Fluorescent Sensors for Ethylene Detection: Anthracene-Selective Fluoroionophores

Caitlyn Bowman and Diane Nutbrown
Department of Chemistry, Juniata College, Huntingdon, PA

What is a fluoroionophore?
A fluoroionophore is a molecule that forms complexes with specific ions and, as a result, experiences changes in either the excitation or emission properties of the molecule. Although fluoroionophores are used to bind a variety of ions, the two synthesized in this investigation have been documented to be Ag(I)-selective:

1. an amine ligand, 6-(9’ anthrylmethyl)-3,9-dithia-6-azaundecane
2. an amide ligand, 6-(9’ anthracenecarbonyl)-3,9-dithia-6-azaundecane

I. Building a Better Fluoroionophore

Why Ag(I)?
Coinage metal ions are known to bind ethylene. Ag(I) is used in industry to separate gaseous alkanes and alkenes.

Ag(I) can be coordinated to S, or emission properties of the molecule. Although fluoroionophores are used to bind a variety of ions, the two synthesized in this investigation have been documented to be Ag(I)-selective:

1. an amine ligand, 6-(9’ anthrylmethyl)-3,9-dithia-6-azaundecane
2. an amide ligand, 6-(9’ anthracenecarbonyl)-3,9-dithia-6-azaundecane

II. Synthetic Routes to Ag(I)-selective Fluoroionophores

The ionophore: 3,9-dithia-6-azaundecane

III. The Theory Behind Expected Photophysical Changes

(1) Amine Ligand
6-(9’ anthrylmethyl)-3,9-dithia-6-azaundecane

Lone pairs of the basic nitrogen quench the fluorescence of the anthracene by photoinduced electron transfer (PET).

- **Turn-On sensor for Ag(I)**
  - The interaction of the Ag(I) ion with the nitrogen will relieve the quenching of the anthracene (no more PET), so the intensity of the fluorescence will increase. The Ag(I) will also quench the anthracene to a small extent, but the relief of PET has the greater effect.

(2) Amide Ligand
6-(9’ anthracenecarbonyl)-3,9-dithia-6-azaundecane

The valence electrons of the amide occupy a lower energy molecular orbital than those of the anthracene, so the amide cannot participate in PET.

- **Turn-On sensor for Ag(I)**
  - The Ag(I) will quench the π-bonds of the anthracene, decreasing the intensity of the fluorescence.

IV. Spectroscopic Characterization of Amine Ligand (1) with Ag(I)

- **Absorbance**
  - 80 μM solutions of the amine ligand (1) in 70:30 dichloromethane:ethanol were used for these spectroscopic studies. 5.5 mM AgF, and 4.9 mM KF, solutions were used to probe the Ag(I)-binding selectivity of the amine ligand (1), and were titrated into separate solutions of the amine ligand in 0.2 mM equivalents.

  - The absorbance spectrum (left) shows that the absorbance progressively decreases and experiences a slight bathochromic (red) shift of 4 nm (from 380 nm to 372 nm) upon the addition of 0.0 to 1.0 eq. Ag(I). Beyond 1.0 eq. Ag(I), the absorbance begins to increase but does not shift to a longer wavelength.

- **Emission**
  - 5.5 mM AgF, and 4.9 mM KF, solutions were used to probe the Ag(I)-binding selectivity of the amine ligand (1), and were titrated into separate solutions of the amine ligand in 0.2 mM equivalents.

  - The emission spectrum (right) shows that the fluorescence increases progressively upon the addition of 0.0 to 1.0 eq. Ag(I). Beyond 1.0 eq. Ag(I), the fluorescence does not increase significantly. Amine ligand (1) does serve as a turn-on sensor for Ag(I).

V. Next Steps
- Introduce ethylene gas to the Ag(I)-bound amine ligand (1)
- Conduct these studies in different solvents because ethylene has differential solubility in different solvents
- Conduct competition studies with a variety of metal ions
- Conduct spectroscopic studies with the amide ligand (2)

Acknowledgements:
Thank you to my advisor, Dr. Diane Nutbrown, and the other professors in the Chemistry Department for their continual assistance. Thank you to the UNI chemistry faculty and staff, especially our lab-host, Dr. Judith Bursyn. Thank you to the other students who work in the lab, Cameron Stevens, John Milligan, and Shelly Perry.