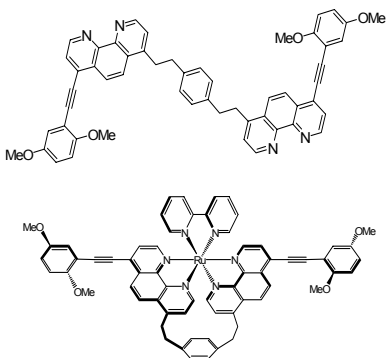


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Objective: The purpose of our research is to synthesize new supramolecular building blocks and investigate their photochemical and photophysical properties.

What are we trying to accomplish?

Problem: Most researchers^{1,2,3,4} have explored polymers (A) with pendant transition metal complexes. When excited by light, the polymer and transition metal tend to interact on their own.



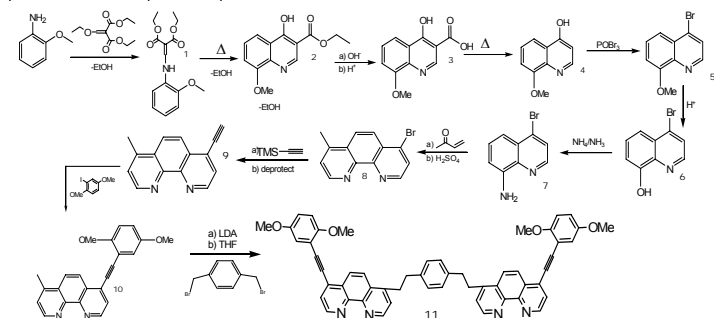
Solution: Our solution is to directly incorporate the transition metals into the backbone of the polymer using a ligand inspired by Sauvage⁵. This adaptation would be beneficial in enhancing the interaction of the metal and polymer backbone which could be seen in the observed photophysical properties and making it considerably easier to tune the properties of the polymer. The ability to tune the properties would open the door for these systems to be useful in new solar energy conversion systems including solar cells and molecular wires.

How are we going to do this?

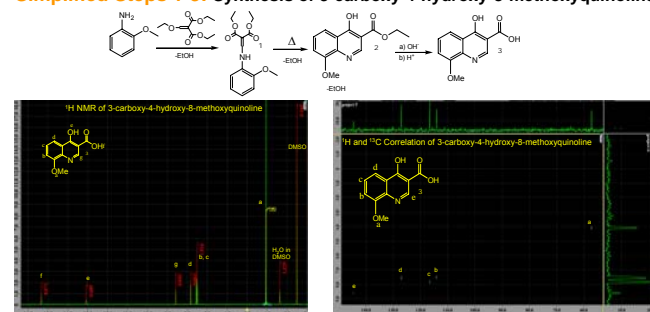
- Create a supramolecular linear directing ligand through a multi-step synthesis
- Incorporate transition metals (such as ruthenium or rhenium) into the ligand
- Investigate the photochemical and photophysical properties of the ligand through spectroscopy

Synthesis of Model Ligand

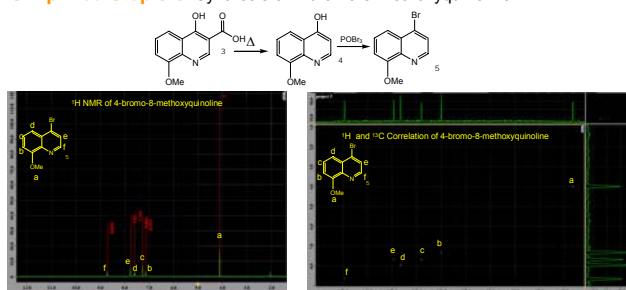
The current focus of the synthesis is optimizing Step 8. We are currently working on synthesizing previous products in order to optimize Step 8.



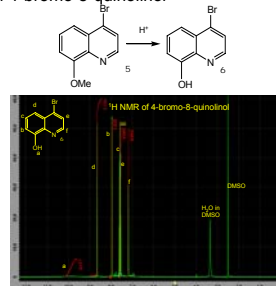
Simplified Steps 1-3: Synthesis of 3-carboxy-4-hydroxy-8-methoxyquinoline



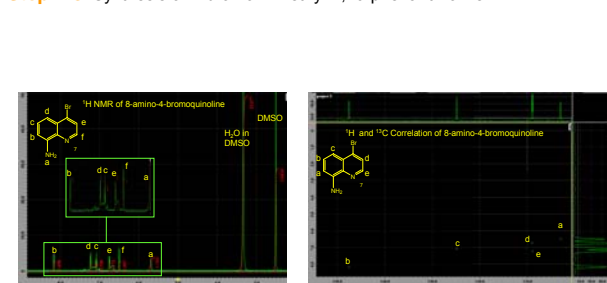
Simplified Step 3-5: Synthesis of 4-bromo-8-methoxyquinoline



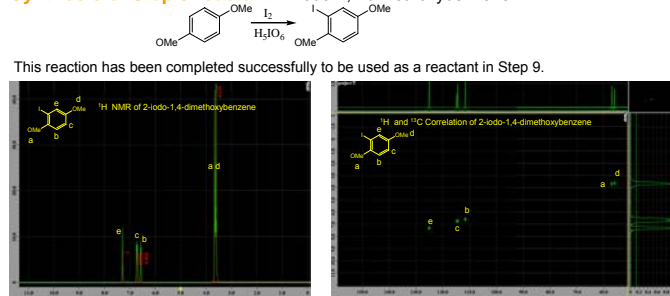
Step 6: Synthesis of 4-bromo-8-quinolindol



