



Synthesis and Study of Cyano-Donor /Methoxy-Acceptor Biphenyl and Terphenyl Lactones

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Mission

Our mission is to explore a biaryl compound capable of dihedral angle modification through a reversible tethered lactone bridge. These compounds will find themselves pertinent to the fields of molecular electronics and sensing. The compound can exist in two states: open and planar. In the open state π -orbital overlap is minimal and communication between the rings is insignificant. In the closed state substantial π -orbital overlap enhances conductance and fluorescence, and also alters UV-Vis properties. An efficient switching mechanism must be implemented to survey these changes. The compound switches conformation based on the pH of environment (high pH –open, low pH–closed). The goals of the project are three fold: the synthesis and characterization of the ring-closed 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

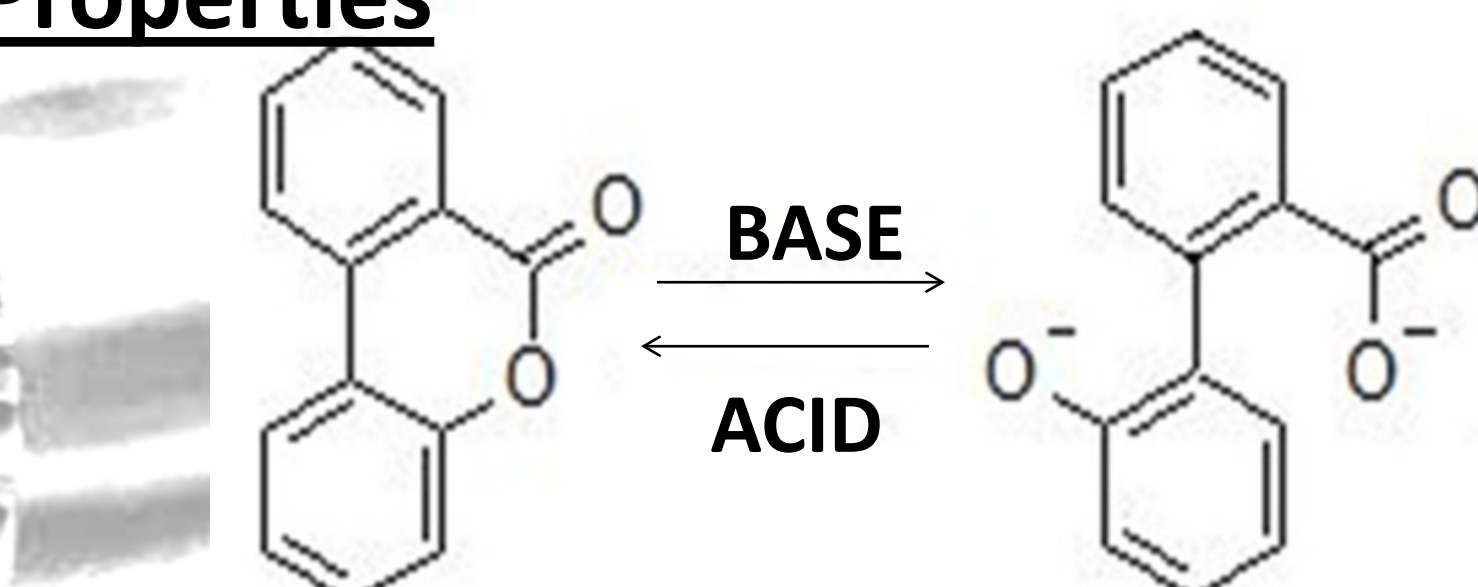
- A chemical system capable of existing in at least two forms exhibiting different spectral, electrochemical, or magnetic properties.
- Interconversion should only occur as a result of a defined energy stimulus.

