Water-Soluble Fluorescent Zinc Complexes: Potential Sensors for Hydrogen Sulfide in Aqueous Solution

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Abstract: Hydrogen sulfide (H2S) has long been known as a corrosive and toxic gas. In the past few years, however, hydrogen sulfide has also been recognized as a key player in cell growth, neuropa-thways, and the regulation of blood pressure and inflammation. Attention to hydrogen sulfide, especially in the medical community, has increased rapidly in recent years, leading to the need for a reliable, biocompatible sensor. This project is concerned with the development of a fluorescence-based, water-soluble hydrogen sulfide sensor that is selective against other thiols in solution. Our approach is to form a cationic LznOR complex, where L is a water-soluble ligand and R is a fluorophore. Upon reaction with H2S in solution, we hypothesize that the fluorophore will be displaced by a hydrosulfide group at the zinc site, resulting in an Lzn-SH complex and quenching of the fluorescent absorbance of the fluorophore. These changes in fluorescence could then be used to detect and quantify the amount of hydrogen sulfide in an aqueous solution. The result is a hydrogen sulfide sensor capable of selectively detecting hydrogen sulfide in an aqueous solution, with potential applications for quantifying hydrogen sulfide levels in blood samples.

Background/Approach:
- Hydrogen sulfide is present primarily in its anionic HS- form in aqueous solution
- Approach is similar to procedures developed by Galardon, et al

I. SYNTHESIS: Identify a system that can (a) stabilize a [Zn-SH]- moiety and (b) be easily modified to increase its water solubility.

Tris(2-pyridymethyl)amine (TPA) from previous research

Figure 1. NMR Spectra of 1 in CD3CN

II. STRATEGY FOR DEVELOPMENT OF HYDROGEN SENSOR

Figure 2. Structure of cationic portion of 1.

Figure 3. 1H NMR Spectrum of 2 in CD3CN

Table 1. Synthesis of Complex 2

Noelle Held, Eric Brown

Synthesis of Complex 2

Results:

Figure 4. Right: 5mM Complex 2 Left: 5mM Complex 2 + 5equiv. NaSH in solution under UV light at 354nm

Figure 5. Right: 5mM Complex 2 Left: 5mM Complex 2 +5equiv NaSH under normal light

Figure 6a. UV Spectra of TPA/Zn Complex + NaSH in Various Equivalents

Figure 6b. Absorbance Intensity at 385nm vs. Equivalents NaSH Added

Figure 7a. Fluorescent Emission Spectra of Complex 2 + Various Equivalents NaSH at 324nm Excitation

Figure 7b. Fluorescent Intensity at 424nm vs. Equivalents NaSH Added

Discussion/Next Steps:

- Improve water solubility by using more polar ligand:
- Explore and improve detection limits at low concentrations
- Explore selectivity of sensor against other physiological thiols such as cysteine and glutathione

Acknowledgements:

This project was funded and a summer fellowship provided to NAH by NSF-REU Grant # 1005159. Special thanks to Galice Garcia for training in spectroscopy, and to Benjamin Ingalls and Ian Shaw for guidance in lab.