

Electronic Supplementary Information for

Sensitive and selective detection of cesium via fluorescence quenching

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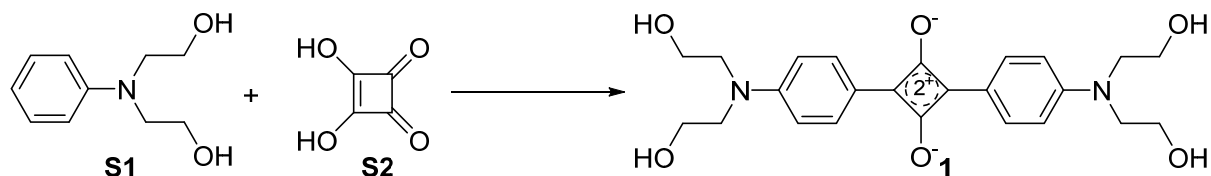
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Materials and Methods

All reagents and solvents were purchased from Sigma Aldrich and were used as received without further purification. ^1H NMR spectra were recorded on a Bruker 300 MHz spectrometer. Fluorescence measurements were recorded on Shimadzu RF 5301 spectrophotometer with a 3 nm excitation slit width and a 3 nm emission slit width. All spectra were integrated vs. wavenumber using OriginPro software.

Synthesis of Compound 1

Compound 1 was synthesized following literature-reported procedures for analogous compounds (see for example *J. Am. Chem. Soc.* **2006**, *128*, 13320)



Phenyldiethanolamine **S1** (0.88 mmol, 160 mg, 2.0 eq.) and squaric acid **S2** (0.44 mmol, 50 mg, 1.0 eq.) were dissolved in a 1:1 mixture of toluene and *n*-butanol. The reaction mixture was equipped with a Dean-Stark trap and condenser, and the reaction mixture was stirred in the dark at reflux overnight. The reaction mixture was cooled to room temperature and then to 0 °C. The precipitate was collected by vacuum filtration and thoroughly dried to yield 19 mg of compound **1** (12.5% yield).

Screen of Other Metals

All non-interacting metals were screened using the following procedure:

All metal salts were dissolved in distilled water to a final concentration of 10 mM. Compound **1** was dissolved in DMSO to a final concentration of 1.0 mM.

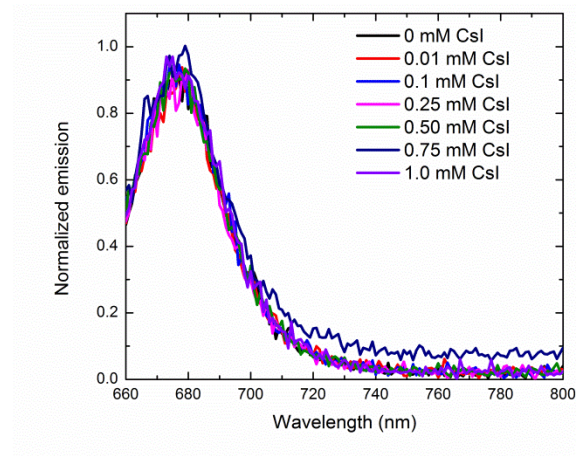
The following solutions were added to a quartz cuvette: 20 μL of the aqueous solution, 980 μL of distilled water, 20 μL of the compound **1** solution, and 980 μL of DMSO. This created a 1:1 water: DMSO solution with final concentrations of $[\text{metal}] = 0.1 \text{ mM}$ and $[\text{compound } \mathbf{1}] = 0.01 \text{ mM}$.

After thorough mixing, the fluorescence spectra were recorded from 650 nm excitation with 3 nm excitation slit width and 3 nm emission slit width.

