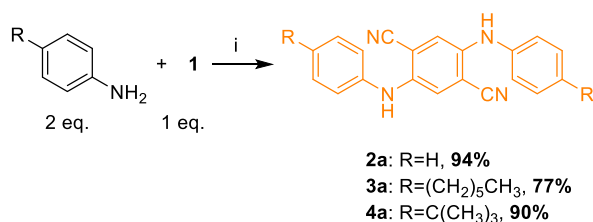


**PRF# 57251-ND7 “Development of New Synthetic Routes to Aromatic Ladder Polymers”
Christopher Gorman, PI, Department of Chemistry, North Carolina State University**

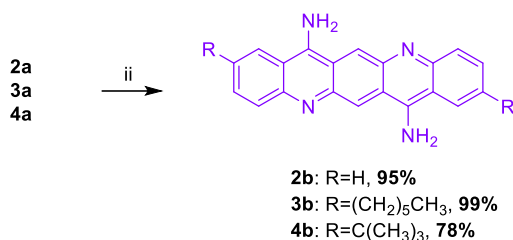
In year two of the ACS Petroleum Research Fund grant, we have generated results for the proposed work that are now published.¹ We have successfully shown an efficient synthetic route for the synthesis of novel oligo(N-heteroacene)s. N-heteroacenes are a class of molecules valued for their potential as 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.²

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

Synthesis of Precursors



Cyclization of Precursors



Our synthesis is a two-step approach for the synthesis of N-heteropentacenes, Scheme 1). The first step involves forming a C-N bond and the second step involves an acid-mediated cyclization 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.^{3,4}

We have fully characterized these molecules using mass spectrometry and ¹H and ¹³C NMR spectroscopy, ultraviolet-visible absorption spectroscopy and electrochemistry (Figure 1). We have also characterized their emission. When the neutral molecule **2b** was excited at 450 nm, negative Stokes shifts were observed. This may be due to emission from S_n→S₀ where n>1. It is also possible that excited state proton transfer, can occur. However, the emission spectrum of the fully protonated species of **2b** (vide infra) has a positive Stokes shift of 17 nm (Figure 1b), suggesting that additional photophysical complexities are eliminated in these species. Furthermore, a single exponential decay time constant of 13.6 ns was found for the fully protonated **2b**.

The diazapentacenes **2b**, **3b**, and **4b** possess four nitrogen atoms that could be protonated, and thus these molecules are expected to exhibit acidochromism upon the addition of up to four equivalents of acid. Because there are two different types of nitrogen atoms, it was hypothesized the first two equivalents of acid would protonate the pyridyl nitrogen atoms since their lone pairs are orthogonal to the π-system. Then, the addition of two more equivalents of acid should protonate the amino nitrogen atoms.

The absorption spectra for **2b** do not change significantly with the addition of the first two equivalents of TFA (Figure 2a) which is congruent with the protonation of the pyridyl

