# Pi-Expanded Coumarins with Switchable Propeller Geometries

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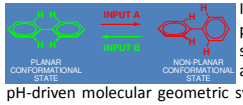
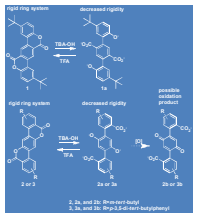
## Mission

The focus of this project is analyzing planar conjugated molecules as molecular geometric switches. Our mission is to synthesize and study different classes of pi-expanded oligocoumarins with Crankshaft and Propeller architectures. The aryl-aryl torsional angle of the oligophenyl subunits is controlled by lactone bridging groups to force planar conjugation. The lactone bridges could be reversibly cleaved and re-formed by changes in pH to form an open and closed conformation. Planar compounds with extended pi-conjugation suffer from poor solubility due to strong pi-stacking interactions. The synthesis with various solubilizing groups and switching studies of these compounds could lead to applications in areas such as organic electronics, molecular machines, light-harvesting materials, drug administration and sensors.

## Background




In this project we are focusing on analyzing planar conjugated compounds as molecular switches. Specifically, analyzing the architectures of Crankshaft and Propellers as pH-driven molecular geometric switches. With these architectures the planar conjugation of the aryl system could be reversibly altered by cleavage and re-formation of the lactone bridging of the arenes. The physical properties including spectroscopic and electronic properties of compounds containing aryl-aryl bonds are highly dependent on the torsional angle between the arene subunits. This allows us to determine if the molecule switched conformation by analyzing the compounds after differing pH. In previous studies we focused on pi-expanded mono-coumarin biphenyl systems to analyze their ability to act as a pH-driven molecular geometric switch. After characterization and switching abilities were confirmed, the basic concept was extended to pi-expanded oligocoumarin terphenyl system containing two lactone bridges. We recently reported the syntheses and studies of three such compounds (see crankshaft compounds, and picture below).



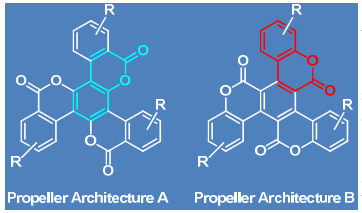
Our current research is focused on Propellers. Propeller architectures are compounds with three lactone bridges with the potential to act as pH-driven molecular switches. Compounds like propellers are being studied in organic solar cells, field effect transistors, light-emitting diodes and non-linear optical devices. Switching abilities of propellers could also lead to very useful pH-reversible binding agents for application in drug delivery.

## Crankshaft Compounds


Three highly fluorescent dilactone bridged terphenyls with crankshaft architectures have been synthesized. These compounds have been characterized by fluorescence and UV-vis spectroscopy. For all three compounds, a direct correlation between the rigidity of the terphenyl system and the strength of absorption and emission of light has been observed. This confirms the ability for these molecules to act as geometric switches.

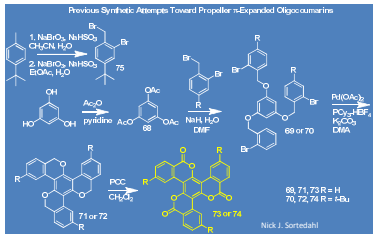
## Characterization Studies

### Propeller Studies



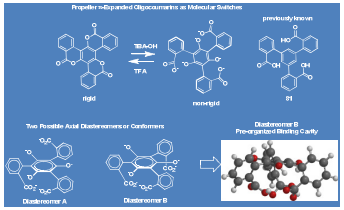

Propellers are biphenyls and terphenyls arranged in a linear fashion with lactone bridges to force rigidity. Our studies will focus on syntheses of Propeller A. Propeller B would not be planar and would have high steric strain. Propeller A would not have this strain enabling the synthesis to be more tractable and its potential physical properties more compelling, including the potential to act as a molecular switch.

### Synthesis of Prototype



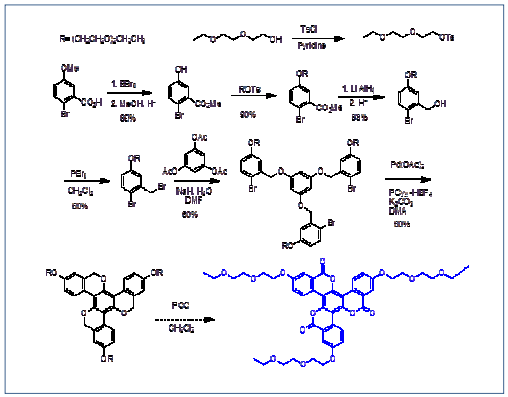

In previous work with Propellers, once the final compound (74) was made it was very insoluble in many solvents. We are attempting to address this solubility issue by attaching oligoethylene glycol groups to the outer benzene rings. The addition of these groups are expected to increase polarity. More importantly, these groups should allow for repeated pH-driven switching, greatly enhancing desirability for practical applications. However, the synthesis of Propeller A with the oligoethylene groups has posed difficulties that will be addressed. Currently more of Propeller A with *t*-butyl groups is being synthesized and visual switching studies will be performed.

### Application of Propellers




Propellers can be switched to a non-planar conformation with the treatment of a base, and switched back to a planar conformation with the treatment of an acid. Interest in pH-reversible binding agents has been high due to the possibility for application in drug delivery. Base-promoted ring-opening could lead to two possible axial diastereomers, A and B. Diastereomer B, with all carboxyls pointing unidirectionally, could be an excellent ligand for electron deficient species. Especially considering the very electron rich trianionic central arene ring. This property allows for the molecule to have the potential to act as a drug delivery agent, by binding the drug at high pH and releasing the drug at low pH. When the molecule is in planar conformation it will fluoresce and detection could be determined through visual studies.

## Improving Solubility



## Future Studies

The final reaction with PCC in the synthesis is oxidizing the oligoethylene groups as well as the desired points of oxidations. After this was observed, PCC was added in smaller amounts and the time of the reaction was shortened, but the result was the same. During the summer, other oxidizing agents will be explored in attempt to yield the target molecule. Other oxidizing agents such as $KMnO_4$, have the potential to specifically oxidize the desired positions. After Propeller A has been synthesized with the oligoethylene groups the solubility of Propeller A will be greatly improved and characterization studies will be performed to test the ability of the compound to act as a molecular geometric switch.

## Acknowledgments

- Dressler, Justin J.; Miller, Sarah, A.; Meeuwsen, Brian T.; Riel, Asia Marie S.; Dahl, Bart J. "Synthesis of Dilactone Bridged Terphenyls with Crankshaft Architectures. " *Tetrahedron* **2015**, *71*, 283-292.
- Carlson, Erik J.; Riel, Asia Marie S.; Dahl, Bart J. "Donor-Acceptor Biaryl Lactones: pH Induced Molecular Switches with Intramolecular Charge Transfer Modulation." *Tetrahedron Lett.* **2012**, *53*, 6245-6249
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