Synthesis of a Novel Molecule for Supramolecular Polymerization

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Introduction

A fundamental goal of supramolecular chemistry is the creation of nanoscale structures through the control of intermolecular forces that have many applications in the pharmaceutical, chemical, and electronics industries. An amphiphilic monomer, which forms metastable nanotubes, was a template for the growth of silver iodide nanowires as reported by a different group (Figure 1).[1] This monomer consisted of a core composed of a cyanine dye, a sulfonate region providing polarity, and an alkane region of eight carbons. The structures (Figure 2) formed from this monomer were only stable for a limited range of pH, ionic strength, and organic solvent concentration. This work aims to synthesize a comparable monomer by replacing the alkane region with a terminal diacetylene tail (Figure 3). It has been demonstrated that assembled diacetylene monomers can polymerize in the presence of UV light,[2] and ideally this modified monomer with the capability to form nanotubes can also be polymerized to create a more rigid structure.

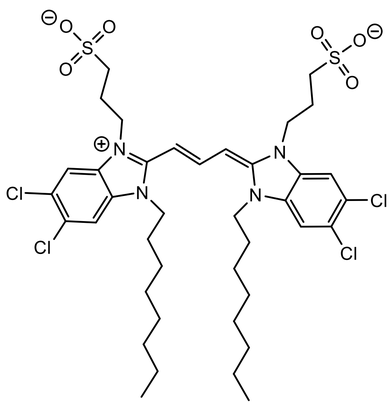


Figure 1. Previous groups' monomer.

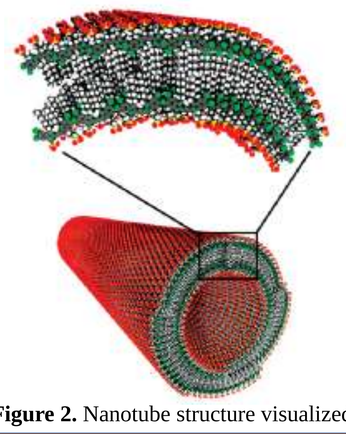


Figure 2. Nanotube structure visualized.[3]

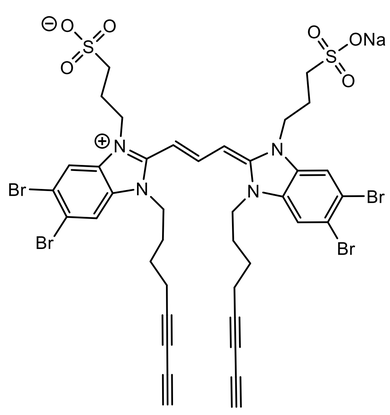
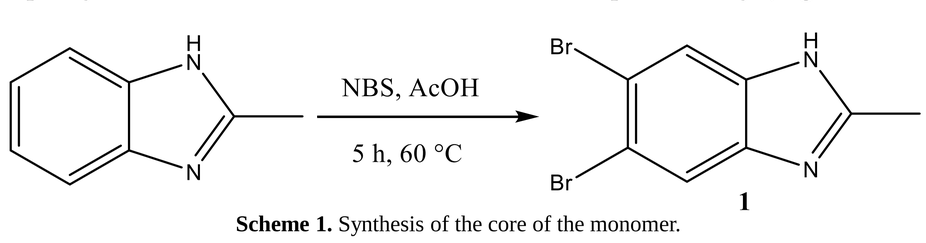


Figure 3. Proposed monomer.

Completed Synthetic Procedure

The synthesis of the monomer has been divided into 6 steps and closely follows that conducted by a previous group.[4] Three of these steps have thus far been completed. The first step involves the synthesis of 5,6-dibromo,2-methylbenzimidazole (**1**) which acts as the core of the monomer (Scheme 1). Thus far, 12 g has been synthesized which represents a 28% yield (Figure 4). Identity and purity were confirmed with ^{1}H NMR and mass spectrometry (Figures 5 & 6).[4]



Scheme 1. Synthesis of the core of the monomer.

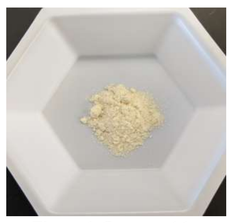


Figure 4. Compound **1**.

