THE MOLECULAR WIRE CONCEPT CONTINUED

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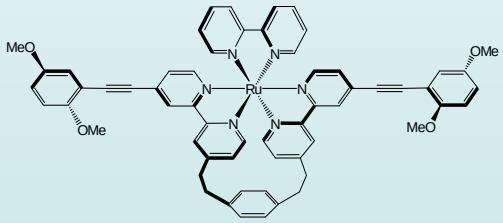
Introduction:

The goal of our supramolecular research is to create a molecular wire subunit which will transfer electrons over a highly conjugated organic polymer. This unit will wrap around a metal center thus bringing the metal directly in line with the conjugated polymer backbone creating a macromolecule, a polymer incorporating metals for the purpose of transferring energy. This project first requires the synthesis of a series of ligands followed by the synthesis of the final molecular wire subunit.

Originally, organic polymers did not successfully incorporate metals due to their linear qualities. The advantage of our structure is that interaction of the metal with the surrounding ligands is forced through coordination. Once achieved, the electron flow will be greatly increased and optimized.

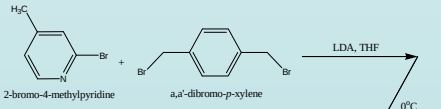
Steps:

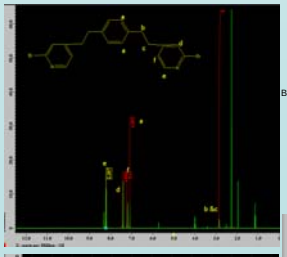
-Construct ligands through synthesis
-Form the multimetallic system by incorporating a transition metal into the backbone of the ligand
-Utilize the supramolecule in solar cell development, in molecular devices and in computer technology



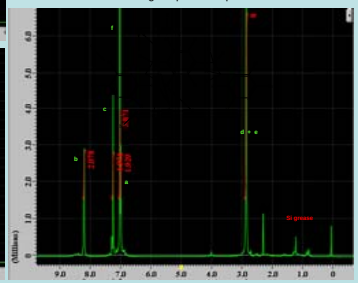
Step 1: Ligand Precursor

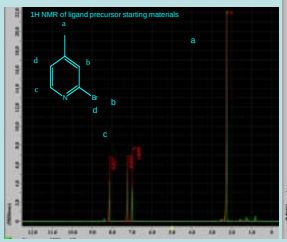
The reaction to synthesize the ligand precursor, is very sensitive to the LDA which is made from n-BuLi. A significant amount of the time spent on this reaction was finding satisfactory proportions and using fresh n-BuLi. The reaction is also very sensitive to temperature and the atmosphere.



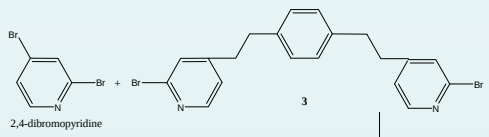


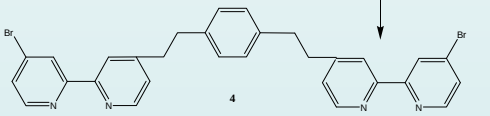
1H NMR of ligand precursor product.



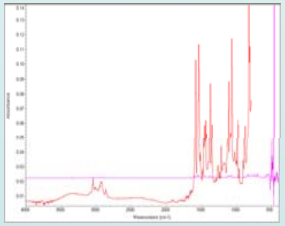


Step 2: Bipyridine Ligand

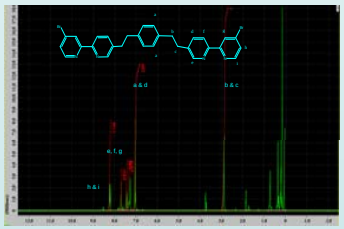




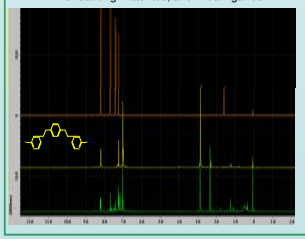
ATR-FTIR spectrum of bipyridine ligand.



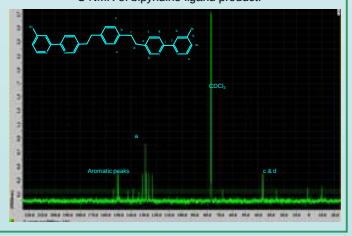
^{1}H NMR of bipyridine ligand product.



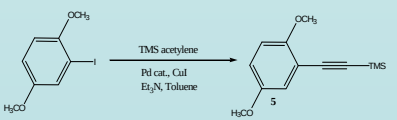
^{1}H NMR of starting materials, and initial ligands.



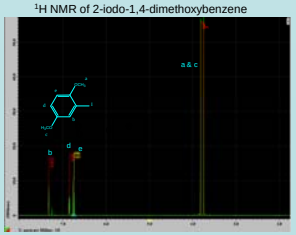
^{13}C NMR of bipyridine ligand product.

