Synthesis and Characterization of "Smart" Biaryl Sultines

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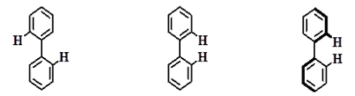
Rationale

Biphenyl – containing compounds, applicable to many nanoscience applications such sensors and molecular machines, can be imagined to exist in two states: non-planar or planar. In the non-planar, open state, the π-orbital overlap is minimal, which creates a large dihedral angle between the two rings, thus attenuating electronic communication. In the planar, closed state, π-orbital overlap is substantial, therefore electronic communication between the two rings is facile.



Dihedral Angle = 180 Dihedral Angle = 0 Dihedral Angle =90

In reality, most biphenyl containing compounds have been known to exist at a dihedral angel of static equilibrium, making these two-states impossible to achieve. However, physical properties such as electron absorption, emission, and conductance are highly dependent on this angle. By synthesizing a reversible tethered sultine bridge, a switching mechanism can be implemented to achieve a two-state switch, and as a result, the fundamental properties of these compounds can be controlled. Thus, the goal of this project is twofold: a) the synthesis and characterization of a donor-acceptor biaryl compound containing a reversible tethered sultine bridge and b) the exploration of dihedral modulation via pH and UV-Vis spectroscopy.

Background

Dihedral Angle:

The angle between two phenyl rings with a single bond as an axis.

Dihedral Angle – Dependent Properties:

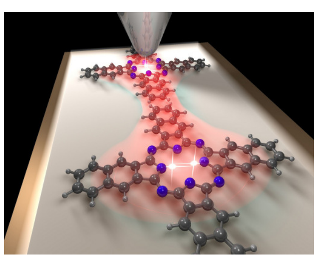
- Absorption wavelength
- Fluorescence
- Electrical Conductance

Molecular Machine:

A discrete functional molecular scale system that is designed to produce quasi-mechanical movements in response to a defined energy stimulus.

Molecular Switch:

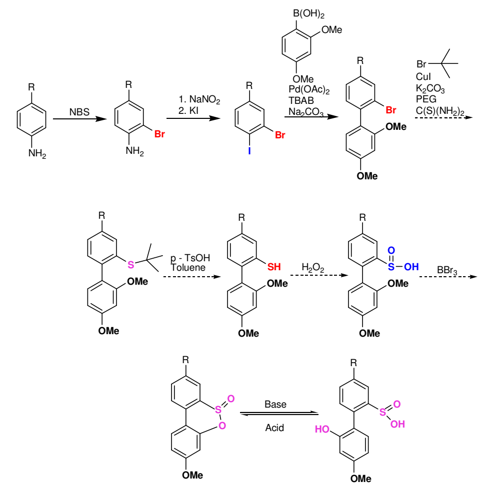
A chemical system, capable of existing in a minimum of two forms, that exhibits different spectral, electrochemical, or magnetic properties. *Interconversion* of each chemical form should only occur as a result of a defined energy stimulus.



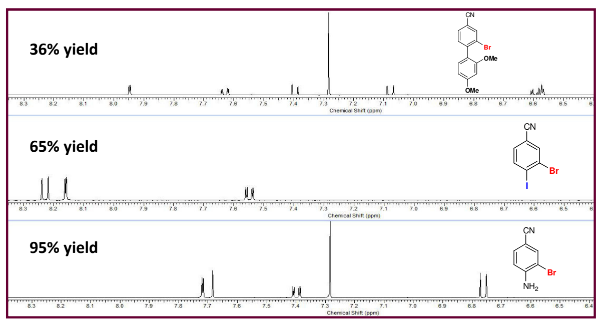
Switching Modes:

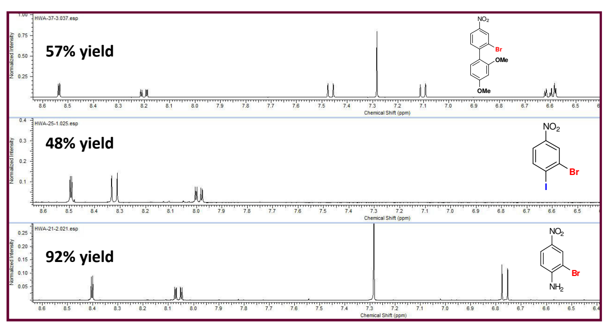
- pH environment
- Fluorescence Spectroscopy
- UV-Vis Spectroscopy

Pathway Synthesis



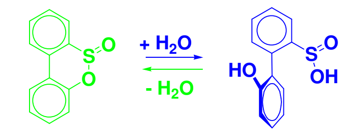
NMR Characterization





Expected Results

pH Reversible Sulfinate Ester Tether



Stable at acidic pH **Stable at basic pH**

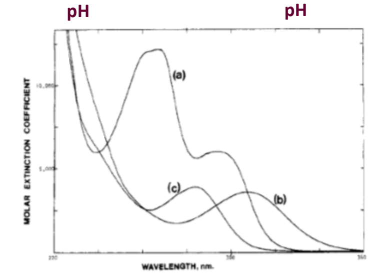
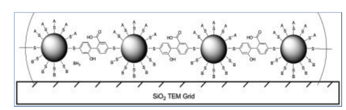


Figure 1. Dependence of the ultraviolet spectrum of biphenylene sultine (2) on pH: (a) biphenylene sultine (2), (b) dipotassium salt of 2-(2-hydroxyphenyl)benzenesulfinic acid (7), (c) 2-(2-hydroxyphenyl)benzenesulfinic acid (8). See Experimental Section for details.

Future Studies

- Synthesis and exploration of alternate novel switches
  - -> Terphenyl analogs
  - -> Redox switchable biaryls
  - -> Light labile bridges
- Conduction of linker containing molecules onto a gold nanoparticle



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