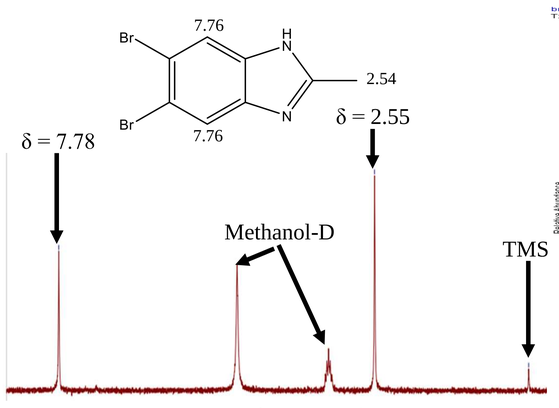


Figure 5. ^{1}H NMR of **1.**

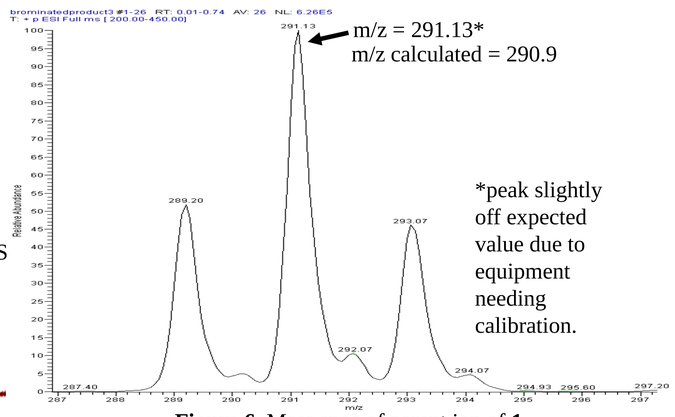
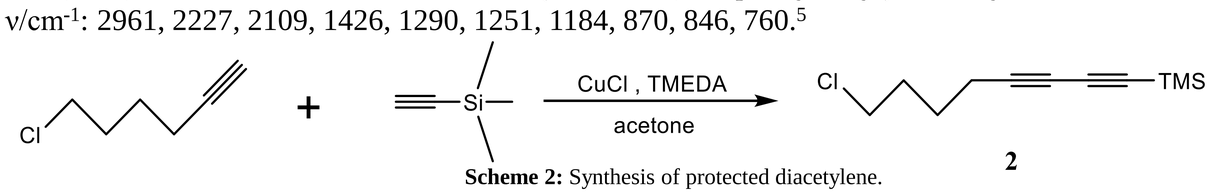


Figure 6. Mass spec of parent ion of **1.**

The second step involves the synthesis of a precursor (8-chloroocta-1,3-diyn-1-yl)trimethylsilane (**2**) (Figure 7) which will form the polymerized backbone of the supramolecular structure (Scheme 2). The identity of **2** was confirmed via ^{1}H NMR (Figure 8) and IR, and 1.0 g was successfully synthesized representing an 18% yield. Experimental IR of **2**: IR ν/cm^{-1}: 2958, 2225, 2107, 1250, 1182, 759, 651. Similar structure IR data of (7-chloro-1,3-heptadiyn-1-yl)-trimethylsilane: IR ν/cm^{-1}: 2961, 2227, 2109, 1426, 1290, 1251, 1184, 870, 846, 760.[5]



Scheme 2: Synthesis of protected diacetylene.