Dihedral Angle-Dependent Properties

- Absorption wavelength
- Absorptivity
- Fluorescence
- Conductance

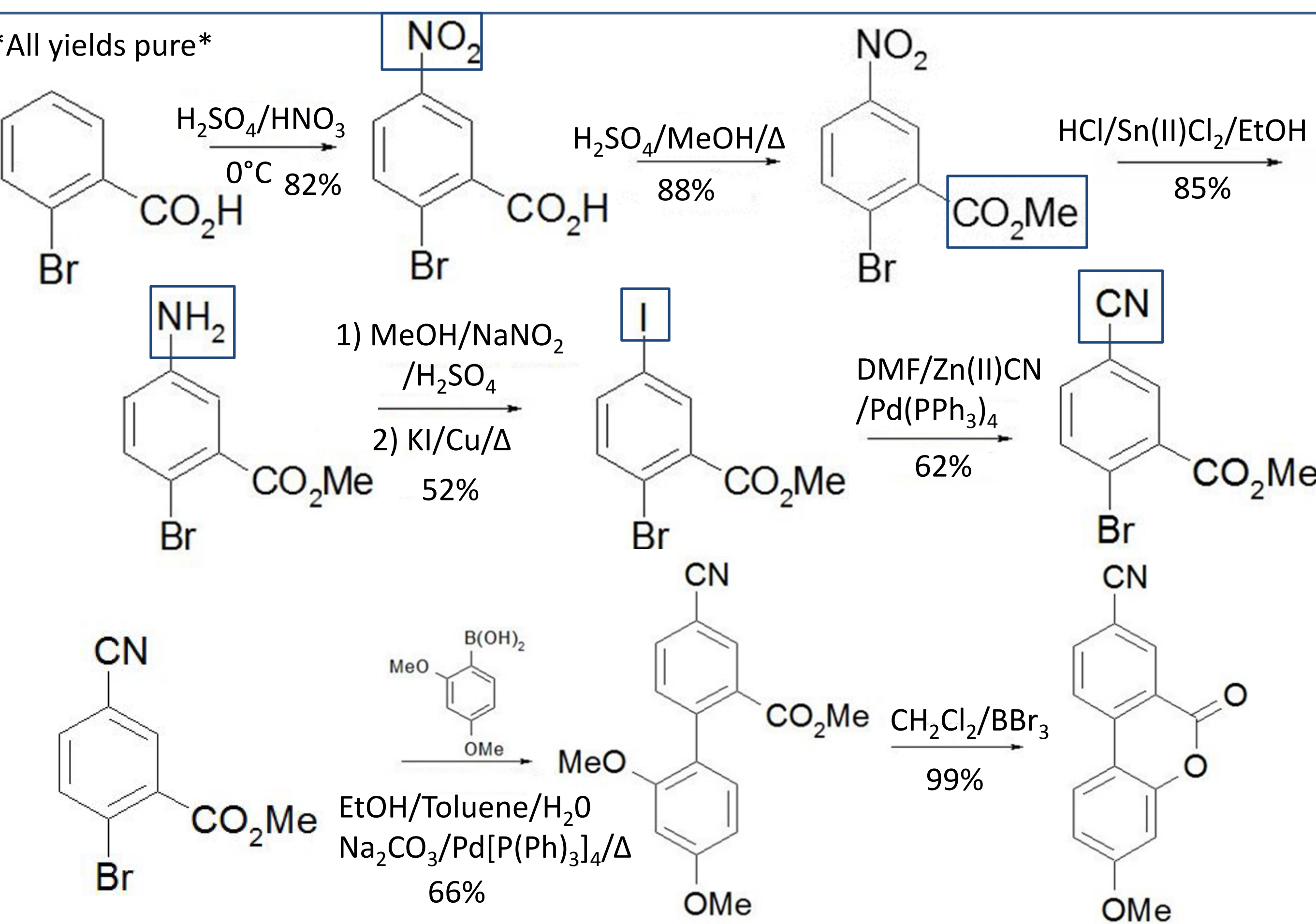
Switching Methods

- pH of environment
