

Pattern-based recognition of thiols and metals

using a single squaraine indicator

Supporting Material

Experimental details

General

Single-cuvette fluorescence measurements were made using a Photon Technology International QuantaMaster spectrofluorimeter. 96-well plate fluorescence intensity data was gathered using a Biotek Synergy 2 Multi-detection Microplate Reader. All chemicals and reagents were bought from Aldrich or Fluka and used without further purification. DMSO was degassed *via* displacement with N₂ and dried over molecular sieves for at least 6 hours prior to use. Dilutions and aliquots were performed using Fisher Brand Finnpiquette micropipettes calibrated by mass.

Fluorescence Titrations of SQ in DMSO with thiol

A stock solution of **SQ** (1.27×10^{-4} M) was prepared by dissolving **SQ** (0.6 mg) in 10 mL 1:9 CH₂Cl₂/DMSO. This stock solution was then used to prepare a 2×10^{-6} M solution of **SQ** using pure DMSO. A separate stock solution of propanethiol (2.87×10^{-2} M) and 1 eq. of Hunig's base was also prepared in pure DMSO. This second solution was then used to prepare a 4×10^{-5} M solution of propanethiol. 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 10 μL aliquots of the propanethiol solution to the cuvette and recording the spectrum 5 minutes after each aliquot injection.

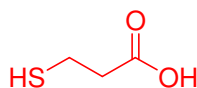
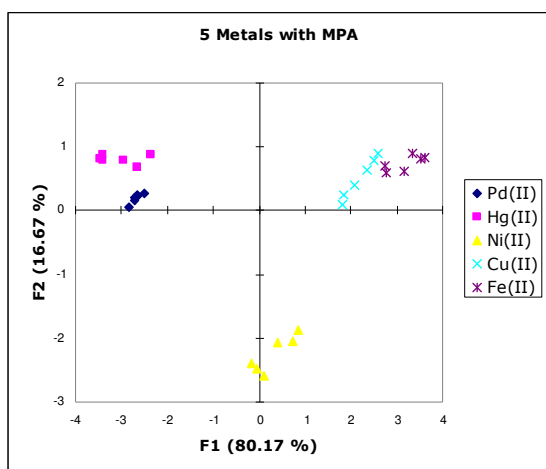
Fluorescence Titrations of SQ:thiol complex in DMSO with metals.

A 2×10^{-6} M solution of **SQ** was prepared in DMSO analogously to the previous method. A separate solution of 4×10^{-4} M propanethiol and 1 eq Hunig's base was also prepared. The palladium(II) nitrate stock solution was prepared by dissolving 6.7 mg of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 10 mL DMSO. This solution was then diluted to make a 4×10^{-5} M Pd(II) titrant solution. A 2 mL aliquot of the **SQ** solution was transferred to the fluorescence cuvette and the initial fluorescence was measured. **SQ**:thiol complex formation was achieved by adding 10 μL aliquot of thiol solution to the cuvette and decoloration was completed after 15 minutes. The titration was performed by administering successive 10 μL aliquots of the Pd(II) solution to the **SQ**:thiol complex and spectra were recorded 5 minutes after each aliquot injection.

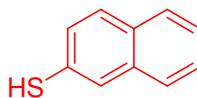
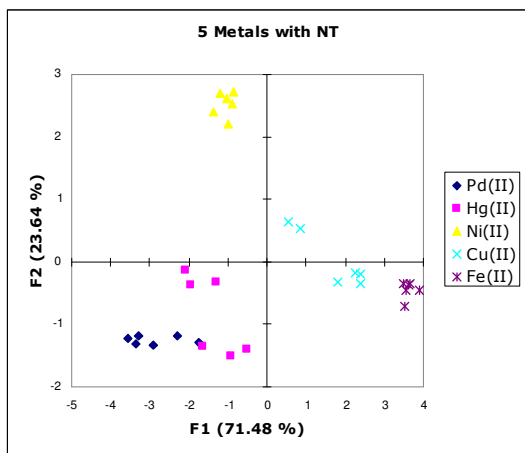
96-well plate experiments

All the experiments were carried out using three standard 96 well assay plates having 8 rows and 12 columns. First 5 rows of plates were loaded with 200 μL of 2×10^{-6} M solution of squaraine in DMSO. To rows 1-5 50 μL of 8×10^{-6} M thiol solutions 1 to 5 were added. The first 6 columns of the plate containing **SQ**:thiol complexes were then treated with 50 μL of 8×10^{-6} M solution of the first metal, whereas the last 6 columns were treated with 50 μL of 8×10^{-6} M solution of the second metal. This process was

repeated with metals 3, 4 and 5. All of these analytes were added using micropipetting systems. The 96 well assay plate was then submitted to measurements of fluorescence intensity. The fluorophore solutions were excited using a tungsten light source with a 645/15 bandwidth filter. The emitted radiation was selected using a 680/30 bandwidth filter.



Pattern based recognition of five metals with 3-mercaptopropionic acid (**MPA**).



Pattern based recognition of five metals with naphthalene thiol (**NT**).