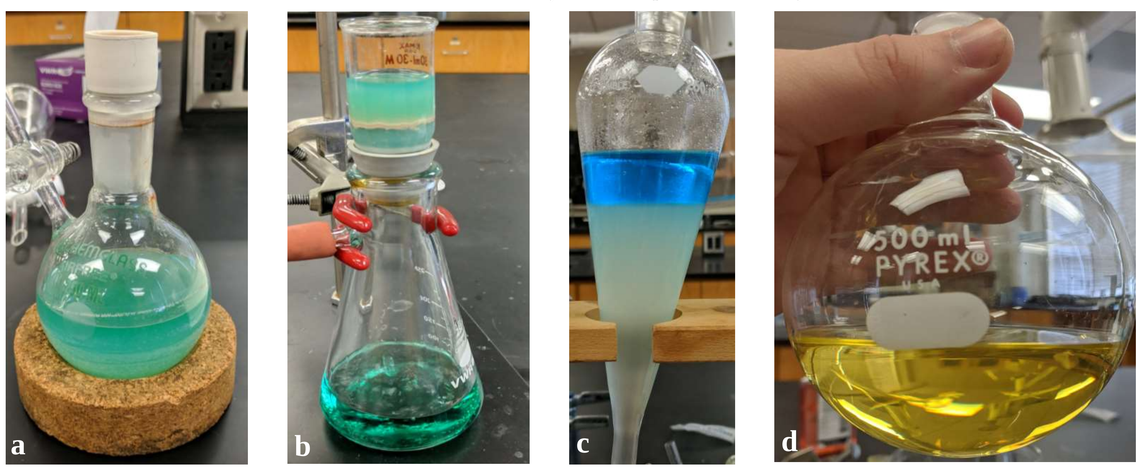
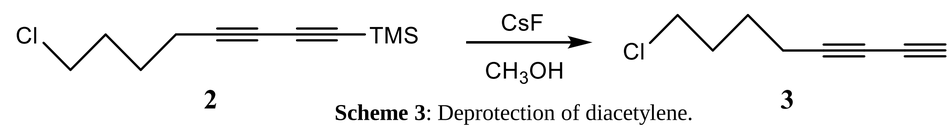


Figure 7. Workup of **2** involving the filtration of the crude mixture (a) through a silica pad (b), followed by extraction and washings (c) and the collection of combined organic layers (d).

The third step involves the synthesis of the final diacetylene (**3**) via removal of the TMS from the terminal alkyne (Scheme 3). The identity of **3** was confirmed via ^{1}H NMR (Figure 9), and 0.40 g was successfully synthesized representing a 58% yield.



Scheme 3: Deprotection of diacetylene.

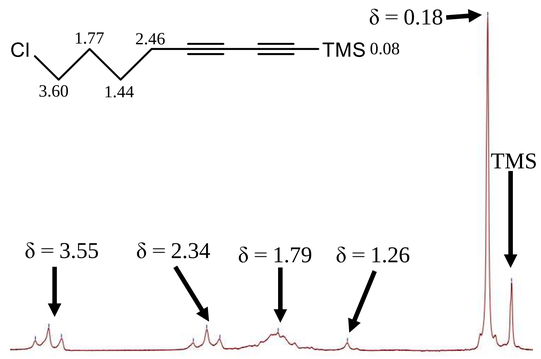


Figure 8: ^{1}H NMR of protected **2**.

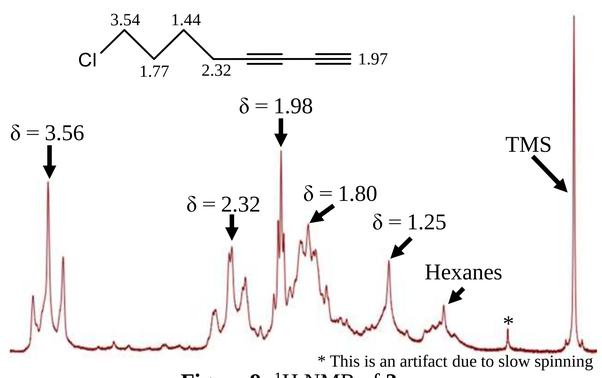
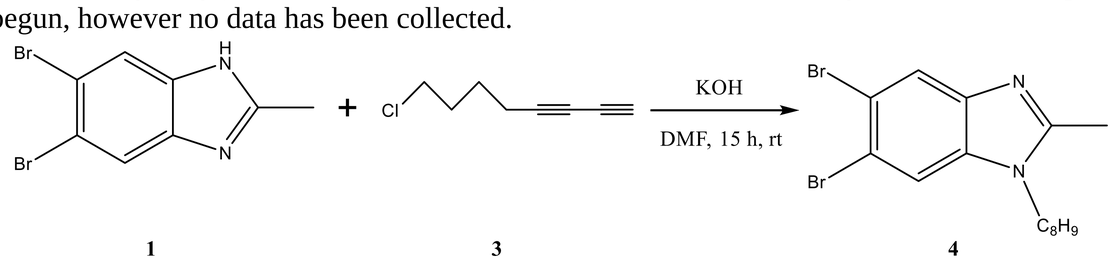


Figure 9: ^{1}H NMR of **3**.