- Oxidation/Reduction
- UV-light



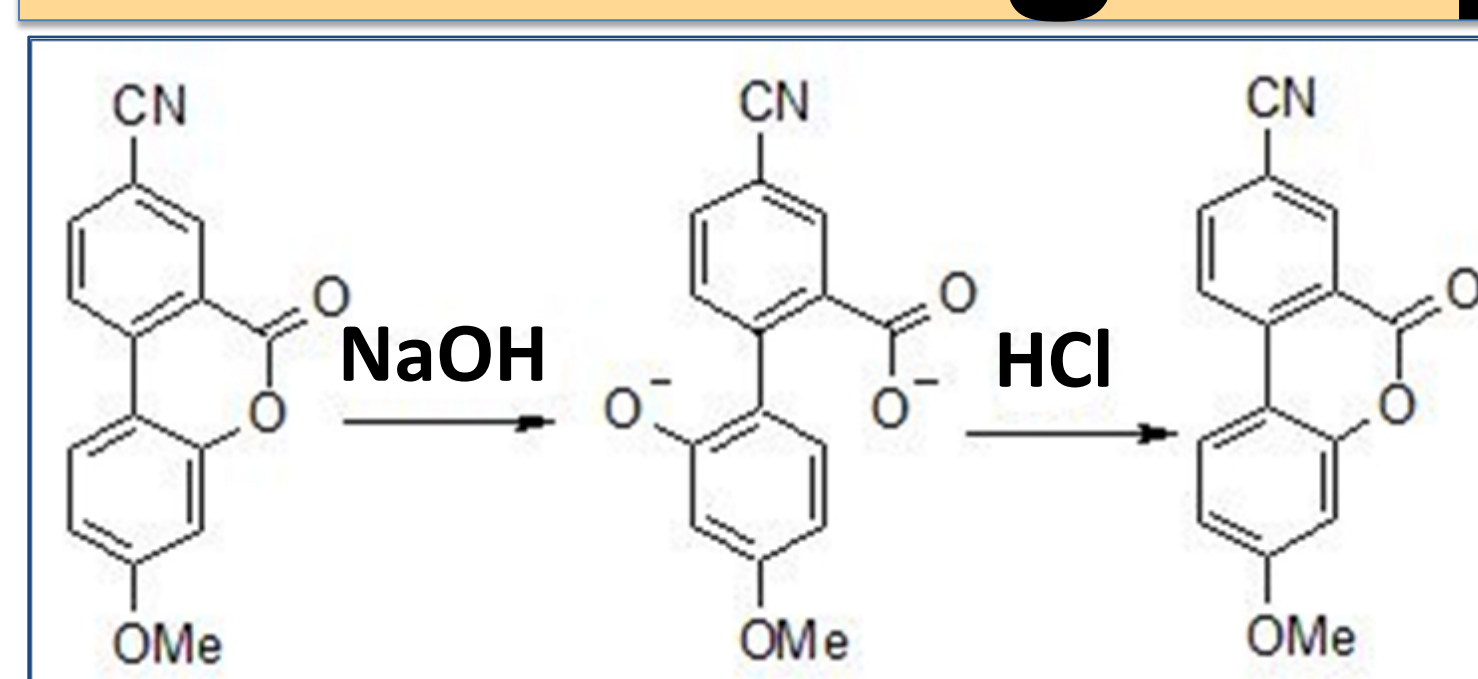
Short	Absorption Wavelength	Long
High	Absorptivity	Low
Strong	Fluorescence	Weak
High	Conductance	Poor

