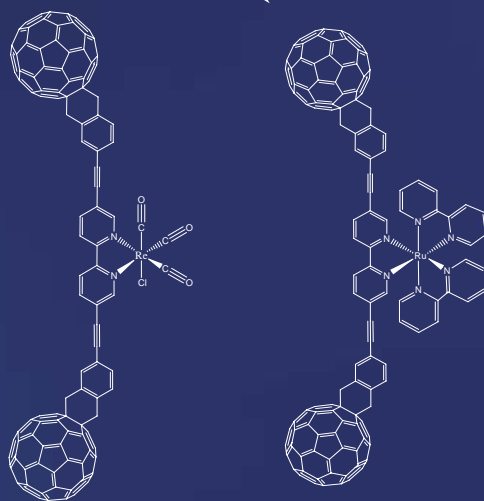
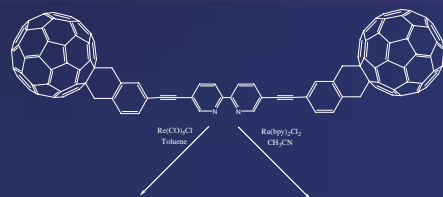


Synthesis of a novel fullerene-bipyridine ligand for photoelectric applications

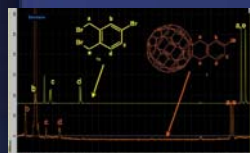
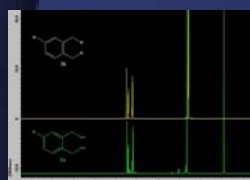
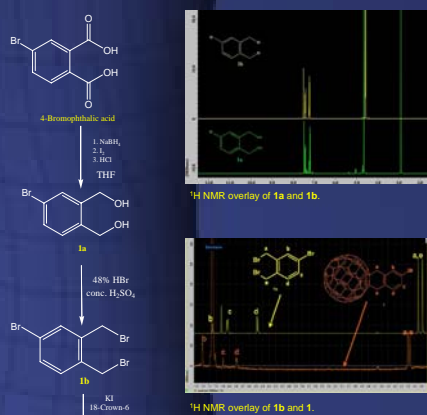
Joel DeYe Faculty Mentor: Keith A. Walters
Department of Chemistry, Northern Kentucky University, Highland Heights, KY 41099



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 transfer 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.

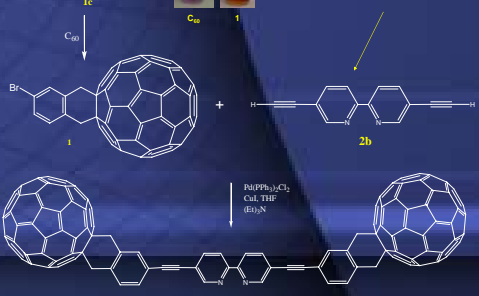


Fullerene "Handle" Synthesis

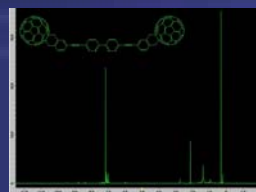
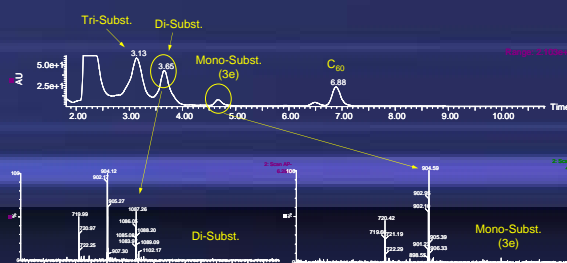


Bipyridine "Bridge" Synthesis

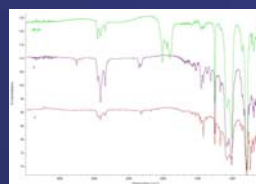
See neighboring poster by Celeste Morris & Sean Goins



HPLC/MS (IPA/Hexanes) of 1



¹H NMR of ligand 2.

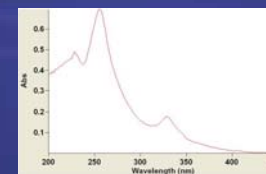


ATR-FTIR overlay of "handle" 1, ligand 2, and the 2M-Re complex.

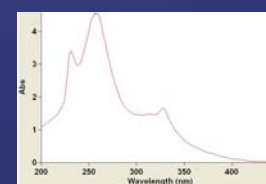
As shown in the IR overlay above, the telltale stretches associated with the fullerene are consistent throughout supporting successful syntheses. Also, the carbonyl stretches from the rhenium complex are quite evident, further indicating success.

