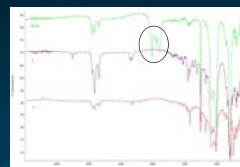
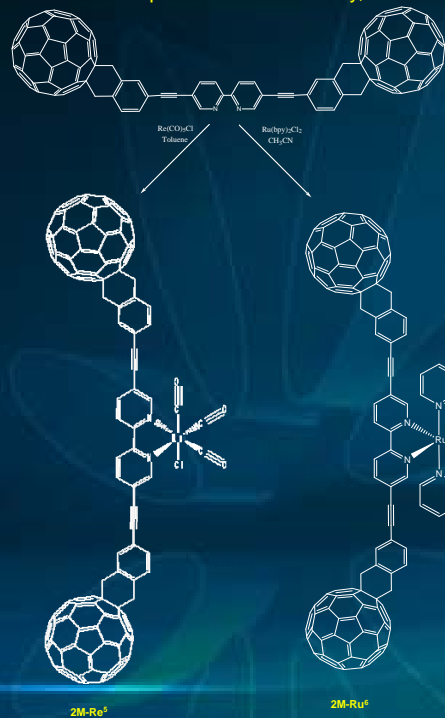


Synthesis of a novel fullerene-bipyridine ligand for photoelectric applications



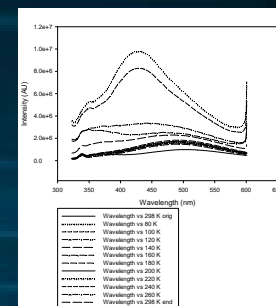
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Objective: The primary objective of our research is to synthesize supramolecular systems that move electrons efficiently when excited by a photon of light. One such system is in development: two fullerene "handles" connected through a conjugated bipyridine "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 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.



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

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



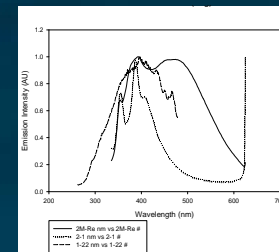
Variable temperature emission plot of the rhenium complex

The graphs at right are examples of variable temperature emission. The key thing to note is the difference in the emission at 298 K of the different species ("handle" **1**, ligand **2**, and the rhenium complex) in the lower plot. This red shift likely represents metal to ligand charge transfer (MLCT). Also, each species clearly has its own unique emission characteristics, which further supports the success of our syntheses.

Quantum yields of the complex (in THF) were determined using perylene and anthracene (in EtOH) actinometers. The quantum yield of the complex was calculated (equation 1) to be approximately 2%.

$$\Phi_{em}^s = \Phi_{em}^r \left(\frac{1 - 10^{-A_s}}{1 - 10^{-A_r}} \right) \left(\frac{\eta_s^2}{\eta_r^2} \right) \left(\frac{D_s}{D_r} \right)$$

Equation 1, quantum yield calculations



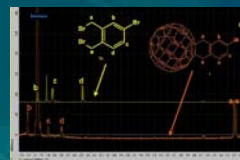
298 K Emission overlay of **1**, **2**, and the rhenium complex



¹H NMR of **2a**



¹H NMR of **2b**



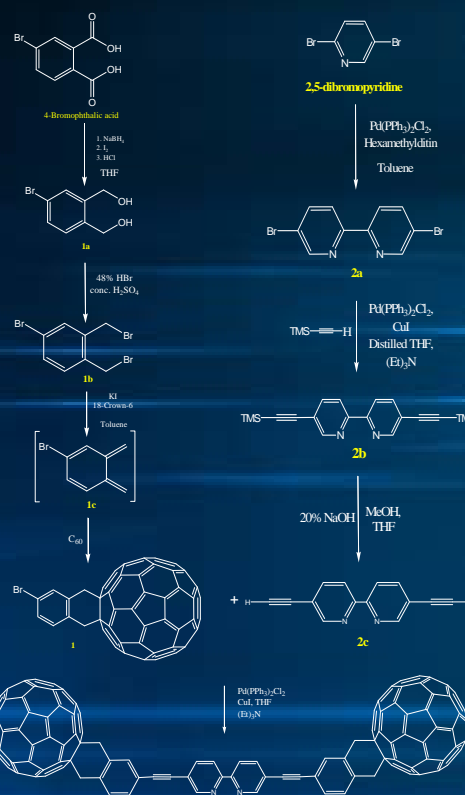
¹H NMR overlay of **1b** and **1**.



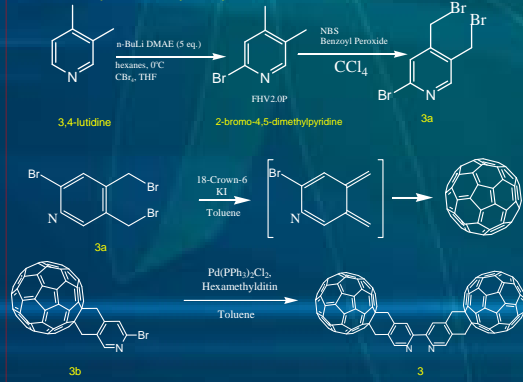
¹H NMR of ligand **2**.

Fullerene "Handle" Synthesis

Bipyridine Bridge Synthesis



Shortened Supramolecular System Synthesis



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Each individual reaction scheme involved in the synthesis of the desired supramolecular system has proven to be successful and each building block is attainable. Schemes for **1a**, **1b** and for **2a** proved to be more straightforward than that of **2b** and compound **1**; a next step will be to perfect those reaction procedures so that they become as repeatable as the others.

Now that the target supramolecular system has been made, the next step is to improve upon the original blueprint. One such improvement is to shorten the distance that electrons have to travel between the fullerene and the transition metal. Not only will electrons flow more rapidly, but the chance that electrons will get lost on their way back to the fullerene from the transition metal will be reduced. This is represented in reaction scheme **3**. Another benefit of this shortened ligand is that two, or even three, of these ligands could be coordinated to the metal (as opposed to ligand **2** where coordinating more than one is sterically improbable).

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. Also, a spectroscopic comparison of ligand **2** and a simplified bipyridine structure, and its metal complexes, will be conducted. These next steps are fast approaching and will be achieved within the next few months, making this an exciting time to be involved with the Walters Research Group.

Acknowledgements

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