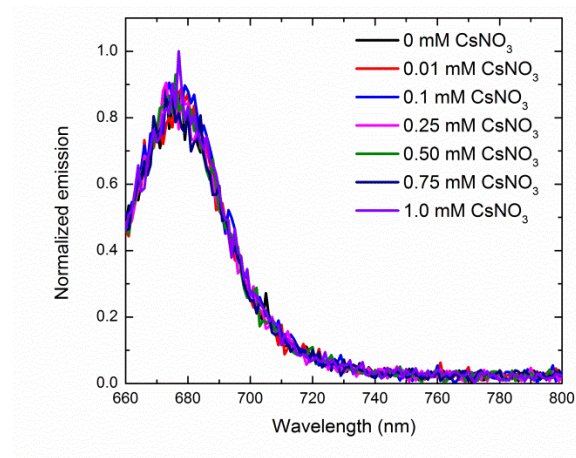
Counterion Effect

The following additional metal salts were screened to probe the effect of the counterion: Cs_2SO_4 , CsNO_3 , CsI , K_2CO_3 , and Na_2CO_3 . None of the cesium salts showed a significant quenching of the squaraine's fluorescence; however, both K_2CO_3 and Na_2CO_3 induced some fluorescence quenching. Summary figures for these salts are shown below.

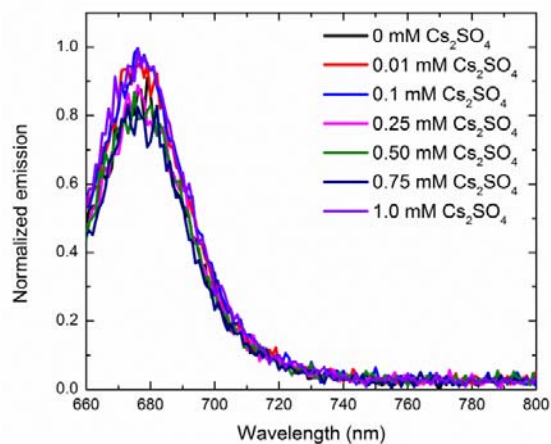
Cesium Iodide:



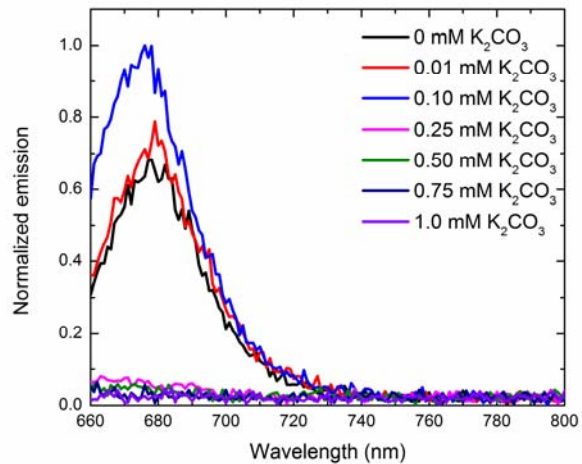
Cesium Nitrate:



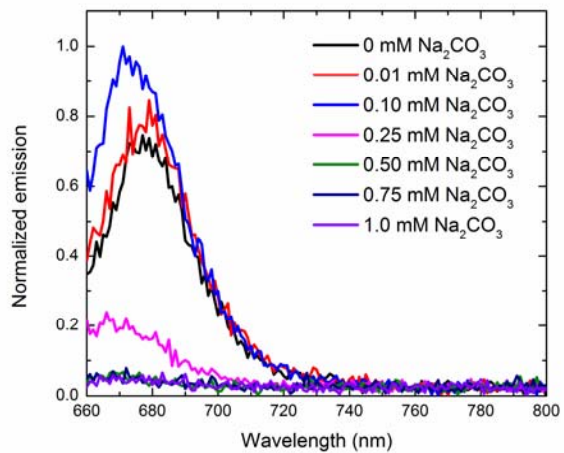
Cesium Sulfate:



Potassium Carbonate:



Sodium Carbonate:



