-trivial when relying on current literature precedent. After much trial and error, my students have developed a very efficient, reliable synthetic protocol for generating precursor **3** that we feel will be quite valuable in the field of viologen chemistry. Following that success, students were able to generate **1a** in two simple steps from the diiodo intermediate. This model system shows reversible two-electron oxidation/reduction via cyclic voltammetry, as expected. From this simple example, it has become apparent that solubility of the ethynyl-substituted bipyridines is going to be a challenge in the generation, purification, and characterization of more elaborate structures. We anticipate that we can mitigate this solubility challenge by using longer alkyl solubilizing groups (e.g. **1b**) rather than the small methyl groups of **1a**.



In the process of generating aryneethynyls that are electrochemically addressable, my students have generated many novel compounds that can act as transition metal ligands. For example, in their pursuit of viologen **4**, students have developed a method for generating ligand **5**. The two cavities that house the ethane linkers in **4** are perfectly sized to accommodate transition metal cations, such as in **6** or **7**. Silver (I) and palladium (II) have the correct orbital geometries for this ligand as linear and square planar arrangements are favorable for these cations, respectively. Careful titrations of metals into solutions of this ligand confirm an equivalence point at a 2:1 metal to ligand ratio, as predicted from the structure. We are currently in the process of reproducing results for these titrations for publication in the near future.



Over the next year, we will expand the scope of these transition metal complex studies in two directions. First, we will investigate the electrochemistry of metal complexes such as **6** and **7** to see what effect transition metal coordination has on the 4,4'-bipyridine unit. Our expectation is that the metal centers may be reversibly reduced and oxidized. We will attempt to establish whether the central bipyridine unit will display viologen type behavior. That is, will it provide two-electron reversible reduction/oxidation as would be expected for **4**? The second direction we will explore with these ligands is the generation of metal-organic grids. Historically, we have used transition metals with accessible valences that are 180° from each other. However, if we use metals with four open valences, such as  $\text{Pd}(\text{CH}_3\text{CN})_4(\text{BF}_4)_2$ , we should be able to generate perpendicular complexes as displayed in **A**. When this strategy is applied to ligand **5**, this should lead to molecular grids which could potentially serve as porous materials in the solid-state. Moreover, if the central bipyridine unit behaves as a viologen, these grids will be electrochemically addressable with potential communication between viologen centers within the 2x2 grids.

