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Chromism of spiropyrans

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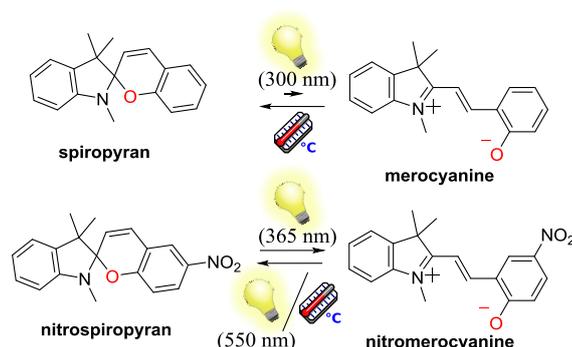
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Summary

Smart molecular systems in which spiropyran based molecular switches play a key role are the central focus of this thesis. These systems respond to stimuli (e.g., light, pH, electricity, etc.) through a change in molecular, and thereby material, properties such as color, acidity, or conductivity, amongst others. The change in macroscopic properties is often the consequence of a change in molecular charge and/or structure, however, it is the arrangement of molecules in a material that dictates the overall expression of the changes of the molecular switches at the macroscopic level. The spiropyran class of molecules, in particular, is interesting as both the charge and structure can be changed by external stimuli, not least irradiation (photochromism, **Scheme 1**), or pH changes (acidochromism).



Scheme 1. Molecular switching of spiropyrans. The NO_2 group facilitates switching back with visible light (of wavelength 550 nanometer) in addition to thermal reversion.

Although spiropyrans and related compounds have been known for over a hundred years, their versatility makes them a staple in applications using molecular based materials and are still ubiquitous in the contemporary scientific literature and, increasingly, in commercial uses (for example the color-changing sunglasses). Responding to multiple stimuli and providing a number of distinct changes to molecular properties can be taken advantage of in many fields, and the potential to use these responsive building blocks increases steadily. Despite the large volume of literature on spiropyrans already present, these compounds continue to provide novel features, which had often gone partly unnoticed, making them an interesting target for study.

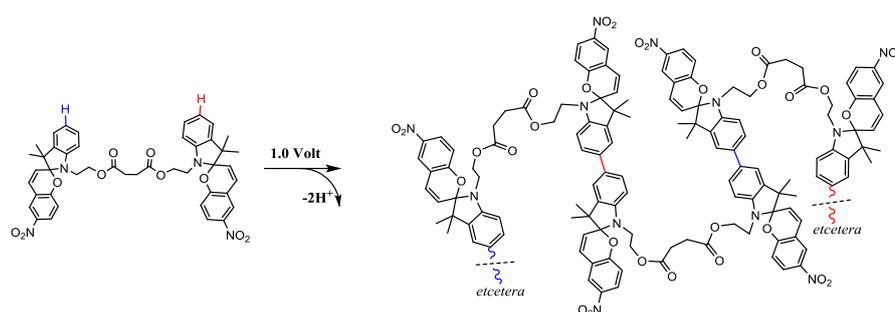
The key challenge, not only with the spiropyran class of molecules but also others, is to translate the changes that occur in a single molecule to the macroscopic world so that we can experience the result and put it to use. For this to work, enough molecules (at an appropriate density) have to undergo the change, and, importantly, the change must have a collective affect and ideally be cooperative. A change in either charge or structure in a neighboring molecule can already dramatically affect the energy required for a molecule to undergo the same change. Harnessing this common issue requires cooperation between the different building blocks of the material, and, e.g., the space to undergo a structural change freely, or the presence of compensating charges and solvent.

In chapter 2 cross-talk, i.e., influence of one component over another and vice versa, that led to complete quenching of the individual photophysical (e.g., photochromism, fluorescence) properties of appended carbazole and naphthalene units was explored. This cross-talk was highly

efficient and resulted in unexpectedly effective quenching of fluorescence of the naphthalene unit, which allowed us to characterize the monomer and the well-behaved redox polymers formed by cyclic voltammetry (electrochemical oxidation). The proof of principle was demonstrated by synthesizing and characterizing model compounds, including a double carbazole with a non-functional linker capable of undergoing the same polymerization, which provided a fluorescent polymer in the absence of cross-talk with a naphthalene core. A key finding in this study is that while the carbazole unit is highly effective in oxidative dimerization itself, tethering of two carbazole units covalently provides for remarkably well-behaved oxidative polymerization.

