

Synthesis of Naphthalene and Biphenylene Tetraimides

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Research Progress

In the reporting period, we continued work on both of the synthetic methods proposed initially for the synthesis of naphthalene and biphenylene tetraimides, namely the “all-at-once” and “stepwise” approaches (Figure 1). The polyoxidation process required to form the requisite arenepolycarboxylic acids has proven to be challenging, not because of inability to achieve reactivity, but difficulty in purification. While we see LCMS evidence for the significant formation of the desired octatetracarboxylic products, we have not been able to remove the byproducts from the mixtures. There are some contaminating underoxidized products, in addition to esterification by the tert-butanol solvent used for oxidation. Currently, we are exploring a suite of other solvent systems that avoid esterification and also facilitate the otherwise tedious workup.

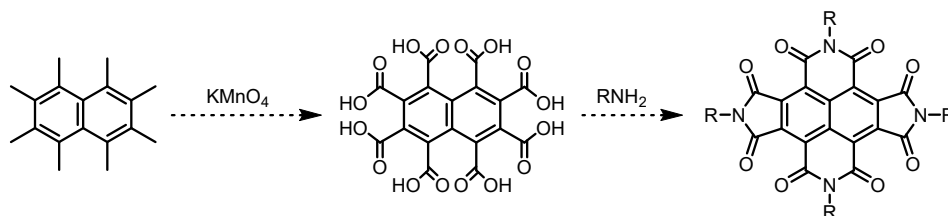


Figure 1. Remaining synthetic steps for the “all-at-once” approach of synthesizing naphthalene tetraimide.

While evaluating our efforts toward biphenylene tetraimide, we considered the possibility of instead synthesizing a benzene *ortho*-diimide (**Br₂-MDI**) prior to performing [2+2] cycloaddition to construct the biphenylene backbone. This benzene diimide is known as mellophanic diimide (MDI), and it is the angled structural isomer of the industrially relevant linear pyromellitic diimide. We learned in the course of this work that 1,2,3,4-tetramethylbenzene, the starting material for our synthesis of mellophanic diimide, has no major industrial utility despite being a significant fraction of the C₄ benzene petroleum extracts and a byproduct of durenne synthesis. Therefore, we became interested in pursuing the synthesis of mellophanic diimide and its derivatives, with the eventual aim of obtaining the biphenylene tetraimide targeted initially in this proposal. A summary of this work, which was recently published (*J. Org. Chem.* **2019**, *84*, 10362), follows below.

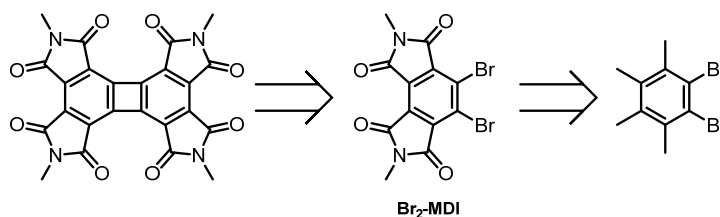


Figure 2. Retrosynthetic disconnection for biphenylene tetraimide through a [2+2] cycloaddition of a dibrominated mellophanic diimide **Br₂-MDI**.

Prior to our work, there have been only scattered reports describing the MDI scaffold. The literature focuses on its incorporation into polyimides either in concert with or in contrast to pyromellitic diimide. We discovered instead that solid-state dehydration of ammonium carboxylate salts could afford the novel chlorinated MDIs in up to 50% yield, an outcome that was achieved in a five-gram-scale synthesis of **Cl₂-MDI-Hex**. When exploring the reactivity of **Cl₂-MDI-Hex** with various nucleophiles, we serendipitously observed an unexpected annulation reaction between 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and **Cl₂-MDI-Hex** to form **DBU-MDI** (Figure 3). Based on this finding, we decided to instead investigate bidentate nucleophiles.

1,2-Disubstituted benzenes reacted efficiently with **Cl₂-MDI-Hex** to produce a series of fine-tuned donor-acceptor chromophores (Figure 3). We then assessed reactivity of **Cl₂-MDI-Hex** with tetradentate nucleophiles and were rewarded by the isolation of heteropentacene tetraimides **NONO** and **NSSN** (Figure 3), which can be regarded as the longer acene analogs of the naphthalene and biphenylene tetraimides proposed initially for this work. It was facile to oxidize dihydro compounds **NN** and **NSSN** with **MnO₂** to their azaacene forms **oxNN** and **oxNSSN**, respectively. In

the case of **oxNSSN**, the bandgap was narrowed significantly so its absorption takes place at the edge of the visible region. Its extinction coefficient is nearly $10^5 \text{ M}^{-1} \text{ cm}^{-1}$, a feature that can be attributed to its incorporation of S atoms and quinoidal conjugation pattern.