Synthetic Pathway



Characterization Studies

Switching Experiments

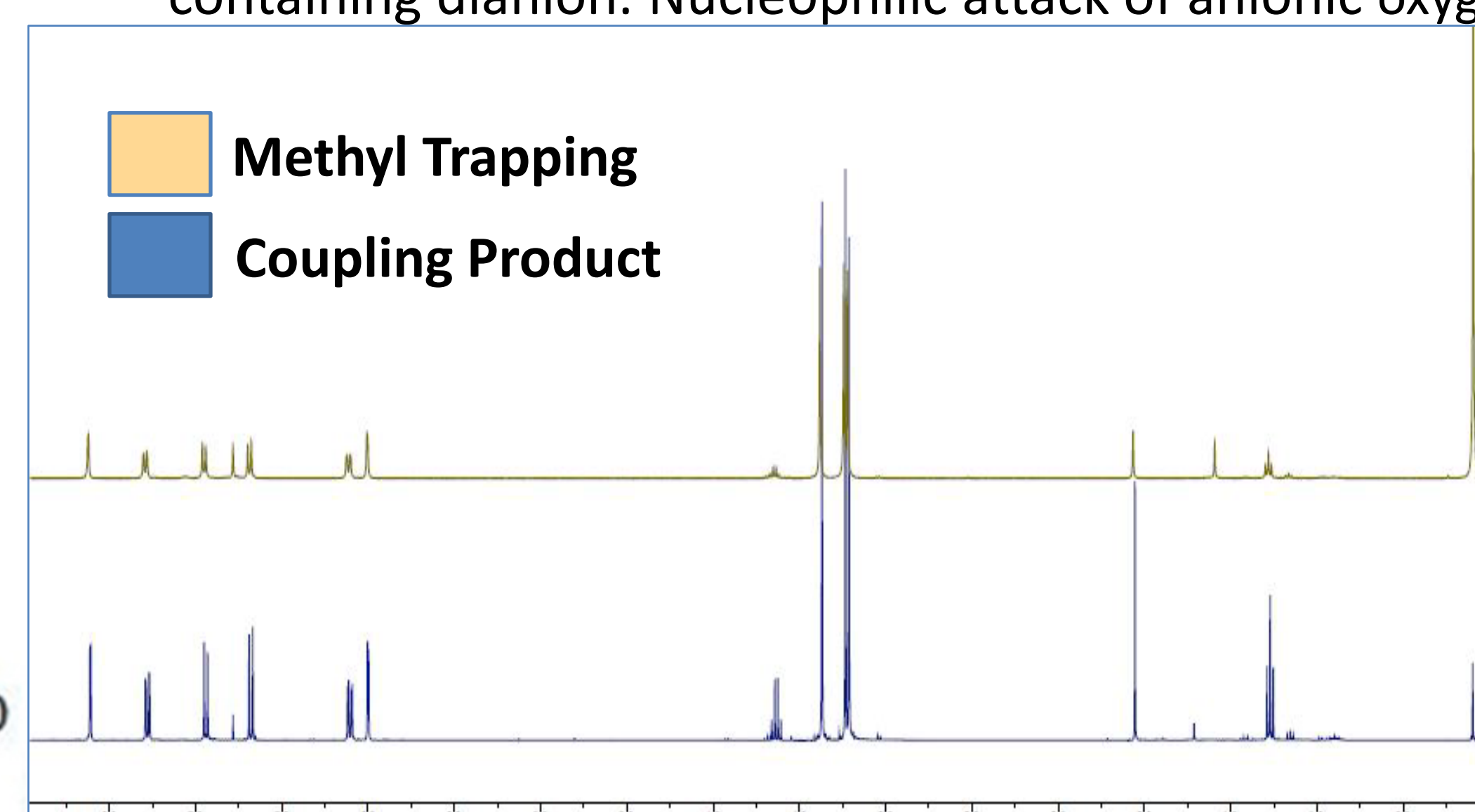


Switching studies designed to probe efficacy of pH as switching method and confirm structure of dianion. Opening/ closing studies exploit solubility differences due to ionic nature of dianion.

Does changing pH open/close ring? Yes: Addition of 4M NaOH to solution of 1:1 THF:MeOH containing lactone resulted in loss of compound from organic layer. Compound returns to organic layer upon addition of conc. HCl.

What is the percent recovery for 1 open/close cycle? 98.7% recovered with very little di-protonated side product observed.

Structure confirmation of dianion. Structure confirmed through addition of methyl donor (Me_2SO_4 or MeI) to solution of MeCN containing dianion. Nucleophilic attack of anionic oxygens on methyl



