



# A "Smart" Biphenyl Lactone containing a Nitro Acceptor and Methoxy Donor

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## Objective

- Our objective is to investigate the synthesis of tethered organic biaryl systems for ultimate application in sensing and molecular electronics.
- We aim to synthesize biaryls with a tether that can be reversibly opened and closed. Thus, these molecules can be "tethered" shut ( $\theta=0^\circ$ ) or left "open" ( $\theta \gg 0^\circ$ ), depending on external stimuli such as pH, thereby reversibly and controllably affecting their physical properties such as conductance and fluorescence.
- This can be observed with conductance and fluorescence studies. In the open state, the  $\pi$ -orbital overlap is at a minimum and electron communication is negligible.
- By changing the pH of the environment we can confirm these conformation switches.
- The molecules made during the project have broad application in the field of material science and the synthetic pathway represents a novel strategy for the synthesis of biaryl lactones.
- Our mission is to synthesize and characterize the donor/acceptor compound, the determination of the efficacy of pH as a switching method and the detection of a unique UV-Vis and/or fluorescence signal associated with each state.

## Background

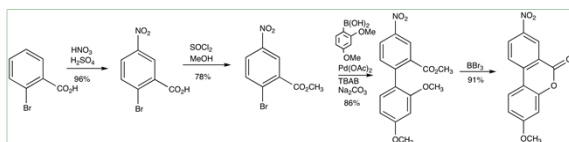
### Molecular Switch

- A chemical system capable of existing in at least two forms exhibiting different spectral, electrochemical, or magnetic properties.
- Interconversion should only occur as a result of a defined energy stimulus.

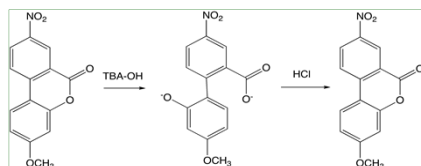
### Dihedral $\theta$ -Dependent Properties

- We can observe this drastic angle change by UV-Vis and fluorescence spectroscopy, absorption wavelength and absorptivity.
- We can switch the angle by changing the pH of the environment, redox reactions and UV Light.

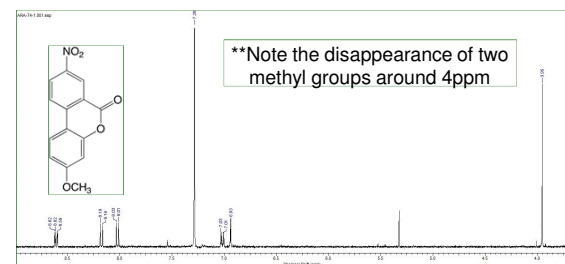
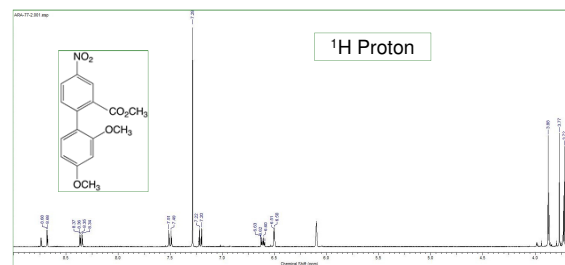
## Synthetic Pathway



## Switching Pathway



## NMR Analysis



## Switching Studies

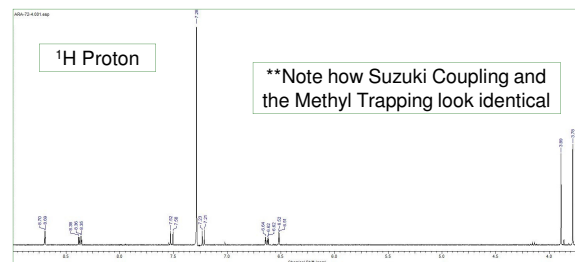
BELOW: Vials containing (from left to right) Lactone, Dianion, Lactone.



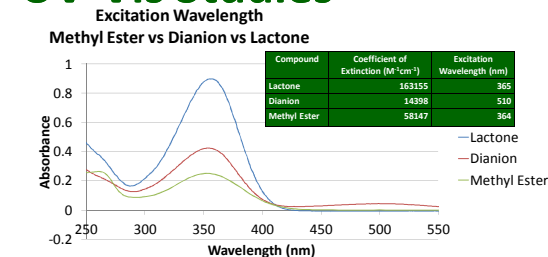
The switching studies are designed to determine if we can reversibly open and close the biphenyl lactone and to confirm the structure of the dianion.

**Changing the pH of the environment.** To see how efficiently the ring opens and closes. Addition of 4M NaOH to the lactone dissolved in Acetonitrile (MeCN) resulted in loss of compound from organic layer. Compound returns to organic layer upon addition of conc. HCl.

**Confirmation of dianion.** The structure was confirmed through addition of methyl donor ( $\text{Me}_2\text{SO}_4$ ) to solution of MeCN containing dianion. This was confirmed by NMR analysis.

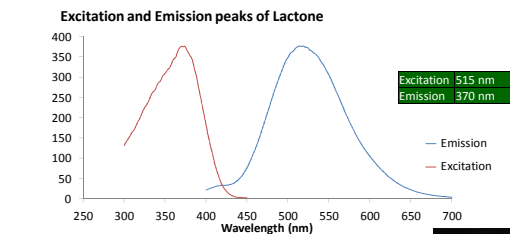


## UV-Vis Studies



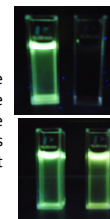
UV-Vis studies confirm previous hypotheses about absorptivity and absorption wavelength. Ring-open dianion and methyl ester display attenuated coefficient of extinctions ( $14398$  and  $58147\text{M}^{-1}\text{cm}^{-1}$ ) compared to ring-closed lactone ( $163155\text{M}^{-1}\text{cm}^{-1}$ ).

## Fluorescence Studies



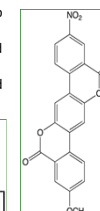
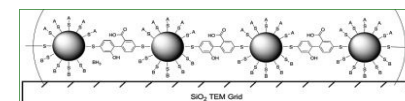
The fluorescence data confirms our UV-Vis data with the lactone emitting at 370nm.

**TOP RIGHT:** Cuvette on the left contains lactone dissolved in MeCN. Cuvette on the right contains the dianion. This shows the loss of fluorescence when the rings are non-planer. **BOTTOM RIGHT:** Cuvette on left is the lactone in MeCN. The right cuvette is fluorescent after the addition of HCl to the dianion.



## Future Studies

- Synthesis of alternate novel switches including expansion into terphenyl analogues.
- Condensation of linker-containing molecule onto a gold nanoparticle.
- Exploration of alternate means of switching including redox- and light-labile bridges



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