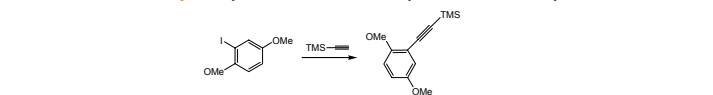
Step 7-8: Synthesis of 4-bromo-7-methyl-1,10-phenanthroline



Synthesis of Step 9 reactant: 2-iodo-1,4-dimethoxybenzene



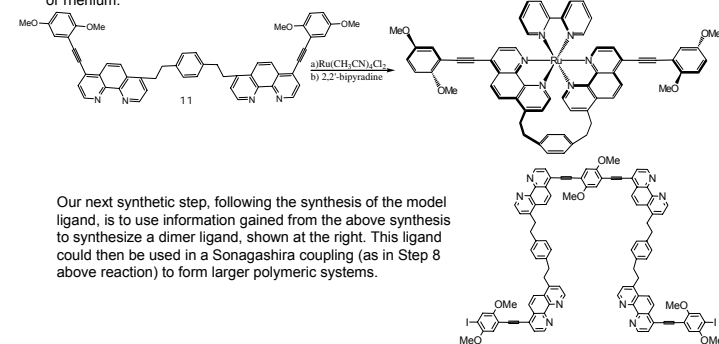
Alternative to Step 9: Synthesis of 2-TMS-acetylene-1,4-dimethoxybenzene



As an alternative route to coupling TMS-acetylene to the phenanthroline and then couple 2-iodo-1,4-dimethoxybenzene, we decided to attempt the coupling of 2-iodo-1,4-dimethoxybenzene to TMS-acetylene. This is one of the things we are currently focused on in our research.

The Next Step

Following synthesis of the model ligand (11), it will be bound to transition metal centers, such as ruthenium or rhenium.

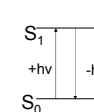


Our next synthetic step, following the synthesis of the model ligand, is to use information gained from the above synthesis to synthesize a dimer ligand, shown at the right. This ligand could then be used in a Sonogashira coupling (as in Step 8 above reaction) to form larger polymeric systems.

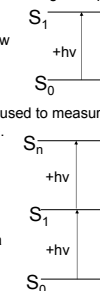
Spectroscopic Studies

Following synthesis of the model ligand and metal ligand complexes, a detailed spectroscopic study will be conducted. This will help in understanding how the ligand and transition metal are interacting with light. Along with the methods shown, we will also use Stark spectroscopy to determine the distance of charge transfer within the molecule following excitation by measuring the change in dipole moment.

Absorption Spectroscopy will be used to determine how the molecules absorb light.



Emission Spectroscopy will be used to measure the emission, or light given off, by a molecule.



Transient Absorption Spectroscopy will be used to measure the absorption of a molecule that has already been excited to higher excited states using a pulsed laser.

References:

- Ley, K. D.; Schanze, K. S. *Coord. Chem. Rev.* **1998**, *171*, 287-307.
- Walters, K. A.; Ley, K. D.; Cavalaheiro, C. S. P.; Miller, S. E.; Gosztola D.; Wasielewski, M. R.; Bussandri, A. P.; Van Willigen, H.; Schanze, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 8329-8342.
- Wang, Y.; Liu, S.; Pinto, M. R.; Dattelbaum, D. M.; Schoonover, J. R.; Schanze, K. S. *J. Phys. Chem.* **2001**, *105*, 11118-11127.
- Kingsborough, R. P.; Swager, T. M. In *Prog., Inorg. Chem.*; Karlin, K. D. Ed.; John Wiley & Sons, 1999; Vol. 48, p 123.
- Pomeranc, D.; Heitz, V.; Chambron, J. C.; Sauvage, J. P. *J. Am. Chem. Soc.* **2001**, *123*, 12215-12221.
- Azadi-Ardakani, M.; Wallace, T. W. *Tetrahedron*, **1988**, *44*, 5939-5952.
- Price, C. C.; Roberts, R. M. *J. Am. Chem. Soc.* **1946**, *68*, 1204-1208.
- Gershon, H.; Clarke, D. D. *Montash. Chem.* **1991**, *122*, 935-941.
- Lauer, W. M.; Arnold, R. T.; Tiffany, B.; Tinker, J. *J. Am. Chem. Soc.* **1946**, *68*, 1268-1269.
- Burckhalter, J. H.; Edgerton, W. H. *J. Am. Chem. Soc.* **1951**, *73*, 4837-4839.
- Belser, P.; Bernhard, S.; Guerig, U. *Tetrahedron*, **1996**, *52*, 2937-2944.
- Mobian, P.; Kern, J. M.; Sauvage, J. P. *J. Am. Chem. Soc.*, **2003**, *125*, 2016-2017.
- Sonogashira, K. In *Comprehensive Organic Synthesis*, Trost, B. M., Fleming, I. Eds.; Pergamon Press: Oxford, 1991; Vol 3, p 521.
- Juris, A.; Balzani, V.; Barigelli, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1998**, *84*, 85-277.
- Worl, L. A.; Duesing, R.; Chen, P.; Della Ciana, L.; Meyer, T. *J. Chem. Soc. Dalton Trans.* **1991**, 849-858.

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