Overcoming cross-talk between individual functional components in a molecular material is not only accomplished through new synthetic designs, so called molecular engineering, but can also be overcome by recognizing the cause of the cross-talk and physical engineering of a material. This latter approach is the focus of chapter 3, in which a molecular based system that loses its photochromic and other excited state properties due to intermolecular interactions called H-aggregation, i.e., close stacking of the polymer chains that lead to excited state quenching, is brought back to life again by disrupting these stacking interactions physically rather than by molecular redesign. The polymer made up of repeating units of a sexithiophene/dithienylethene hybrid was shown earlier to be entirely photochemically inactive and in chapter 3, we show that when these interactions are disrupted by swelling the polymer with solvent (i.e., solvent molecules intercalate between the polymer chain to break up the stacking interaction) all excited state properties are restored, including singlet oxygen generation, emission, and photochromism.

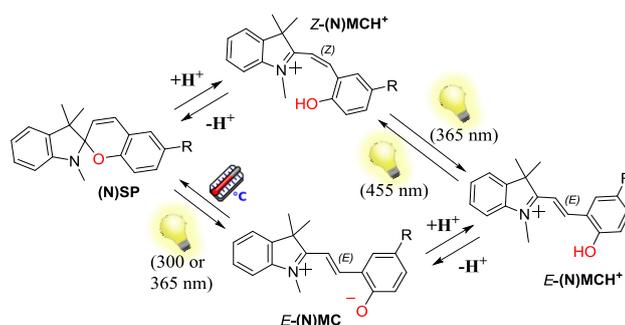
Chapter 4 applies the experience and knowledge gained in chapters 2 and 3, i.e., electropolymerization (making a polymer upon oxidation of the building block) at electrodes and avoiding deactivation of photochromic properties in the polymer form, to the spiropyran class of photochromes. Spiropyran dimers generated by (electro)chemical oxidation provide access to a set of new properties. By attaching two spiropyrans together through a different site in the molecule, analogous to chapters 2 and 3, we were able to create double spiropyrans that each could still couple by electrochemical oxidation to another spiropyran (**Scheme 2**).



Scheme 2. Approach to use electrochemical dimerization (i.e., single coupling) of spiropyrans to achieve polymerization by having each building block able to couple twice.

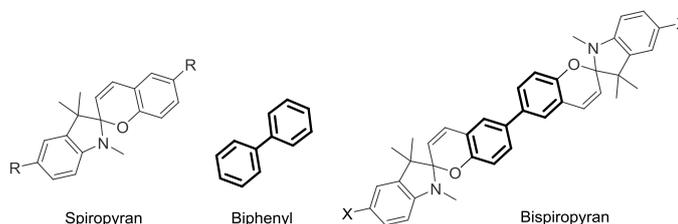
The key finding in this chapter was that the molecular units within the polymers formed were also able to undergo visible light driven ring-opening when oxidized, thus allowing electrochemical control over ring-opening and ring-closing with only visible light irradiation once in the polymer form.

In chapter 5, the acidochromism (i.e., acid-induced color changes) of spiropyrans is explored. Though it has been suggested many times that an intermediate acidified *cisoid* should exist, and the thermally generated acidified *cis*-merocyanine was observed spectroscopically, the first report that was able to demonstrate a response between the pK_a (acid strength) and photochemical bistability was only in 1995. In this report, a large excess of hydrochloric acid was used to effect a modest change in UV/vis absorbance. In this chapter, however, we show that matching the pK_a of the acids used and the acidity of the merocyanine forms is essential to achieving acid induced switching (**Scheme 3**).



Scheme 3. The discovered interconnecting behavior of spiropyran in presence of *sufficiently* strong acid and irradiation.

In chapter 6 and 7, a new design of spiropyran is investigated. In contrast to chapter 4 where two spiropyrans were connected through a long flexible side-chain, here the approach of fusing them through a biphenyl unit was taken (**Scheme 4**).



Scheme 4. The newly designed bispiropyran molecular switch, inspired by the spiropyran and biphenyl motifs.

Chapter 6 focuses on the photochromic properties of bispiropyrans, which largely follow those of the “regular” spiropyran. However, an additional colored species is observed, linked to the direct connection of the two components, which may also give insights into the reactivity of the more usual spiropyran forms. Lastly, in Chapter 7, the electrochemical properties of bispiropyrans are studied, which turn out to differ largely from their mono-spiropyran analogues. Due to the direct connection between the switching moieties, the electrochemical oxidation, which is normally not involving the phenol unit, is now centered on the central bisphenol motif, which opens new opportunities in electrochromic as well as photochromic behavior. Under certain conditions ring-opening coupled with oxidation can be out-competed and electropolymerization can be achieved, yielding novel redox and photo responsive polymers of this new bispiropyran photochrome.

As a whole, this thesis contributes to the advancement of the exciting field of spiropyran photochromes and at the same time we have answered key fundamental questions regarding the chromism of spiropyrans. Of course many more questions have been raised in the process.