

Contents

1. Synthesis and characterisation of new compounds

2. X-ray crystallography

3. Qualitative titrations

4. Quantitative titrations

5. Control Experiments

6. ^1H NMR displacement experiments

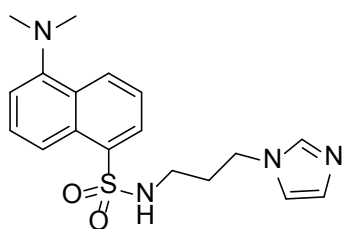
7. References

Commercially available solvents and chemicals were used without further purification unless otherwise stated. Where dry solvents were used, they were degassed with nitrogen, dried by passing through an MBraun MPSP-800 column and then used immediately. Triethylamine was distilled from and stored over potassium hydroxide. Water was deionised and microfiltered by using a Milli-Q Millipore machine. Routine 300 MHz NMR spectra were recorded on a Varian Mercury 300 spectrometer, ^1H NMR operating at 300 MHz, ^{13}C at 75.5 MHz. All 500 MHz ^1H Spectra and all ^1H NMR titrations were recorded on a Varian Unity Plus 500 spectrometer. All chemical shift (δ) values are given in parts per million.

Low resolution mass spectra were recorded on a Micromass LCT Premier XE spectrometer. Accurate masses were determined to four decimal places using Bruker μTOF and Micromass GCT spectrometers. For the mustard simulant (CEMS) UV/visible experiments were carried out on a PG instruments T60U spectrometer at 293 K and luminescence experiments were carried out on Varian Cary-Eclipse spectrophotometer. For sulphur mustard agent (HD) UV/visible experiments were carried out on a StellarNet SL5-DH Deuterium-halogen light source linked via fibre optics and an in-line cuvette holder to a StellarNet Blue Wave UV/vis spectrometer at 293 K and luminescence experiments were carried out on Horiba Jobin Yvon Fluoromax-4 Spectrofluorimeter. For transmission electron microscopy (TEM), a suspension

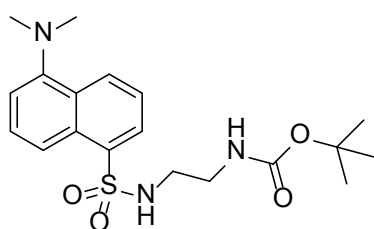
of nanoparticles was allowed to air dry onto a carbon film supported by a TEM copper grid and viewed in a FEI CM12 TEM operating at 80 kV. Images were acquired using a Keenview G2 digital camera and particle size distribution determined using Image Pro Plus v. 6.3 software (Media Cybernetics).

Synthesis of Dansylimidazole 1



N-Aminopropyl imidazole (0.32 g, 2.55 mmol) and Et₃N (0.77 g, 7.60 mmol) were dissolved in dry CH₂Cl₂ (50 mL) at 0°C and stirred prior to the dropwise addition of dansyl chloride (0.75 g, 2.80 mmol) in 75 mL dry CH₂Cl₂. The reaction was allowed to warm to ambient temperature, and was further stirred for one hour. Water (30 mL) was added, the organic layer separated, dried over MgSO₄ and the solvent removed *in vacuo*. Purification by column chromatography (silica; MeCN/ Et₂O, 3:1) gave **1** as a yellow oil (0.70 g, 77 %). ¹H NMR (300 MHz, CDCl₃) δ 8.57 (2H, m, ArH), 8.25 (2H, m, ArH), 7.57 (2H, m, ArH), 7.27 (1H, s, ImH), 7.20 (1H, m, ImH), 6.98 (1H, s, ImH), 3.91 (2H, t, ³J = 6.7 Hz, CH₂), 2.90-2.83 (10H, m, CH₃, CH₂CH₂N); ¹³C NMR (75 MHz, CDCl₃) δ 151.9, 148.7, 136.7, 134.0, 129.4, 128.4, 128.1, 123.0, 118.3, 118.2, 115.1, 115.0, 45.7, 45.1, 39.5, 29.4; HR-ESMS: *m/z* calc. for [M + H]⁺ 359.1542 found 359.1552.

