

Continued Synthesis of a fullerene-bipyridine ligand for photoelectric applications

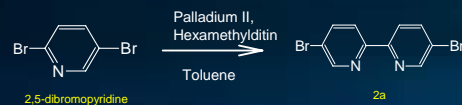


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Objective: The primary objective of our research is to synthesize supramolecular systems that move electrons efficiently when excited by a photon of light. One such system is in development: two fullerene "handles" connected through a conjugated bipyridine "bridge." Fullerenes (C₆₀) have large cross areas which enable them to absorb photons of light. Fullerenes also have extensive conjugated pi systems, allowing them to be "dumping grounds" for excess electrons. Our supramolecular system (molecule **2**), when coordinated with a transition metal, has great potential for photon induced charge transfer applications. The fullerenes accept a photon of light, exciting electrons to a higher energy state, and transfers those electrons to the coordinated metal which conducts the charge out of the system, or vice-versa. Practical uses for our system include solar cells, molecular devices, computer applications, or other areas where molecules need to interact with light.

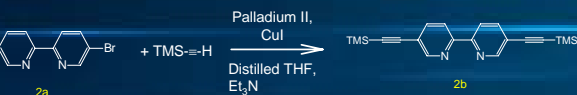
Bipyridine Ligand Synthesis

Step 1: Synthesis of 5,5'-dibromo-2,2'-bipyridine (**2a**)



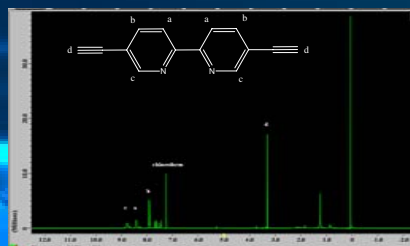
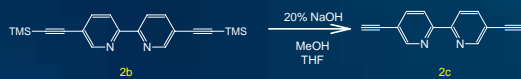
Step 2: Synthesis of 5,5'-trimethylsilylethynyl-2,2'-bipyridine (**2b**)

This is known as a Sonogashira coupling. The coupling of TMS with the bipyridine molecule, protects the molecule and allows for the newly synthesized bipyridine ligand to be safely stored.



Step 3: Synthesis of 5,5'-diethynyl-2,2'-bipyridine (**2c**)

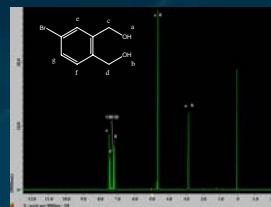
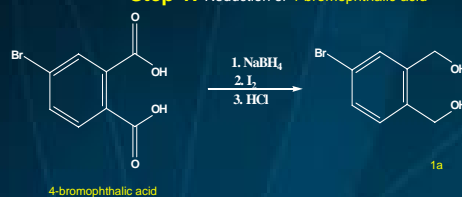
This reaction removed the TMS protecting group from compound **2b**. The resulting bipyridine ligand, **2c**, will degrade after a period of time. For this reason, the TMS groups are necessary until **2c** is ready to be coupled with the fullerene end pieces.



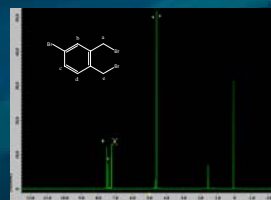
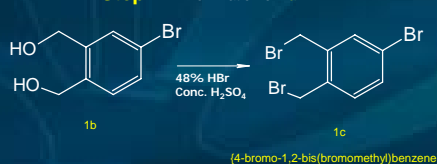
¹H NMR of 5,5'-diethynyl-2,2'-bipyridine, CDCl₃

Fullerene Building Block Synthesis

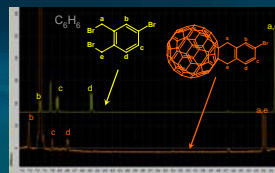
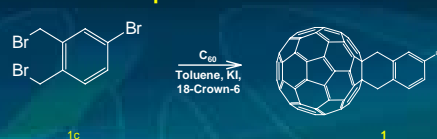
Step 1: Reduction of 4-bromophthalic acid