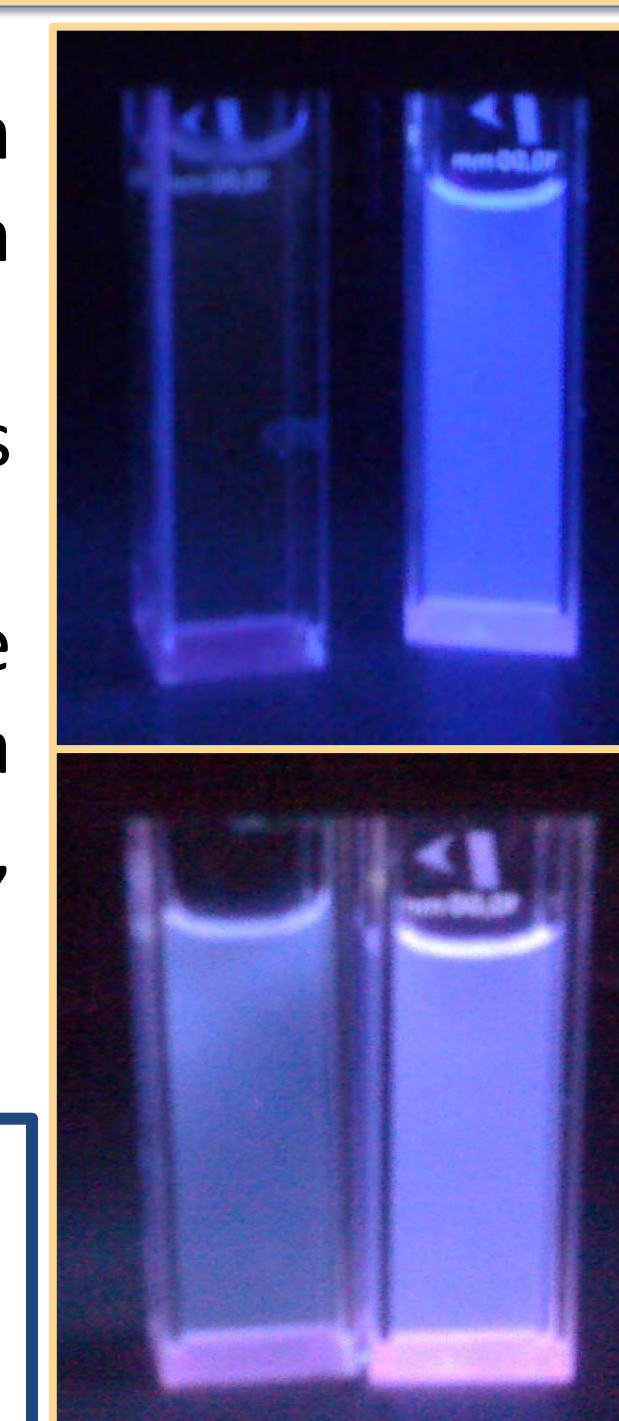
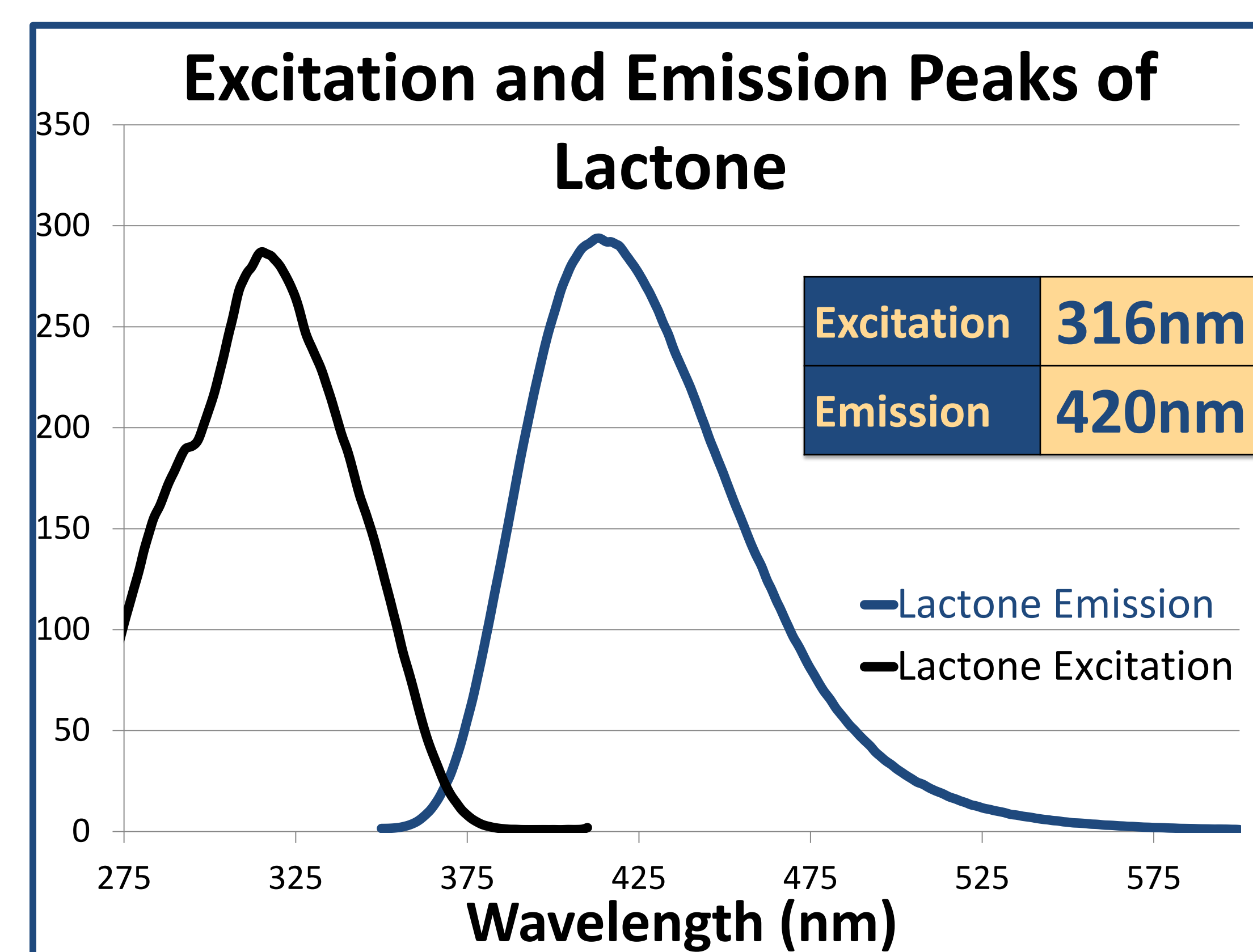
group results in compound that has identical structure to final intermediate. Results and structure confirmed by NMR. (shown at left)

Fluorescence Observations

TOP RIGHT Cuvette at right contains lactone dissolved in MeCN. Left cuvette shows loss of fluorescence upon addition of TBA-OH, which causes ring to open.

