Supporting information

A Selective and Sensitive Chromogenic and Fluorogenic Detection of a Sulfur Mustard Simulant

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Experimental details

General

Fluorescence measurements were carried our using a Photon Technology International Quanta Master spectrofluorimeter with an 814 photomultiplier detection system using a 75W xenon short arc lamp. All chemicals and reagents were bought from Aldrich, Fluka Fisher Scientific and used without further purification.

Caution:CEES *is a blistering agent and potential vesicant so it should be handled inside the fuming hood by wearing hand gloves.*

Procedure for the Naked eye detection of CEES using 1and SQ Solutions

A **1** (0.1 mg, 0.4 mM) was dissolved in 1 mL of methanol containing 3.0 equivalents of K_2CO_3. A solution of **SQ** dye at 14 μM was dissolved in chloroform using sonicator for 1hr. 15 μL of **1** solution was able to bleach 1.2 mL of **SQ** solution instantaneously. A solution of **CEES** (0.11 mg, 0.89 mM) was allowed to react with a **1** (0.4 mM). 25 μL (200 μM of **CEES**) of this solution was treated with 1.2 mL of **SQ** dye solution. These vials were photographed.

Fluorescence Titrations of SQ with thiol in Chloroform

A stock solution of **SQ** (2.65 μM) was prepared in $CHCl_3$. A separate stock solution of **1** (0.4 mM)) and 3.0 equivalents of K_2CO_3 was also prepared in methanol. This solution at 0.2 mM (containing **SQ** was used for titration. A 2 mL aliquot of the **SQ** solution was transferred to the fluorescence cuvette and the initial fluorescence was measured. The titration was performed by adding successive 50μL aliquots of the **1** solution to the cuvette and recording the spectrum.

Fluorescence Titrations of SQ with the solution of CEES treated with 1 (quantitative analysis)

A stock solution of **SQ** (2.65 μM) was prepared in $CHCl_3$. A separate stock solution of **1** (0.4 mM)) and 3.0 equivalents of K_2CO_3 was also prepared in methanol. Increasing amount of 20 μM of **CEES** the 220

μM with respect to **1** was reacted at 80 ^{o}C for a minute. Each time, this solution was titrated with 2 mL of stock solution of **SQ** (2.65 μM) in a fluorescence cuvette and the fluorescence was measured.

Calibration curve

The fluorescence response of **SQ** (2.65 μM) with various concentrations of **CEES** starting from 20 μM to 220 μM was measured in chloroform. In a similar manner as described above, **1** (0.2 mM) was allowed to react with different concentrations of **CEES** (from 20 μM to 220 μM) at 80 ^{o}C for one minute, followed by the addition of **SQ**. The magnitude of fluorescence intensity depends on the concentration of **CEES**. The results indicate that saturation point was achieved with the addition of 164 μM of **CEES**. Ideally, it should have been 200 μM of **CEES.** We anticipated that some portion of **1** is getting converted into disulfide under given reaction conditions. Consequently, it is not able to react with CEES, thus leaving it unreacted in solution, which leads to the saturation point at 164 μM. In order to achieve a hypothetical saturation point at 200 μM. We have multiplied all the x-axis values by a factor 1.25 and then plotted the calibration curve. This exercise would scale it to 200 μM of the analyte.

Chromogenic detection of CEES on surfaces using SQ

CEES (8 μL) was placed on a surface and absorbed by filter paper. This paper was allowed to react with a solution of **1** (1mg, 4.09 mM) in 1 mL of methanol containing 3.0 equivalent of K_2CO_3 at 80 ^{o}C for 1 min. The solution was cooled to room temperature and then 25 μL of it was mixed with a solution of **SQ** dye (1.2 mL) at 14 μM in chloroform. Same procedure was followed when there is no mustard on the paper. Both these vials were photographed as shown in figure 1.

Figure 1. Detection of **CEES** on paper left (no **CEES**) and right (with **CEES**)

Chromogenic detection of CEES in soil using SQ

2.0 g of soil was mixed with **CEES** in diethyl ether (2mL) and was allowed to stand for 20 min. The solvent from soil sample was evaporated by nitrogen blow down. **CEES** spiked soil sample was reacted

with a solution of **1** (1.0 mg, 4.09 mM) in 1 mL of methanol containing 3.0 equivalent of K_2CO_3 at 80 ^oC for 1 min. The solution was cooled to room temperature, centrifuged and then mixed with a solution of **SQ** dye (1.2 mL) at 14 μM in chloroform. This solution was then photographed.

Chromogenic detection of CEES in gas phase surfaces using SQ

1 (1mg, 4.09 mM) was dissolved in 1 mL of methanol containing 3.0 equivalent of K_2CO_3. 200 μL of it was sprayed over (1" X 2.5") silica coated TLC and it was dried by blowing of air. The treated TLC plate was cut equally into two parts; one part was used for comparison and another part was kept in vapor generation chamber (Figure 2). The vapor generation chamber was placed on the hot place by providing 80 ^oC at chamber surface. **CEES** (10 μL) was placed on the heated surface of chamber. Air was passed through the chamber for 3 min. This pretreated TLC plate was taken out from chamber and drop of **SQ** (30 μM) was placed on the both the TLC plates (treated with and without **CEES**). Both the TLC plates were photographed together.

Figure 2. Gas generation chamber