Step 2: Bromination of **1a**

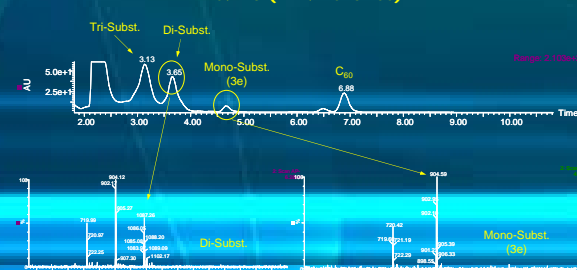


Step 3: Diels-Alder onto fullerene

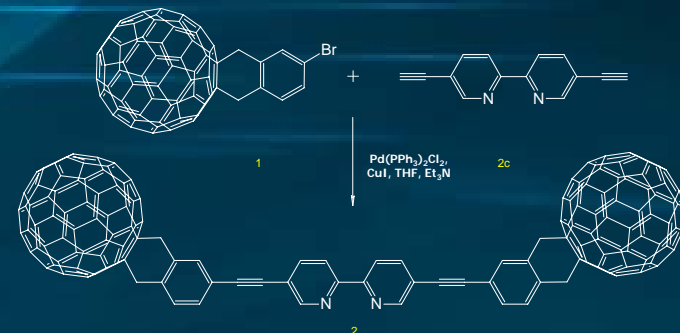


Step 3 is particularly temperamental, as discovered over the summer. Several failed attempts have led to an extensive evaluation of the starting materials and the procedure. However, upon analysis of these facets, thoughts are that these syntheses were successful, though NMR evidence has been elusive. Nevertheless, our reaction has been proven to be successful as shown by NMR spectroscopy and Liquid Chromatography/Mass Spectroscopy data.

HPLC/MS (IPA/Hexanes)

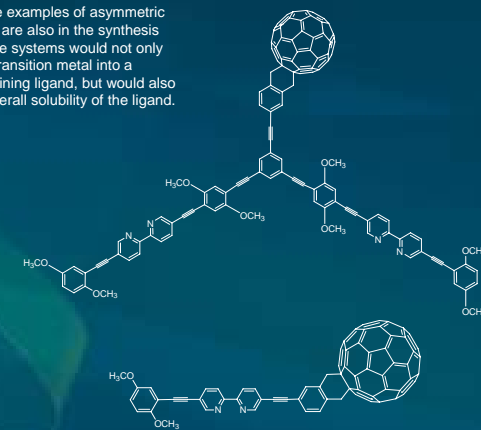


Next Steps: Although the syntheses of **1** and **2c** were successful, the steps need to be repeated and refined to obtain pure compounds. Once pure building blocks are available, the synthesis of the target molecule, **2**, can be attempted. The next phase of the project would be to coordinate **2** with a transition metal and investigate the supramolecular system's photochemical properties. This next phase is fast approaching and could conceivably be achieved within the next year, making this an exciting time to be involved with the Walters Research Group.



Side Chains

To the right are examples of asymmetric molecules that are also in the synthesis process. These systems would not only incorporate a transition metal into a fullerene containing ligand, but would also improve the overall solubility of the ligand.



Acknowledgements

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References

1. Belle, P.; Giget, A.; Kraus, M.W.; Walter, M.; Mullen, K. *J. Org. Chem.* **1995**, *60*, 3307-3310.
2. Bruce, J.; Chambron, J.P.; Kalle, P.; Sauvage, J.P. *J. Chem. Soc., Perkin Trans 1*. **2002**, 1226-1231.
3. Ley, K.D. *Photophysics of Pi-conjugated polymers and oligomers that incorporate metal to ligand charge transfer chromophores*. University of Florida, 2000.
4. Tak, M.; Sugita, S.; Nakamura, Y.; Kasashima, E.; Yashima, E.; Okamoto, Y.; Nishimura, J. *J. Am. Chem. Soc.* **1997**, *119*, 926-932.
5. Sheng-Gao Liu. The dumbbell bis Diels-Alder adduct between tetramethyldiene[4]tetrathialvalene and two C₆₀. *Tet. Lett.* **2001**, 3717-3720.