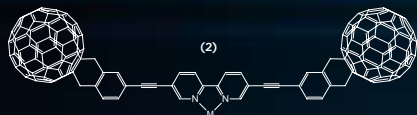


Continued Synthesis of a fullerene-bipyridine ligand for photoelectric applications

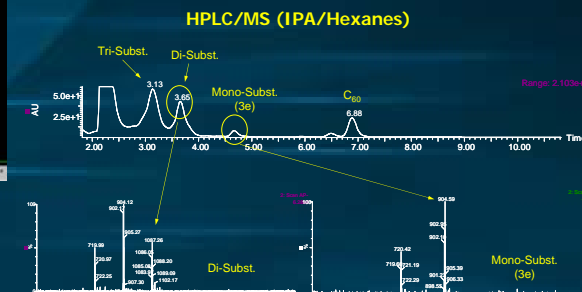
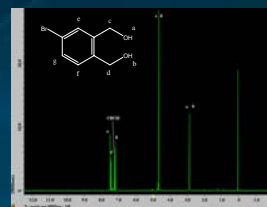
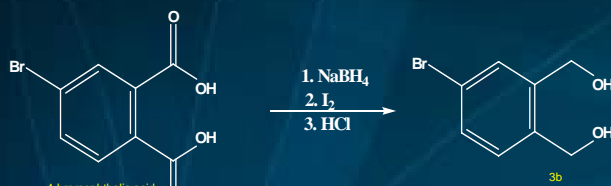


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Fullerene Building Block Synthesis

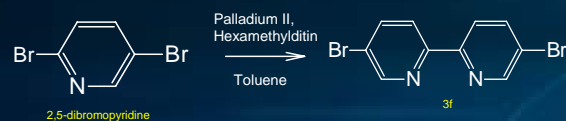
Step 1: Reduction of 4-bromophthalic acid



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.

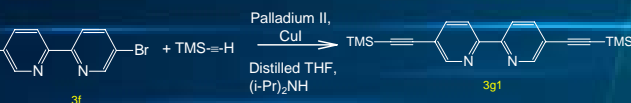
Bipyridine Ligand Synthesis

Step 1: Synthesis of 5,5'-dibromo-2,2'-bipyridine (3f)



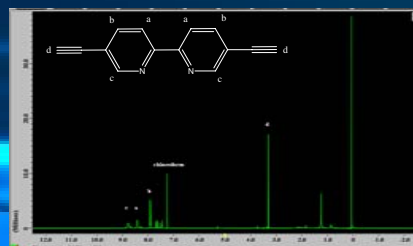
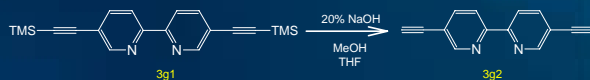
Step 2: Synthesis of 5,5'-trimethylsilylethynyl-2,2'-bipyridine (3g1)

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.



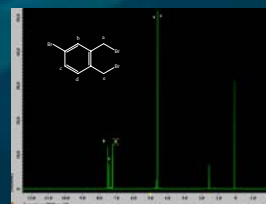
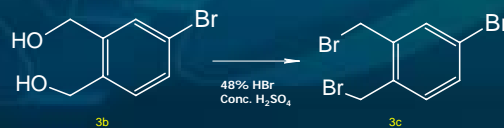
Step 3: Synthesis of 5,5'-diethynyl-2,2'-bipyridine (3g2)

This reaction removed the TMS protecting group from compound 3g1. The resulting bipyridine ligand, 3g2, will degrade after a period of time. For this reason, the TMS groups are necessary until 3g2 is ready to be coupled with the fullerene end pieces.

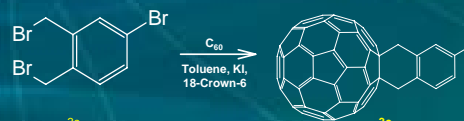


¹H NMR of 5,5'-diethynyl-2,2'-bipyridine, CDCl₃

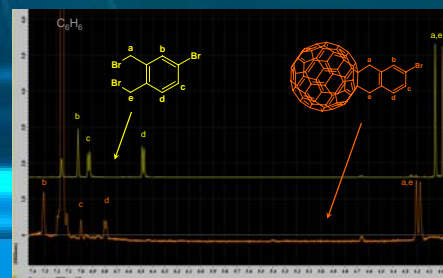
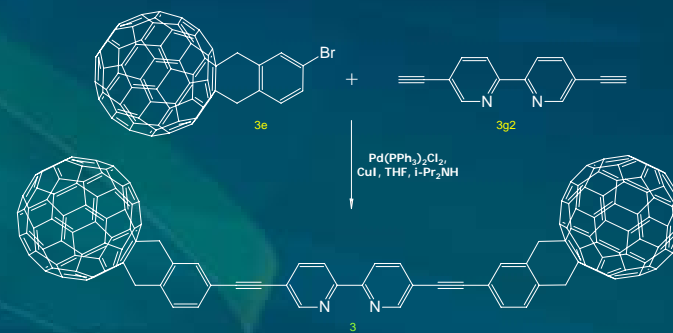
Step 2: Bromination of 3b



Step 3: Diels-Alder onto fullerene



Step 3 is particularly temperamental, as discovered over the summer. Of the ten attempts to synthesize 3e during the summer, only the first was successful. These failures prompted an analysis of the reagents used in the reaction. This process has led to a fresh synthesis of 3c, as the previous amount could have degraded. Nevertheless, our reaction has been proved successful via characterization. New attempts to synthesize 3e are currently underway.



¹H NMR of the "fullerene handle," benzene-d₆

Next Steps: Although the syntheses of 3g2 and 3e 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, 3, can be attempted. The next phase of the project would be to coordinate 3 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.

References

1. Belic, P.; Gügel, A.; Kraus, M.W.; Walter, M.; Müllen, K. *J. Org. Chem.* **1995**, *60*, 3307-3310.
2. Bruce, J.; Chambron, J.P.; Kolle, 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. Taki, M.; Sugita, S.; Nakamura, Y.; Kasashima, E.; Yashima, E.; Okamoto, Y.; Nishimura, J. *J. Am. Chem. Soc.* **1997**, *119*, 926-932.

Acknowledgements

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