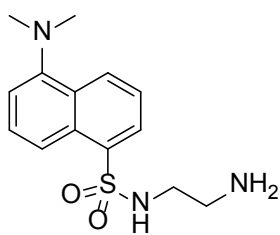
Synthesis of BOC-protected Dansylamine 2a



N-Boc-ethylenediamine (1.07 g, 6.69 mmol) and Et₃N (1.13 g, 11.1 mmol) were dissolved in dry CH₂Cl₂ (100 mL) at 0°C and stirred prior to the dropwise addition of dansyl chloride (1.50 g, 5.57 mmol) in 75 mL dry CH₂Cl₂. The reaction was allowed to warm to ambient temperature, and was further stirred for one hour. Water (30 mL)

was added, the organic layer separated, dried over MgSO_4 and the solvent removed *in vacuo*. Purification by column chromatography (silica; $\text{CH}_2\text{Cl}_2/\text{MeOH}$, 98:2) gave **2a** as a yellow oil (1.50 g, 66 %). ^1H NMR (300 MHz, CDCl_3) δ 8.55 (1H, d, $^3J = 8.7$ Hz, ArH), 8.29-8.21 (2H, m, ArH), 7.61-7.48 (2H, m, ArH), 7.19 (1H, d, $^3J = 6.6$ Hz, ArH), 5.21 (1H, br.s, NH), 4.73 (1H, br.s, NH), 3.19-3.11 (2H, m, NHCH_2), 3.04-2.96 (2H, m, NHCH_2), 2.89 (6H, s, NCH_3), 1.39 (9H, s, ^tBu); ^{13}C NMR (75 MHz, CDCl_3) δ 156.4, 151.8, 134.7, 130.3, 129.8, 129.5, 128.4, 123.1, 118.8, 115.1, 79.3, 45.3, 43.4, 40.2, 28.3; HR-ESMS: m/z calc. for $[\text{M} + \text{Na}]^+$ 416.1614 found 416.1609.

Synthesis of Dansylamine **2**



Compound **2a** (1.37 g, 3.49 mmol) was dissolved in CH_2Cl_2 (20 mL). Trifluoroacetic acid (5 mL) was added dropwise and stirred at ambient temperature for 18 hours. The reaction was basified with sat. $\text{NaHCO}_3(\text{aq})$, extracted with CH_2Cl_2 (3×20 mL) and dried over MgSO_4 . Purification by column chromatography (silica; $\text{MeOH}/25\% \text{NH}_4\text{OH}(\text{aq})$, 9:1) gave **2** as a brown solid (0.84 g, 81 %). ^1H NMR (300 MHz, CDCl_3) δ 8.53 (1H, d, $^3J = 9.0$ Hz, ArH), 8.32-8.21 (2H, m, ArH), 7.60-7.48 (2H, m, ArH), 7.18 (1H, d, $^3J = 7.8$ Hz, ArH), 2.96-2.89 (4H, m, NHCH_2 , NH_2), 2.88 (6H, s, NCH_3), 2.74 (2H, t, $^3J = 5.7$ Hz, CH_2NH_2); ^{13}C NMR (75 MHz, CDCl_3) δ 152.0, 134.7, 130.4, 129.6, 128.4, 123.2, 118.7, 115.2, 45.4, 40.9; HR-ESMS: m/z calc. for $[\text{M} + \text{H}]^+$ 294.1271 found 294.1259.