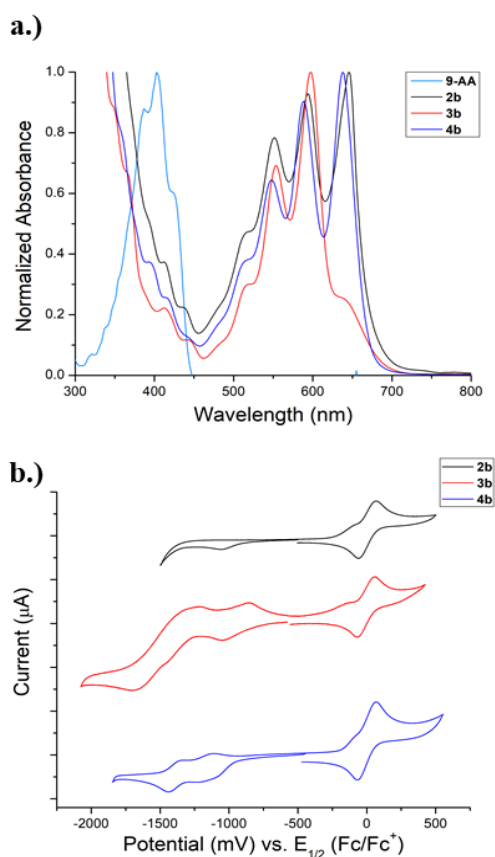


Figure 1. (a) UV-Visible absorption spectra of **9-AA**, **2b**, **3b**, and **4b** in 50:50 THF:MeOH and (b) the cyclic voltammograms of **2b**, **3b**, and **4b** in 0.1 M *n*-Bu₄PF₆ in THF at 50 mV/s.

makes them candidates for metal ion- and proton sensing applications.

The work presented here has been completed successfully, and we are now embarking on extensions of the paradigm. We have also taken these results and have used them in the submission of a proposal to the National Science Foundation.

Thus far, the ACS Petroleum Research Fund has benefited the graduate student working on the project (Rosa Garcia Castrejon) as it allowed her to complete her Ph.D. project and obtain a permanent position (at BASF). Rosa also mentored two undergraduates. These mentoring activities enabled her to gain experience in mentoring and in building a

nitrogen atoms. The addition of two more equivalents of TFA to **2b** (Figure 2b) results in hypsochromic shifts for the longest wavelength from $\lambda_{\text{max}} = \sim 640$ nm to $\lambda_{\text{max}} = \sim 600$ nm. This trend is consistent with the protonation of the amino nitrogen atoms whose lone pairs are no longer in resonance with the π -system, decreasing the number of conjugated atoms. The addition of TFA after roughly four equivalents of TFA does not change the spectrum, as expected, since there are no more sites for protonation. Molecules **3b** and **4b** exhibit the same behavior. This acidochromic behavior of the diazapentacenes

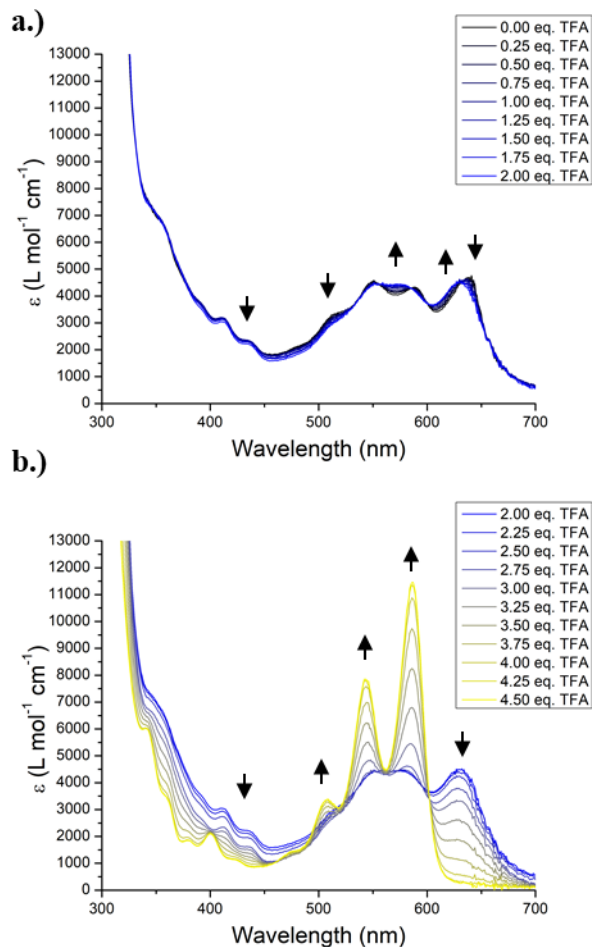


Figure 2. Acidochromism of **2b** (a) upon the addition of 0.0-2.0 equivalents of trifluoro acetic acid and (b) upon addition of 2.0-4.5 equivalents of trifluoro acetic acid in methanol.

functioning team. These qualities were clearly valued by her future employer as evidenced by their post-hiring comments.

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