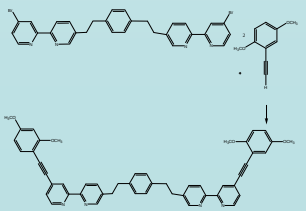


Step 3: End-caps

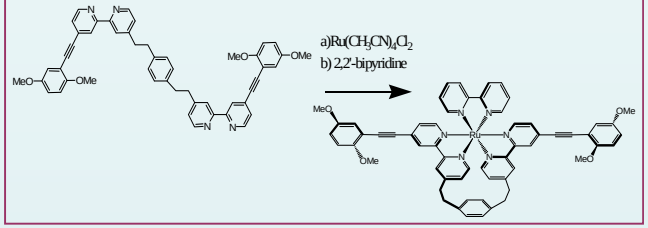


^{1}H NMR of 2-iodo-1,4-dimethoxybenzene

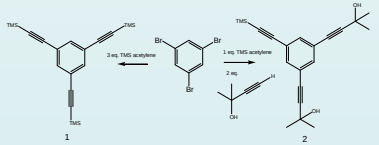




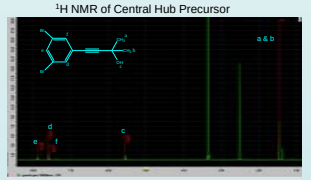
Step 4: Bringing It All Together

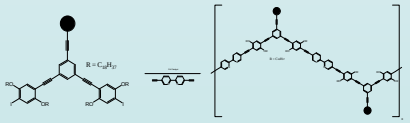


Other Projects:



^{1}H NMR of Central Hub Precursor





Future Work:

-Refine the synthesis and purification of the ligand precursor and bipyridine ligand products
-Couple the bipyridine ligand to the “end-caps”
-Wrap the final ligand around the metal to create the supramolecular system for solar cell development
-Continue combination chemistry on other systems in order to create various supramolecules with photochemical applications using hub molecules synthesized by other members of the Walters Research Group at Northern Kentucky University and the hub molecules which have been synthesized, shown below.

References:

1. Lay, K. D.; Schanze, K. S., Photophysics of metal-organic p-conjugated polymers. *Coordination Chemistry Reviews* **1998**, 171, 287-307.
2. Walters, K. A.; Ley, K. D.; Cavalheiro, C. S. P.; Miller, S. E.; Gosztola, D.; Wasielewski, M. R.; Bussandri, A. P.; van Willigen, H.; Schanze, K. S., Photophysics of p-Conjugated Metal-Organic Oligomers: Arylenethynylenes that Contain the (bpy)Pt(C≡C)2C Chromophore. *Journal of the American Chemical Society* **2001**, 123, (34), 8329-8342.
3. Wang, Y.; Liu, S.; Pinto, M. R.; Dattelbaum, D. M.; Schoonover, J. R.; Schanze, K. S., Excited-State Structure and Delocalization in Ruthenium(II)-Bipyridine Complexes That Contain Phenyleneethynylene Substituents. *Journal of Physical Chemistry A* **2001**, 105, (48), 11118-11127.
4. Kingsborough, R. P.; Swager, T. M., Transition metals in polymeric p-conjugated organic frameworks. *Progress in Inorganic Chemistry* **1999**, 48, 123-231.
5. Pomestano, D.; Nato, V.; Chambron, J.-C.; Sauvage, J.-P., Octahedral Fe(II) and Ru(II) Complexes Based on a New Bis 1,10-Phenanthroline Ligand That Imposes a Well Defined Axis. *Journal of the American Chemical Society* **2001**, 123, (49), 12215-12221.
6. Brocs, J. I.; Chambron, J.-C.; Koelle, P.; Sauvage, J.-P., Synthesis of a linear bis-porphyrin with a Ru(phen)(2+)-complexed 2,2'-bipyridine spacer. *Journal of the Chemical Society, Perkin Transactions 1* **2002**, (10), 1226-1231.
7. Li, Y. Synthesis and Photophysics of Mono-Dispense Phenylene Ethynylene Oligomers. University of Florida, Gainsville, 2001.
8. Smith, A. P.; Lamba, J. J. S.; Fraser, C. L., Efficient synthesis of halomethyl-2,2'-bipyridines: 4,4'-bis(chloromethyl)-2,2'-bipyridine. *Organic Syntheses* **2002**, 10, 107.
9. Smith, A. P.; Lamba, J. J. S.; Fraser, C. L., Efficient synthesis of halomethyl-2,2'-bipyridines: 4,4'-bis(chloromethyl)-2,2'-bipyridine. *Organic Syntheses* **2002**, 78, 82.
10. Kende, A. S.; Fludzinski, P., The stork-danheiser kinetic alkylation procdure: 3-ethoxy-5-methyl-2-cyclohexen-1-one. *Organic Syntheses* **2002**, 7, 208.
11. Kende, A. S.; Fludzinski, P., The stork-danheiser kinetic alkylation procedure: 3-ethoxy-6-methyl-2-cyclohexen-1-one. *Organic Syntheses* **2002**, 64, 68.
12. Myers, A. G.; Gleason, J. L., Asymmetric synthesis of a-amino acids by the alkylation of pseudoephedrine glycinamide: l-allylglycine and n-boc-l-allylglycine. *Organic Syntheses* **2002**, 10, 12.
13. Myers, A. G.; Gleason, J. L., Asymmetric synthesis of a-amino acids by the alkylation of pseudoephedrine glycinamide: l-allylglycine and n-boc-l-allylglycine. *Organic Syntheses* **2002**, 78, 57.
14. Synthesis and chemical properties of polyacetylenic derivatives of benzo- and dibenzo- crown ethers, Russian journal article.

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