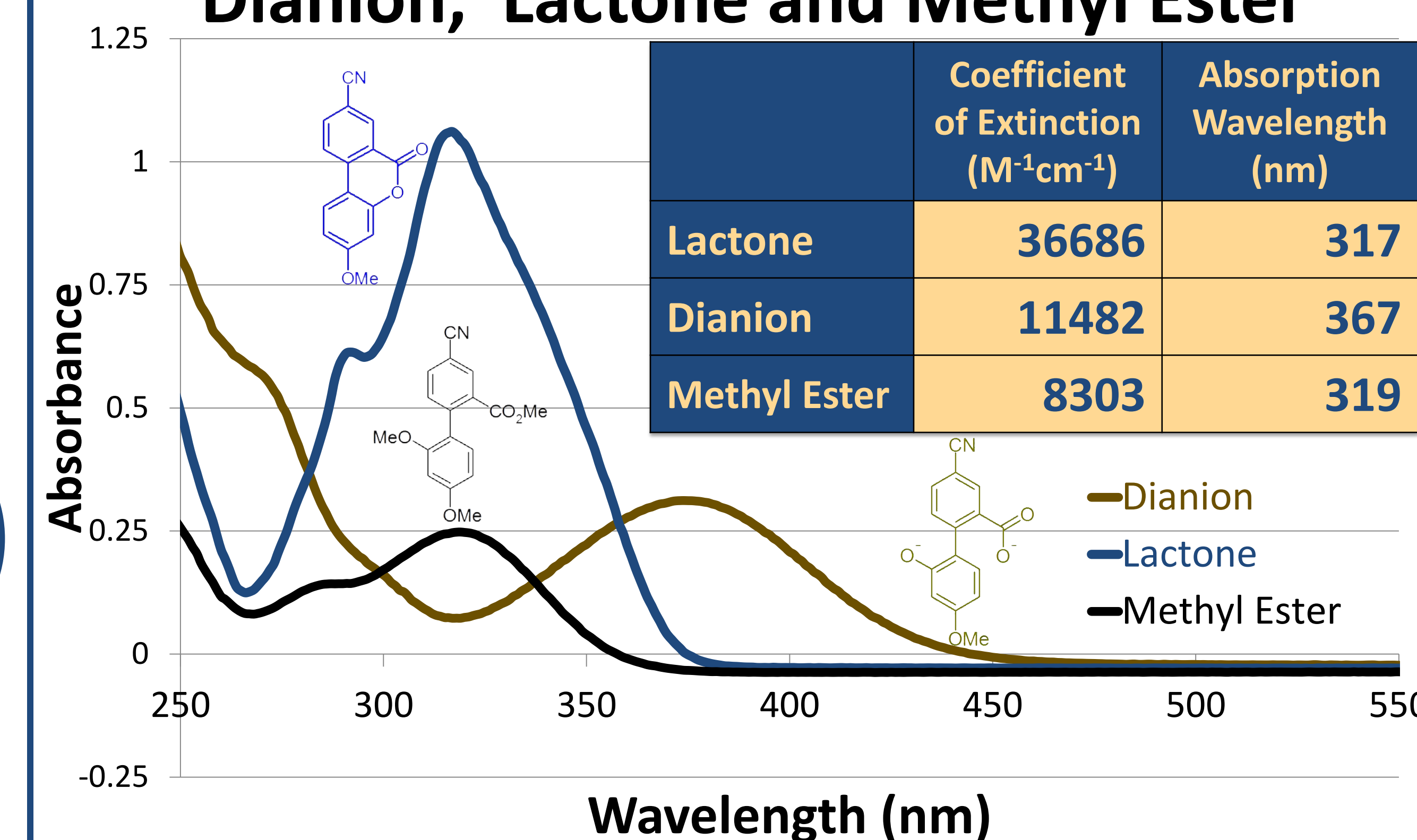
LOWER RIGHT Cuvette at left fluoresces anew when ring is closed following addition of HCl.