General Procedure for Synthesis of Gold Nanoparticles

H[AuCl₄] (100 mg, 0.29 mmol) was dissolved in H₂O (20 mL). Aliquat336 (130 mg) was dissolved in toluene (20 mL). The two solutions were combined and stirred vigorously for 10 minutes. The aqueous layer was discarded and the organic phase transferred cooled to 0°C. The dansyl ligand (3 eq.) was dissolved in CH₂Cl₂ (20 mL) and added to the cooled toluene solution. NaBH₄ (60 mg, 1.47 mmol) was dissolved in H₂O (5 mL) and added dropwise at 0°C. The reaction mixture was stirred for two hours at ambient temperature after which the CH₂Cl₂ was removed *in vacuo* and the remaining solution washed with H₂O (3 × 50 mL). The solvent volume was concentrated *in vacuo* and MeOH (100 mL) was added. Filtration and washing with copious MeOH afforded the nanoparticles as a dark solid.

Au·1

CHNS Analysis Found C, 10.5 ; H, 1.2 ; N, 2.3; S, 1.4; UV-vis (CHCl₃) 348, 529; TEM mean diameter 3.1 nm (± 0.7, n = 104)

Au·2

CHNS Analysis Found C, 7.9; H, 0.9; N, 1.8; S, 1.5; UV-vis (CHCl₃) 342, 524; TEM mean diameter 3.2 nm (±0.7, n = 104)

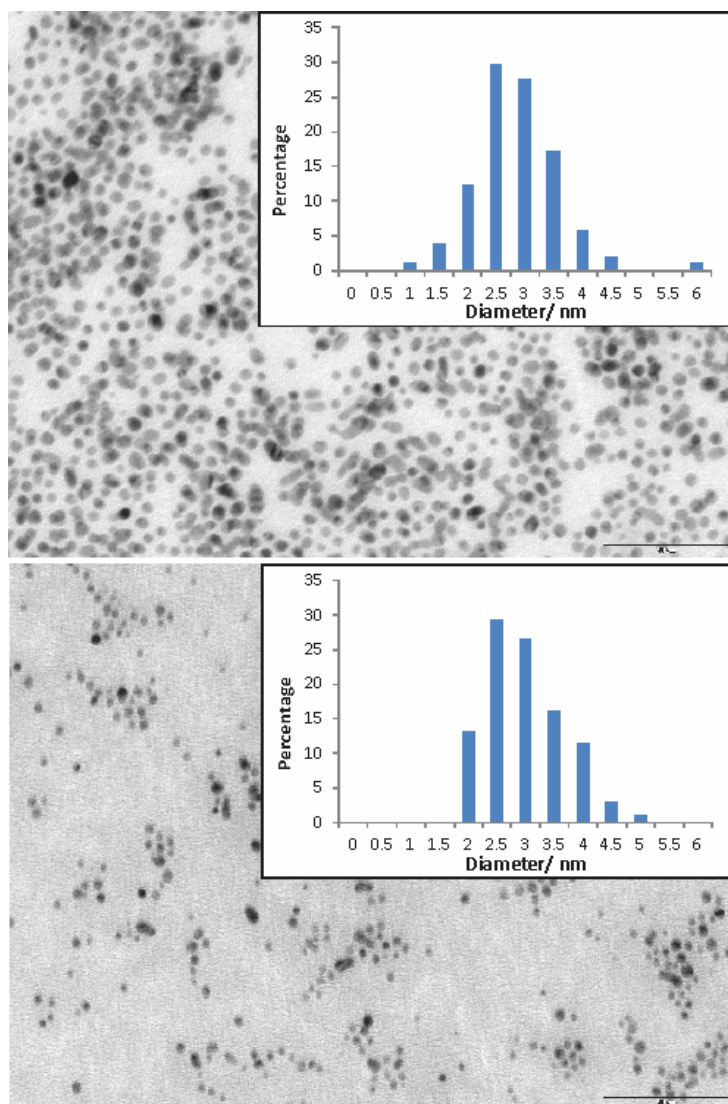


Figure S1: TEM images with histograms inset of **Au-1** (top) and **Au-2** (bottom)

