Sensitive and Selective Detection of Cesium via Fluorescence Quenching

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Sensitive and selective detection of cesium via fluorescence quenching

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Herein we report a robust and easy method for detecting cesium metal ion (Cs⁺) in partially aqueous solutions using the fluorescence quenching of 2,4-bis-[4-(N,N-dihydroxyethylamino)phenyl]squaraine. This squaraine dye was found to be both highly sensitive (low limits of detection) and selective (limited response to other metals) for cesium ion detection. The detection is likely based on the metal complexing to the dihydroxyethanolamine moieties, which disrupts the donor-acceptor-donor architecture and leads to efficient quenching.

Cesium, which is found in industrial, medical and nuclear wastes, can cause a number of negative health effects, including cardiovascular disease and gastrointestinal distress. Current methods for detecting cesium in complex environments include atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectroscopy (ICP-MS), and solid state sensors. Fluorescence-based methods have rarely been used for cesium detection, even though such methods have the potential to be both cheaper and non-destructive, and have been used successfully for the many analytes. In one example of fluorescence-based cesium detection, researchers synthesized a substituted calixarene that bound cesium with high affinities, resulting in a significant fluorescence enhancement and a 0.3 μM detection limit. Reported herein is a highly sensitive and selective method for cesium detection that relies on the fluorescence quenching of a near-infrared emitting squaraine fluorophore (compound 1).

Compound 1 was synthesized following literature-reported procedures. The fluorescence response of the squaraine to various metal ions was tested by mixing a squaraine solution in DMSO with aqueous solutions of metal ions, and comparing the fluorescence spectra of the resulting solutions with the squaraine fluorescence spectra in the absence of any metal ion (but in the same DMSO-water ratio). The squaraine solution was made fresh daily due to partial degradation under the experimental conditions.

The addition of 1.0 mM of cesium carbonate led to a significant quenching of the squaraine fluorescence to 7.6% of its initial value, as well as a complete disappearance of the characteristic squaraine absorption band (Figure 1). Even as little as 0.010 mM of cesium carbonate caused the squaraine fluorescence to decrease to 92% of its initial value (red line, Figure 1). Plotting this fluorescence quenching as a function of cesium concentration yielded a plot that rapidly approached saturation at high cesium concentrations (Figure 2).

Fig. 1. The absorbance and fluorescence spectra of compound 1 with increasing amounts of cesium carbonate (0.10 mM compound 1; 650 nm excitation).

Fig. 2. Illustration of the relationship between cesium concentration and fluorescence quenching.
This complete cesium binding was easily detected by visual inspection of the squaraine solution (Figure 3). The addition of 1.0 mM of cesium carbonate rapidly turned the light blue squaraine solution colorless, whereas other common metal ions displayed no measurable color change.

The sensitivity of this method was determined by calculating the limit of detection. Although this limit is typically defined as three times the standard deviation of the background noise (or ten times the standard deviation for quantification limits), in this case that definition led to a value that was effectively zero. Using 30 times the standard deviation of the background noise for these calculations led to a limit of detection of 0.096 µM, which provides an upper boundary for the detection limit. This detection method is more sensitive than previously reported fluorescence-based methods for purely aqueous solutions, as well as for cesium ion detection in mixed solvent systems.

The selectivity of this detection method was determined by screening a wide variety of other metals, including transition metals, alkali metals, and alkali earth metals in a variety of oxidation states. Most of these ions led to no significant changes in the squaraine’s fluorescence spectra (Figure 4).

The mechanism of cesium-induced fluorescence quenching is currently under investigation, but the following conclusions can already be drawn: (a) The lack of any bathochromic or hypsochromic shift in the squaraine fluorescence spectra indicates that metal-induced aggregation is unlikely to be a significant contributing factor; (b) the relatively linear relationship between cesium concentration and fluorescence quenching (for low cesium concentrations) indicates that a well-defined ion-squaraine interaction is occurring; and (c) Job plot experiments do not yield a clear stoichiometry between the metal ion and the squaraine fluorophore.

The observed fluorescence quenching is in line with a literature report of a crown-ether containing squaraine whose fluorescence was quenched in the presence of alkali and alkali earth metals. In that report, the authors concluded that the metal ions caused fluorescence quenching through binding in the crown ether moieties, which disrupted the donor-acceptor-donor nature of the squaraine chromophore. Similarly, in this case we expect that the cesium cation binds strongly to diethanolamine, attenuating its strongly donating character and leading to highly efficient fluorescence quenching.

Conclusions

In conclusion, reported herein is a sensitive and selective method for detecting cesium via fluorescence quenching of a squaraine fluorophore. This detection method has a number of advantages compared to previously-reported systems, including (a) low limits of detection; (b) marked insensitivity to a variety of other common metals; (c) ease of operation; and (d) monitoring of a fluorescent signal in the near-infrared spectral region, which has limited interference from other analytes and will enable detection in complex media. The mechanism of cesium-induced fluorescence quenching and the applicability of this quenching in multiple environments are currently under investigation, and results will be reported in due course.

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Notes and references

† Electronic Supplementary Information (ESI) available: Synthesis of compound 1; detailed procedures for fluorescence quenching experiments and limit of detection experiments, screen of all non-interacting metal ions. See DOI: 10.1039/b000000x/

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