BELOW Emission spectrum of the lactone was taken while exciting at 316nm. Lactone dissolved in MeCN at a concentration of 2.4 μM , emission slit kept at 2.5nm, excitation slit kept at 10nm.



UV-Vis Studies

Excitation Wavelength of Dianion, Lactone and Methyl Ester

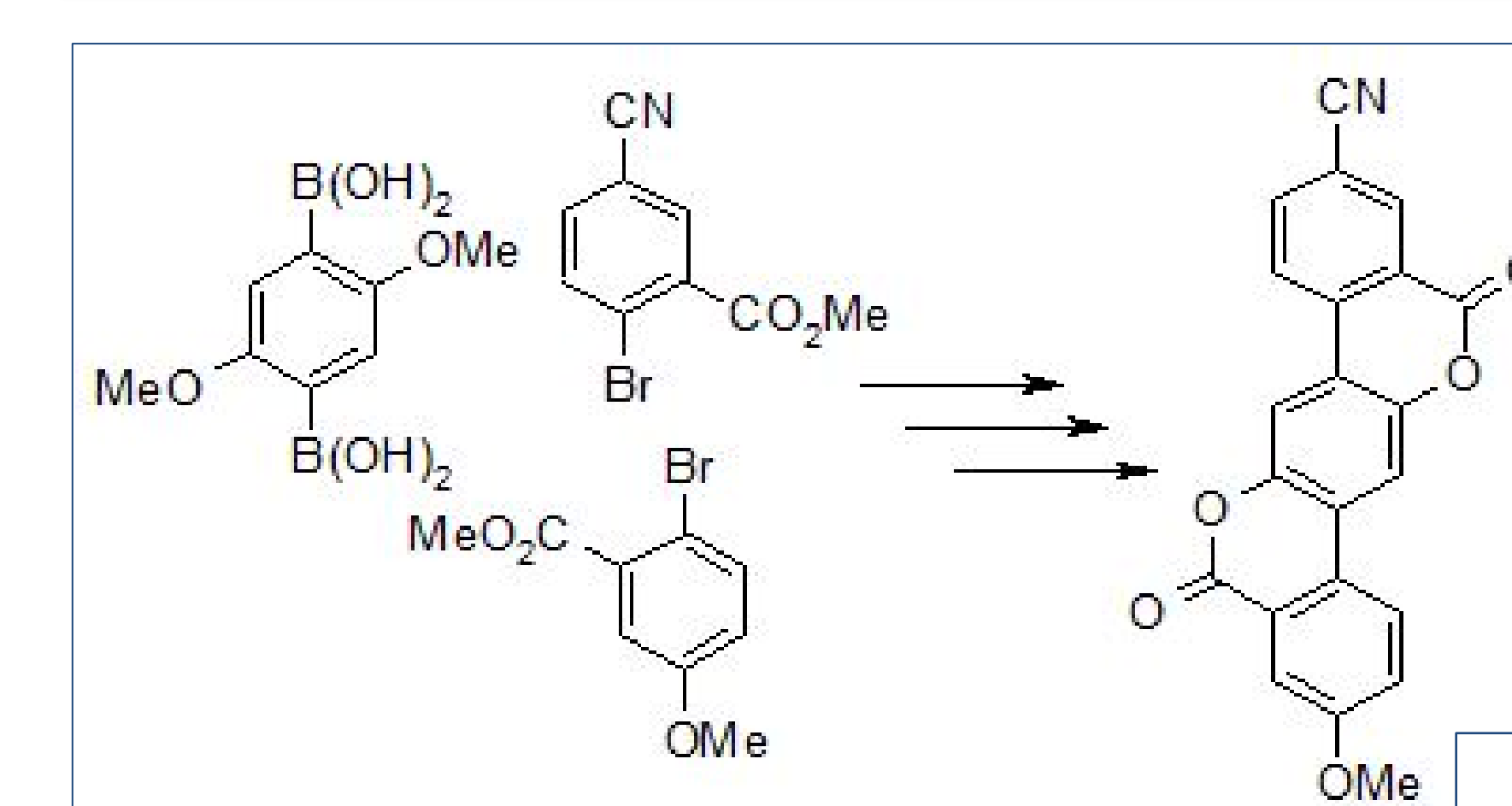


UV/Vis studies confirm previous hypotheses regarding absorptivity and absorption wavelength. Ring-open dianion and methyl ester display attenuated coefficient of extinctions (11482 and 8303 $\text{M}^{-1}\text{cm}^{-1}$, respectively) compared to ring-closed lactone (36686 $\text{M}^{-1}\text{cm}^{-1}$). Also, a visible upfield shift of absorption wavelength is observed in dianion (316nm \rightarrow 367nm).