Job Plot Data

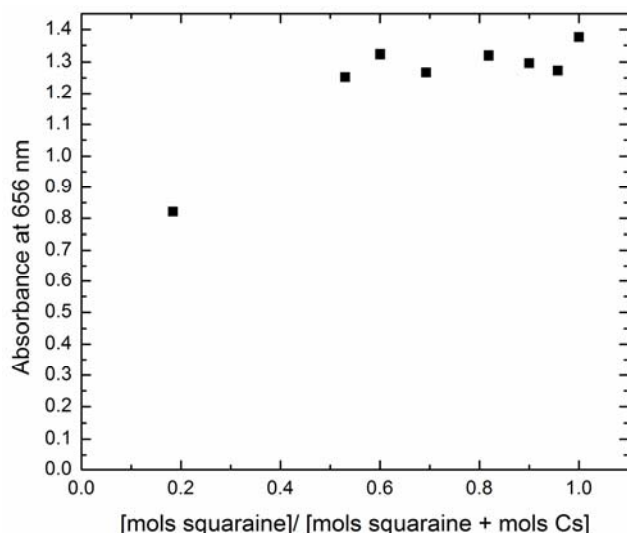
Job plot experiments were conducted as follows:

1. A stock solution of the squaraine (0.01 mg/ mL) in DMSO was formed.
2. 1.25 mL of the stock solution of squaraine was mixed with 1.25 mL of pure water. The absorbance of the solution was measured.
3. 1.25 mL of the stock solution of squaraine was mixed with 1.25 mL of cesium solution A and the absorbance was measured.
4. 1.25 mL of the stock solution of squaraine was mixed with 1.25 mL of cesium solution B and the absorbance was measured.
5. 1.25 mL of the stock solution of squaraine was mixed with 1.25 mL of cesium solution C and the absorbance was measured.
6. 1.25 mL of the stock solution of squaraine was mixed with 1.25 mL of cesium solution D and the absorbance was measured.
7. 1.25 mL of the stock solution of squaraine was mixed with 1.25 mL of cesium solution E and the absorbance was measured.
8. 1.25 mL of the stock solution of squaraine was mixed with 1.25 mL of cesium solution F and the absorbance was measured.
9. 1.25 mL of the stock solution of squaraine was mixed with 1.25 mL of cesium solution G and the absorbance was measured.

Cesium solutions A-G are defined as follows:

	initial conc (M)	initial conc (mM)	final mols delivered	molar ratio
solution A	0.0001	0.1	1.25E-05	4.432624113
solution B	0.00001	0.01	1.25E-06	0.443262411
solution C	0.000001	0.001	1.25E-07	0.044326241
solution D	0.000005	0.005	0.000000625	0.221631206
solution E	0.0000025	0.0025	3.125E-07	0.110815603
solution F	0.00002	0.02	0.0000025	0.886524823
solution G	0.000015	0.015	0.000001875	0.664893617

The results of these experiments were plotted with the [moles of squaraine]/ [moles of squaraine + moles of Cesium] on the X-axis, and the absorbance at 656 nm (the absorption maximum of the squaraine) on the Y-axis:



Details for Limit of Detection Experiments

The limit of detection (LOD) is defined as the lowest concentration of analyte at which a signal can be detected. To determine the limit of detection, the following experiments were conducted:

1. Dilutions of the cesium carbonate stock solution were made to yield the following seven solutions:

Solution number	Initial concentration	Final concentration in squaraine solution
1	0 mM	0 mM
2	1 mM	0.010 mM
3	10 mM	0.10 mM
4	25 mM	0.25 mM
5	50 mM	0.50 mM
6	75 mM	0.75 mM
7	100 mM	1.0 mM

2. 20 μL of each solution was combined with 980 μL of distilled water, 20 μL of the squaraine solution, and 980 μL of DMSO. The solutions were excited at 650 nm and the emission spectra were recorded 6 times for each cesium concentration.

3. All fluorescence emission spectra of the fluorophore were integrated vs. wavenumber, and calibration curves were generated, with the analyte concentration on the X-axis (in mM) and $1-F/F_0$ on the Y-axis, where F = the integrated fluorophore emission at a particular cesium concentration and F_0 = the integrated fluorophore emission in the absence of cesium. The lower cesium concentrations yielded a linear relationship, and the equation for the line was determined.

4. The limit of the blank was taken to be the average of the blank (squaraine emission without cesium) + 30 times the standard deviation of the blank.

5. This value was entered into the equation determined in step 3 (for the Y value), and the corresponding X value was determined. This value provided the LOD in mM.