Oligoethylene Glycol Substituted Isomeric Pi-Expanded Coumarins with Crankshaft Architectures

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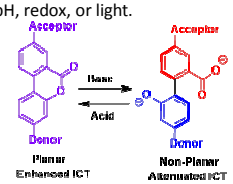
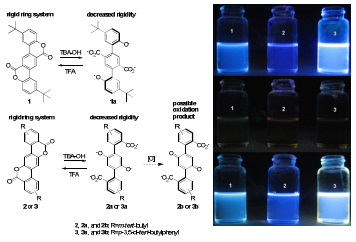
Introduction:

Molecular switches are molecules that are capable of converting between two geometries and thus exhibiting different properties. The switch between planar and non-planar geometries does not occur unless stimulated by changes in pH, redox, or light.



Background:

The physical properties of terphenyl-containing compounds are known to be highly dependent on molecular geometry, specifically the dihedral angle. Compounds capable of dihedral angle modulation should be useful molecular switches. Planar conjugated aromatics have desirable optical and electronic properties, whereas these properties are highly attenuated in non-planar analogs. Unfortunately, planar compounds tend to be insoluble in most organic solvents. We have synthesized several terphenyl dilactones containing solubilizing substituents, where the two lactones "tether" between the two phenyl rings should force a planar geometry. By varying the pH we can reversibly and rapidly open and close the "tether" and switch the molecule in and out of planarity. Unfortunately, these compounds were insoluble in most organic solvents.



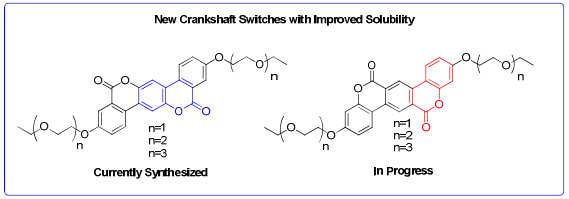
Top: solutions of **1**, **2**, and **3** dissolved in CH_2Cl_2.

Middle: same solutions from top after addition of 1 drop of 40% aq. TBA-OH treated with $Na_2S_2O_4$.

Bottom: same solutions from middle after re-acidifying with TFA.

Soluble Oligoethylene Glycol Terphenyl Switches

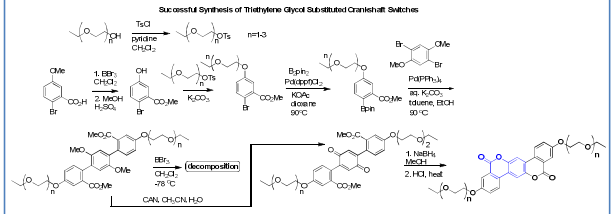
More recent work has been directed at the solubility of the lactone switches and trying to improve the solubility through the use of oligoethylene glycol groups. This will greatly improve their ability to be applied as molecular switches.



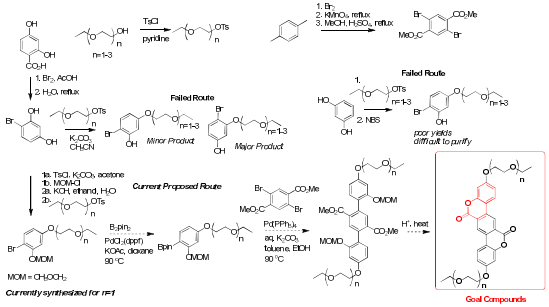
Oligoethylene glycol is chosen as the desired coumarin rather than other solubilizing groups, such as sulfonates or quaternary ammonium groups, because those ionic groups would change their character in differing pH environments.

At this stage, exploration with the ideal solubilizing group is taking place by finding a balance between favorable solubility and ease of purification.

We have currently synthesized small amounts of the following compounds:



Proposed Synthesis of Isomeric Switches:



For this research we propose to synthesize isomeric soluble pi-expanded coumarins. This synthesis begins with 2,4-dihydroxybenzoic acid, which undergoes bromination and decarboxylation to create 5-bromoresorcinol. The phenol groups of the compound will be protected in order to be converted into a pinacol boronate ester, and then Suzuki coupling followed by acid-induced lactonization will produce the desired crankshaft pi-expanded oligocoumarin.

Beginning the synthesis with 2,4-dihydroxybenzoic acid is cost effective, as it is commercially available and inexpensive rather than beginning with 5-bromoresorcinol, which though commercially available, is expensive.

Future work will be to test the isomeric switches for pH-driven switching via NMR, UV-vis, and fluorescence spectroscopy. The main goal of the research is to produce soluble versions of previously synthesized terphyl lactone switches.

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References

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