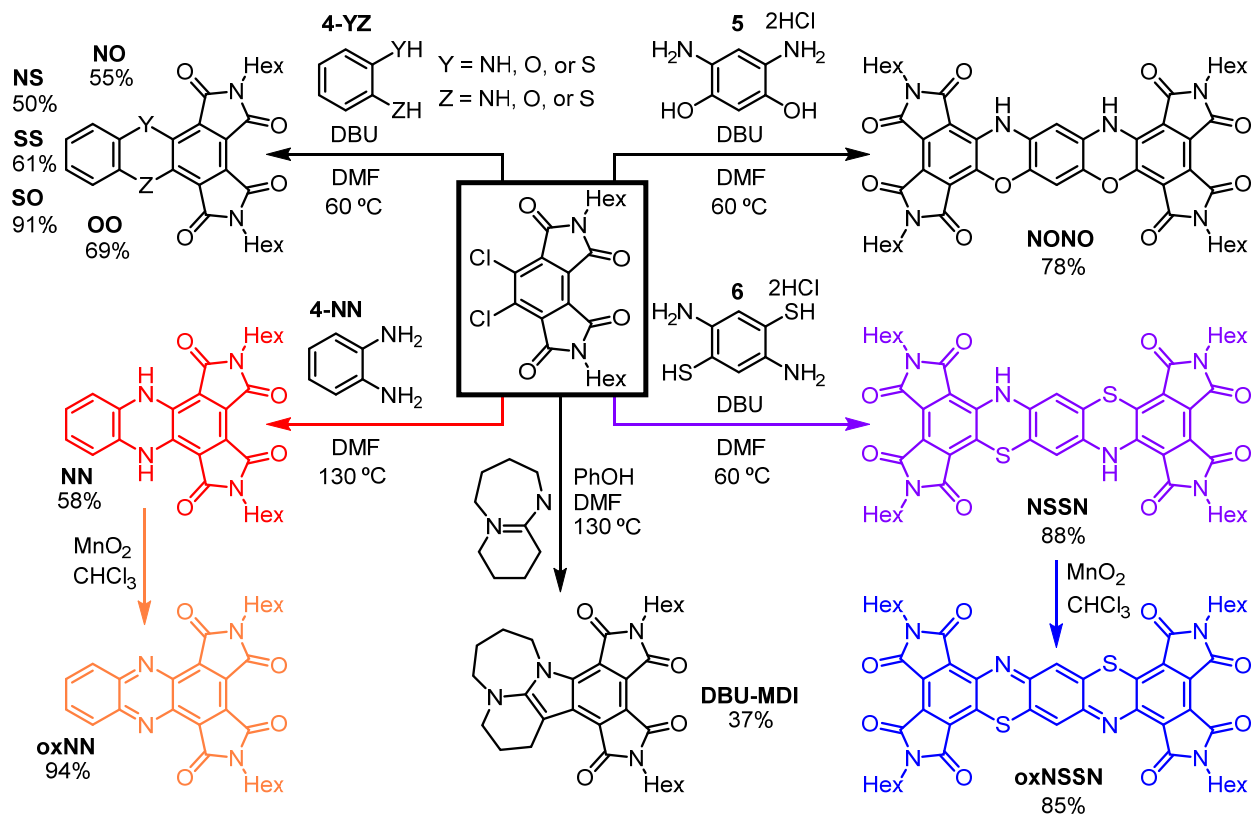


Figure 3. Derivatization of **Cl₂-MDI-Hex** with bi- and tetradentate nucleophiles.

Impact on My Career and on Students

This funding from PRF has been instrumental to my career. During this reporting period, two publications, one of which was discussed here, arose directly from observations made while pursuing the synthesis of the naphthalene and biphenylene tetraimides. These PRF-funded findings and publications served as the foundational preliminary evidence used in a successful grant application to the Research Corporation for Science Advancement Cottrell Scholars Award. Additionally, based on the mellophanic diimide chemistry detailed above, I recently submitted a National Science Foundation proposal that seeks to employ the mellophanic diimide motif as an electron withdrawing motif for the end-capping stabilization of aromatic compounds with unusual electronic structures.

The Macalester undergraduate students who contributed to this research work have all benefited greatly from PRF support of their projects. For example, Min Ji Kim '19 has matriculated into graduate school at University of Wisconsin, Madison. Kellie Stellmach '20 was awarded an ACS Division of Organic Chemistry Summer Undergraduate Fellowship to work on the development of mellophanic diimide synthesis.