



C30 Toward a Dual-Host Approach for Sensing of Ammonium Nitrate and Other Explosive Salts: Intermolecular Interactions Between the Dansyl Fluorophore and Anions Lead to Large Fluorescence Enhancements

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After attending the presentation, attendees will have a better understanding of the interactions between the dansyl fluorophore and anions such as NO_3^- , Cl^- , and Br^- . Such intermolecular interactions lead to significant fluorescence intensity enhancements upon anion addition, and detailed studies of intermolecular interactions by fluorescence and NMR spectroscopic methods will be presented. This can lead to future design of novel sensing devices based on simple combinations of cation and anion hosts for selective detection of ion-pair explosives, such as ammonium nitrate and uronium nitrate.

This presentation will impact the forensic science community by introducing the principles and preliminary results of a simple dual-host extraction method for sensing ammonium nitrate and other salts. The key factor is the combination of cation- and anion-sensing elements for the detection of an ion pair via a dual-host combination. As an initial step, a detailed investigation of the interaction of the dansyl fluorophore with anions, such as nitrate, is presented. The short-term goal is a thorough understanding of the remarkable fluorescence enhancements observed upon addition of anion solution to dansyl chloride, and manipulation of host structure to induce selectivity for nitrate, in particular. The longer term goal is to combine the anion-sensing moiety based on dansyl fluorophore with cationic hosts, selective for ammonium, and achieve selective sensing for specific ion pairs, such as ammonium nitrate.

Detection of explosives plays an important role in national security. After events such as the 1995 Oklahoma City Bombing, the Anti-Terrorism and Effective Death Penalty Act was passed in 1996. The Act requires that all explosives be tagged to assist in the discovery and tracking of explosive devices as well as banning untagged explosives; however, the problem of tagging explosive substances such as ammonium nitrate that are present in common, easily obtained items such as fertilizers, remains. Because of this issue of widespread ammonium nitrate availability, research has been, and is still being done, focusing on the detection of the ammonium nitrate specifically as an ion pair, and detection methods based on solvent extraction by a dual-host supramolecular approach have been proposed.

Analytical techniques that have been used in the past in the detection of ammonium nitrate include gas-liquid chromatography and ion chromatography. These techniques are useful; however, there were still areas for improvement. Gas-liquid chromatography has a limited detection of thermally labile explosives as well as low selectivity and sensitivity for nitrogen-containing compounds. The high temperatures used can easily decompose the thermally labile explosive. The weakness of ion chromatography is that of column depletion. As the column is used and becomes depleted, artifacts can be produced that interfere with the detection of the explosives.

Fluorescence detection presents a sensitive, inexpensive, and potentially portable method for in-the-field detection of explosives. Heteroditopic receptor systems based on dual-host binding and fluorescence offer the potential for unique sensing effects via binding and extraction to the organic phase of both ionic components of the explosive salt as a tight ion pair. The dual-host complex has two different receptors, one for each ion, specific to each of the ions. The low dielectric constant of the organic medium assures close contact of the two hosts, which is essential for unique signals upon ion pair binding as opposed to binding of only one of the components.

Preliminary experiments by fluorescence spectroscopy, NMR spectroscopy, IR, and ESI-MS offer some insight on the utility of the dansyl fluorophore for nitrate detection, via supramolecular interactions. Specifically, fluorescence titrations of a $1 \times 10^{-5} \text{M}$ dansyl chloride solution with tetrabutylammonium nitrate in CH_2Cl_2 showed dramatic fluorescence enhancements upon nitrate addition (Figure 1). The chemical shift changes observed at ^1H -NMR titrations (Figure 2); indicate fast exchange and are apparently due to supramolecular interactions (presumably anion- π interactions) and not to a reaction of the dansyl chloride with any added species. Preliminary determination of the binding constant for the interaction of dansyl chloride with nitrate indicates a high number (in the vicinity of 10^5M^{-1}). It should be noted, however, that there was difficulty fitting the data into a simple 1:1 binding model, and the possibility of multiple equilibria or more complex models is currently being investigated. Experiments investigating the interactions of the dansyl moiety with other anions are also in progress.