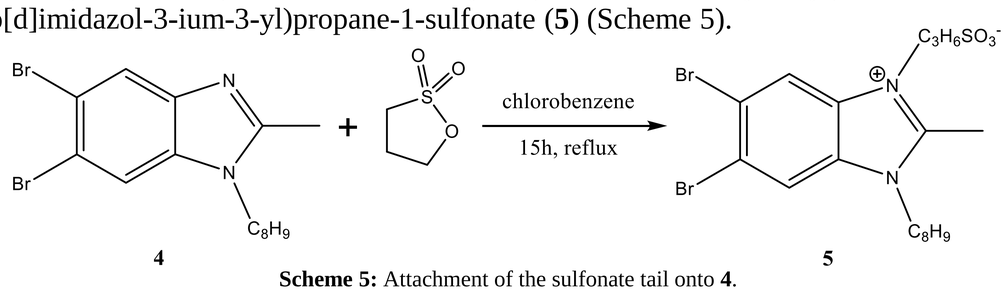
Future Synthetic Plans

The fourth synthetic step involves attaching **3** onto **1** to synthesize 5,6-dibromo-2-methyl-1-(octa-1,3,5,7-tetrayn-1-yl)-1H-benzo[d]imidazole (**4**) (Scheme 4). Preliminary trials for this step have begun, however no data has been collected.



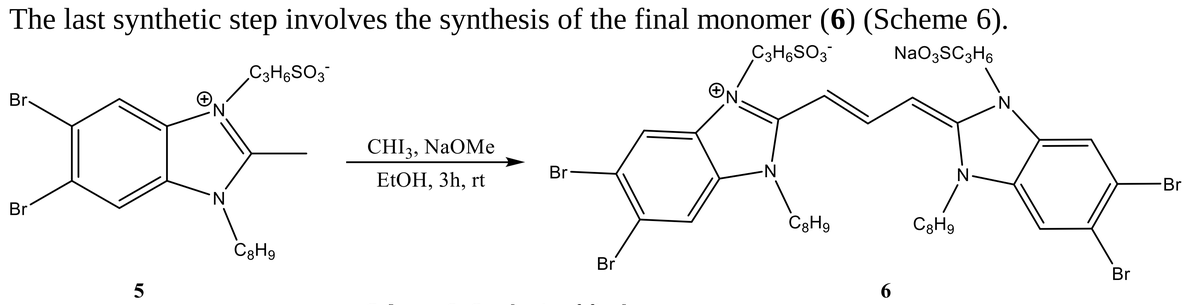
Scheme 4: Attachment of **3** onto **1**.

The fifth synthetic step involves the attaching of the sulfonate tail onto 4 using 1,3-propane sultone to synthesize 3-(5,6-dibromo-2-methyl-1-(octa-1,3,5,7-tetrayn-1-yl)-1H-benzo[d]imidazol-3-ium-3-yl)propane-1-sulfonate (**5**) (Scheme 5).



Scheme 5: Attachment of the sulfonate tail onto **4**.

The last synthetic step involves the synthesis of the final monomer (**6**) (Scheme 6).



Scheme 6: Synthesis of final monomer.

Discussion and Conclusions

The end goal of the overall synthesis is to synthesize at least 100 mg of **6**, which was determined to be the minimal amount needed for full characterization. Given the current amount of **1** & **3** successfully synthesized thus far, as well as the projected yields of **4**-**6**, this goal should be achievable. The strategy of conducting trial syntheses utilizing smaller amount of reactants to work out any issues before moving to a larger scale reaction has proven to be effective. In future work, the utilization of the detailed experimental knowledge and techniques gained from completed work should make later synthetic steps in this project or for other modified monomers easier.

References

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