The Ultraviolet-visible spectra at right show the expected emission(s) for fullerene.¹⁰ However, the rhenium complex shows additional emission which could be evidence of some kind of "communication" between the fullerene and the metal.⁹ This is very exciting as the main goal of this project is to construct a system that allows for such interaction between fullerenes and transition metals.

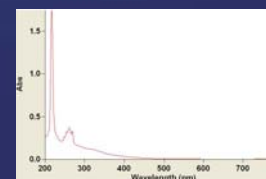
UV-Vis Absorption Spectra



1 in MeCl₂

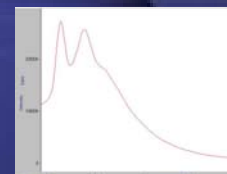


2 in MeCl₂

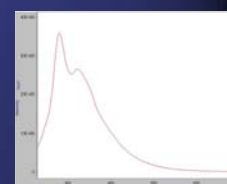


2M-Re in THF

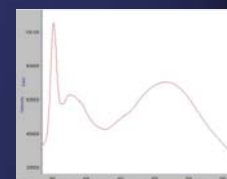
UV-Vis Emission Spectra



1 in MeCl₂



2 in MeCl₂



2M-Re in THF

Next Steps: The next phases of the project are to characterize the metal complexes of **2** and investigate the photochemical properties of these complexes. Studies to be performed include transient absorption (Nd-YAG laser!) and Stark spectroscopy. This next phase is fast approaching and will be achieved within the next year, making this an exciting time to be involved with the Walters Research Group.

Acknowledgements

We would like to thank Northern Kentucky University for their support, and Stuart Oehrle for his separation and spectroscopic assistance. We would also like to thank Kentucky Science and Engineering Foundation, CINSAM, and the Greaves Summer Undergraduate Research Fellowship for their financial support. A special thanks to previous Walters Research Group members Amber Shiveley, Nicole King, Tiffany Tanner, and James Kareth for their contributions to this project.

References

1. Simek, J. W.; Tuck, T.; Bush, K. C., Reduction of carboxylic acids with sodium borohydride and an electrophile. *Journal of Chemical Education* 1997, 74, (1), 107-108.
2. Shiveley, A. N. Synthesis of a new fullerene/transition metal bridge for charge transfer applications. Northern Kentucky University, 2004.
3. Bellik, P.; Guegel, A.; Kraus, A.; Walter, M.; Mueller, K., Diels-Alder Adduct of C₆₀ and 4-Carboxy-o-quinodimethane: Synthesis and Chemical Transformations. *Journal of Organic Chemistry* 1995, 60, (11), 3307-10.
4. Ley, K. D. Photophysics of PI-conjugated polymers and oligomers that incorporate metal to ligand charge transfer chromophores. University of Florida, 2000.
5. Walters, K. A. Photophysical studies of p-conjugated oligomers and polymers that incorporate inorganic MLCT chromophores. Ph.D. Thesis, University of Florida, Gainesville, 2000.
6. Li, Y. Synthesis and Photophysics of Mono-Disperse Phenylene Ethynylene Oligomers. University of Florida, Gainesville, 2001.
7. Davidson, S. K.; Phillips, G. W.; Martin, S. F. Geminal arylation-arylation at a carbonyl center using diethyl N-benzylideneaminoimethylphosphonate: preparation of 2-methyl-2-phenyl-4-pentenal (4-pentenal, 2-methyl-2-phenyl)-. *Organic Syntheses* 1987, 65, 119-34.
8. Tanner, T. M. Synthesis of a Bipyridine Ligand Intended to be Coupled with a Fullerene Supramolecule. Northern Kentucky University, 2005.
9. Worl, L. A.; Duesing, R.; Chen, P.; Della Ciama, L.; Meyer, T. J., Photophysical properties of polypyridyl carbonyl complexes of rhenium(0). *Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972-1999)* 1991, (150th Aniv. Celebration Issue), 849-50.
10. Matsumoto, K. F.; M.; Sato, T.; Onodera, S.; Ito, O., Photoinduced Electron Transfer from Oligothiophene/Polythiophene to Fullerenes (C₆₀-C₇₀) in Solution: Comprehensive Study by Nanosecond Laser Flash Photolysis Method. *J. Phys. Chem. B* 2000, 104, (49), 11632-11638.