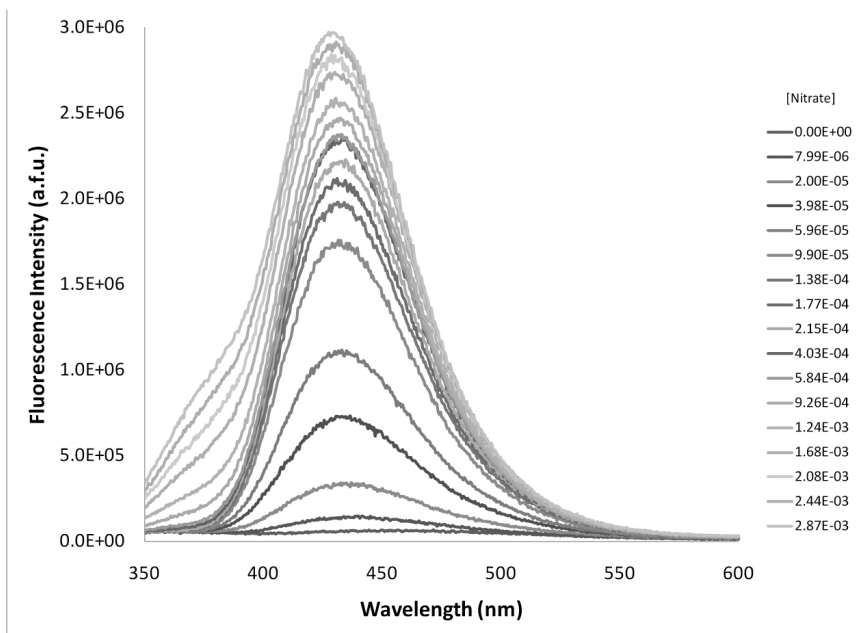


Figure 1: Fluorescence titration ($\lambda_{exc.}$ 310nm) of dansyl chloride ($1 \times 10^{-5}M$) with Bu_4NNO_3

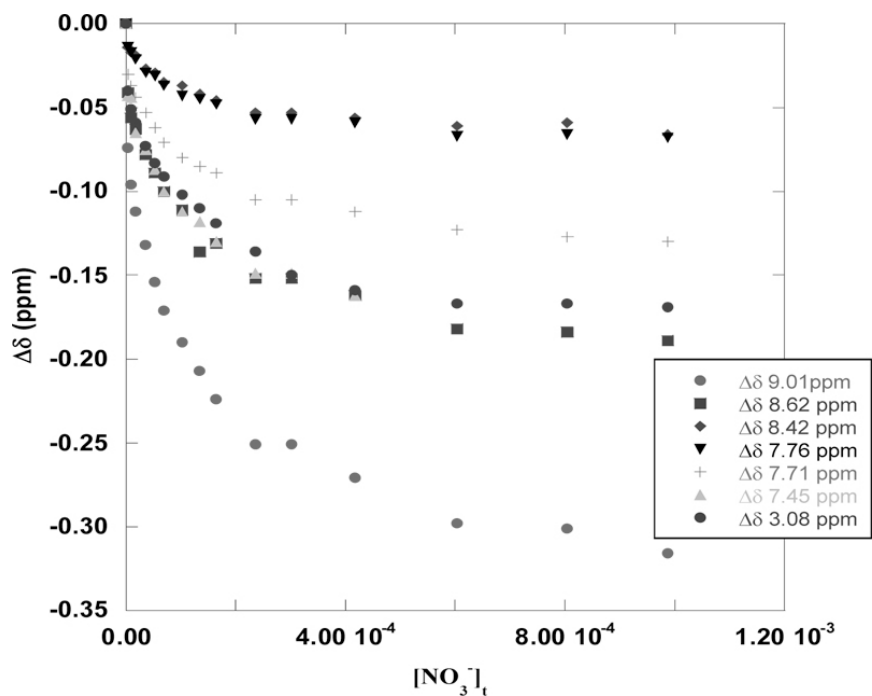


Figure 2: 1H -NMR Chemical shift changes upon titration of dansyl chloride ($5 \times 10^{-4}M$) with Bu_4NNO_3 .

Fluorescence Sensing, Ammonium Nitrate, Dual-Host Extraction