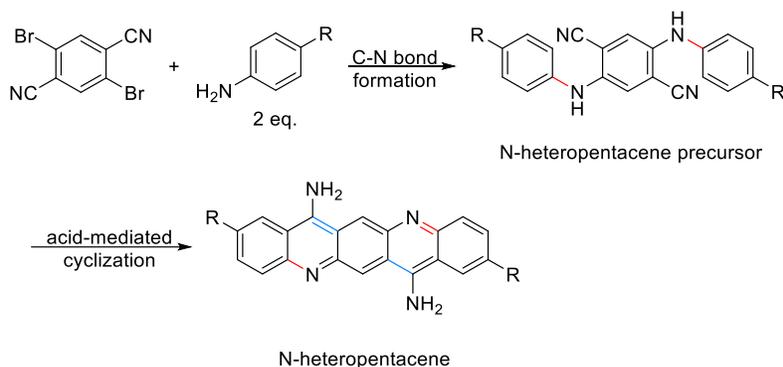


PRF# 57251-ND7 “Development of New Synthetic Routes to Aromatic Ladder Polymers”
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In year one of the ACS Petroleum Research Fund grant, we have generated results that provide proof of concept for the proposed work -- the development of an efficient synthetic route for the synthesis of novel oligo- and poly(N-heteroacene)s. N-heteroacenes are a class of molecules valued for their potential as n-type semiconductors in the next-generation of electronic devices that are flexible, low-cost, and lightweight. By nature, N-heteroacenes suffer from poor solubility and stability as well as challenging and/or inefficient synthetic routes.¹

Scheme 1. Two-step synthesis of N-heteropentacenes.



Our first result is the development of a two-step approach for the synthesis of N-heteropentacenes, Scheme 1). The first step involves forming a C-N bond (bonds in red) and the second step involves an acid-mediated cyclization (bonds in blue) to obtain a fully aromatic structure. This synthetic route is outstanding because the reaction times are short (< 2

h.) and the yields are high. Under the optimized Buchwald-Hartwig amination conditions, the precursor can be prepared in 94% yield. The acid-mediated cyclization is essentially quantitative. This sequence is extremely efficient compared to other methods for the synthesis of N-heteroacenes, particularly those involving late stage oxidation.^{2,3} Using this synthetic technique, we have been able to synthesize a series of N-heteropentacenes with various solubilizing substituents (R, Scheme 1). We currently are exploring structure-property relationships fundamental for emergent technologies based on complementary circuits with p- and n-type organic semiconductors. We are also exploring the extension of this synthetic chemistry to the preparation of longer N-heteroacenes. In addition, we have begun to explore the

synthesis and acid-mediated cyclization of precursors that contain electrophilic groups besides the nitrile group.

The N-heteropentacenes have been characterized to elucidate their structure-property relationships at the oligomeric scale before synthesizing the precursor polymers that can be cyclized to aromatic ladder polymers. From the optical and electrochemical characterization, we have learned that these N-heteroacenes follow the expected trend of a decrease in HOMO-LUMO gap with increasing acene length. For example, the optical HOMO-LUMO gap of 9-aminoacridine (three rings) and the N-heteropentacenes (five

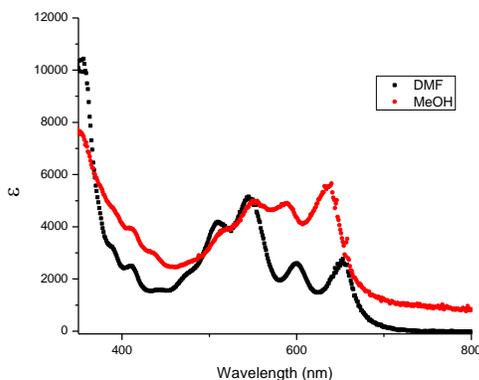


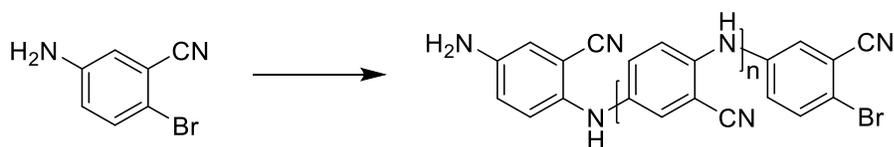
Figure 1. UV-Visible Absorption spectra of the parent N-heteropentacene (R=H)

rings) are 2.92 eV and ~1.86 eV, respectively (Figure 1). We have also added alkyl substituents that increase the solubility and stability of the N-heteroacenes which degrade via the endoperoxide pathway.⁴ Thus, there is interest in installing substituents that further lower the LUMO energy level for increased stability and investigating the effects of these substituents on molecular packing.

The precursor chemistry described above has been extended to the preparation of the polymer as shown in Scheme 2.⁵ An emerald green solid was obtained in 91 % yield. Infrared spectroscopy showed the expected NH and nitrile stretches consistent with the proposed structure. This solid is soluble in dimethyl formamide (DMF) and dimethyl acetamide (DMAc) at a concentration of 1 mg/mL, but we are unsure whether we have a true solution – a typical concern for poly(para-aniline) derivatives.⁶ As a result, we do not yet have molecular weight or polydispersity values for this material.

The work presented here is new and innovative for our group. We are learning how to make ladder polymers which is something we have not done before. We are also obtaining results that will facilitate the submission of a proposal to the National Science Foundation.

Scheme 2. Polymerization of AB-type, 5-amino-2-bromobenzonitrile to form poly(2-cyano-para-aniline).



Thus far, the ACS Petroleum Research Fund has benefited the graduate student working on the project in two ways. First, she has obtained results that

indicate the viability of the project. For example, initially, there were issues with synthesizing the precursor polymers with high molecular weights. She sought to design a model reaction to identify and to address the issue of having low molecular weights. Her solution was to use a highly selective ligand which resulted in a 97% yield in 2 h. versus a 60% yield in 24 h. for the model reaction. These complex problem-solving skills will help her throughout her project and career in an industrial position. Second, as she works on this project, she has had two undergraduates under her supervision. Having two undergraduates enables her to become a better mentor and to better understand the material. Being able to work as a team and to mentor are also qualities that are valued in any environment.

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