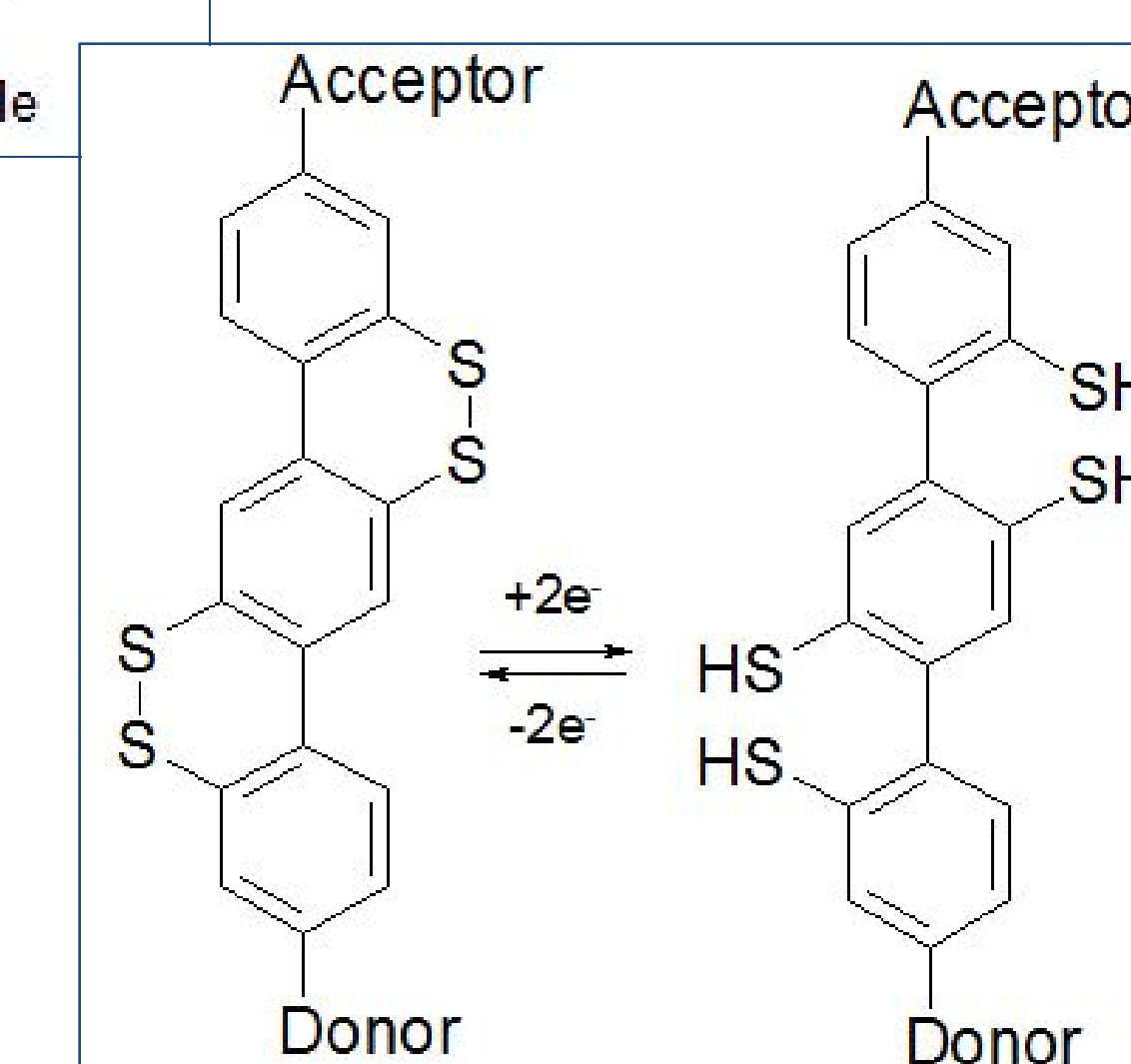


RIGHT vials containing (from left to right) Lactone, Dianion, Methyl Ester. Upfield shift of absorption wavelength visible in dianion.

Future Studies



Synthesis of alternate novel switches, including expansion into terphenyl analogues. Exploration of alternate means of switching including redox- and light-labile bridges.



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