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The ideal sensor would be highly sensitive and selective, require no reagents, inexpensive to produce, reusable and stable for years without need of recalibration. The stability of a sensor is a particularly difficult issue when considering applications such as environmental monitoring and process control, where sensors need to be in situ for several weeks, months or even years. Under these conditions, sensor surfaces often become inactivated due to poisoning, oxidation, etc. This lack of sensor stability is one of the reasons environmental monitoring is still most often performed through grab samples that are analyzed in a laboratory days or weeks after the samples are collected. One method to improve sensor stability for field use is to activate the sensing surface only when needed for a measurement. My research interests combine photo-switchable dyes with molecularly imprinted polymers in an effort to create photo-activated sensors that are reusable and have enhanced protection from poisoning.

Spiroyrans belong to a group of photo-switchable molecules that open upon exposure to UV light and close with visible light. The closed form of a spiropyran is colorless, while the merocyanine (open form) is colored. These types of compounds have been investigated for various applications including optical storage media, optoelectronic devices and molecular switches. Spiroyrans have also been investigated for their ability to complex with cations in solution via the phenolate oxygen atom, but have show little selectivity, chelating with akali earth and transition metal ions. While enhanced selectivity has been obtained by linking crown-ether moieties to spiroyrans, this can be a synthetically challenging approach and requires new dyes to be synthesized for each cation of interest.

Cation selectivity will be introduced by incorporating the spiropyran into a molecularly imprinted polymer (MIP). MIPs are synthetic molecular receptors which are often considered 'biomimetic' due to their substrate selectivity mechanism being comparable to that of antibodies or enzymes. A MIP is formed by complexing the analyte of interest (template molecule) with a functional monomer that has some affinity for the analyte through secondary forces such as ionic or hydrogen bonding. Once complexed, the monomer is polymerized in the presence of cross-linker, and then the template molecule is removed from the polymer leaving binding pockets that are specific to the template molecule's shape and chemical functionality. The template molecules in this work are cations. The availability of the cation binding pocket is then be controlled by opening and closing the spiropyran molecules associated with the binding site. By controlling access to the binding site, this type of sensor surface would be less prone to poisoning effects, extending the sensor surface's useful lifetime. In addition, by closing the spiropyran molecules, the cation is released and the sensor surface is regenerated.

The transduction method to determine cation binding in the imprinted polymers is the spiropyran itself which can exhibit a blue shift of 20-100 nm in the open form absorbance spectrum upon cation complexation. This shift in the spectrum is ready detected with UV-Visible spectroscopy. In addition to the selectivity of the imprinted polymers, the effect that the imprinted polymer matrixes have on the absorption maximum of the

spiropyran/ cation complex can be determined. If the shifts in wavelength are sufficient, the spiropyran polymers could be use in cross-reactive sensing arrays that would take advantage of the solvatochromic nature of spiropyrans to distinguish cations via pattern recognition.

Overall Research Objectives:

- 1) Optimize the MIP polymer matrix: dye concentration, cross-linker identity, etc.
- 2) Establish whether the availability of the binding pockets within the MIP structure be controlled by opening and closing the spiropyran molecules.
- 3) Determine the selectivity of a spiropyran/ MIP film vs. a non-imprinted spiropyran polymer film to establish if enhanced selectivity can be obtained.
- 4) Determine suitability of spiropyran polymer films for use in a cross-reactive sensor array format.
- 5) Combine the polymers with LED sensing platforms, to develop, low-power renewable sensors for environmental applications.