Crystal Structure Data Experimental

Dansylamine **2**. Moiety Formula $C_{14}H_{19}N_3O_2S$; $M = 293.39$; orthorhombic space group $P2_1cn$; green; $a = 8.0889(2) \text{ \AA}$, $b = 11.4745(3) \text{ \AA}$, $c = 15.4252(5) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 1431.71(7) \text{ \AA}^3$; $T = 150 \text{ K}$; $\mu = 0.232 \text{ mm}^{-1}$. $wR = 0.357$; $GooF = 0.89$. Data were collected on the nonius KappaCCD with a graphite monochromator under an open flow of N_2 gas at 150 K .¹ The structure solved with SUPERFLIP,² and refined on F_2 with CRYSTALS.³ All non-hydrogen atoms were modelled with anisotropic displacement parameters, while hydrogen atoms were added geometrically and constrained in further refinement using a riding model.

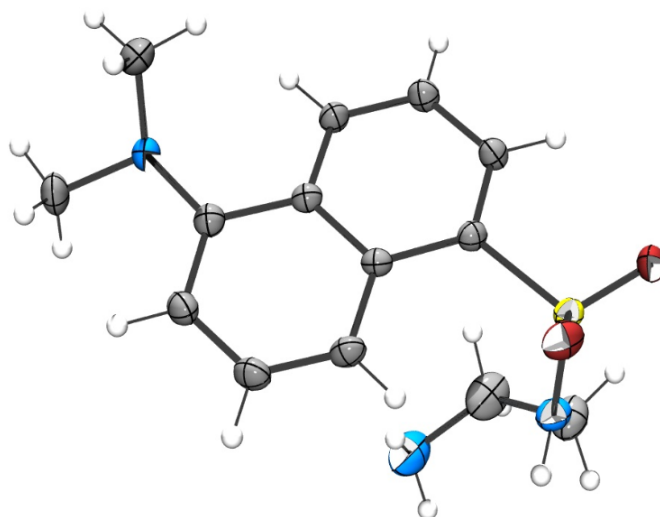


Figure S2: *Crystal structure of dansylamine 2. Thermal ellipsoids displayed at 50% probability*

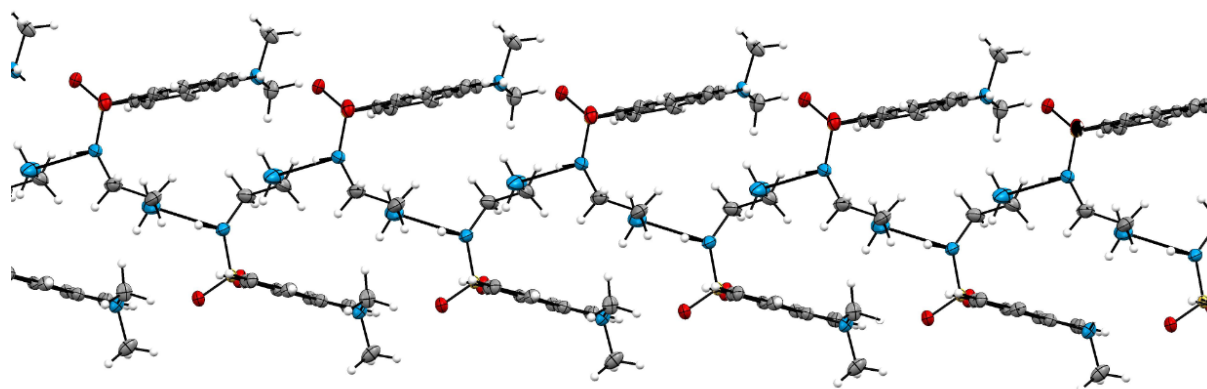


Figure S3: *Solid state packing of dansylamine 2. Hydrogen bonding between primary and amine and sulphonamide*

Titration Protocol

Qualitative Titrations

A 2.5 mL solution of GNPs (0.04 g/mL) was used. 50 μ L of analyte was added to a 2.5 mL solution of the GNPs and the fluorescence and UV-vis spectra monitored directly after addition and at five (fluorescence) or thirty minute (UV-vis) intervals thereafter.

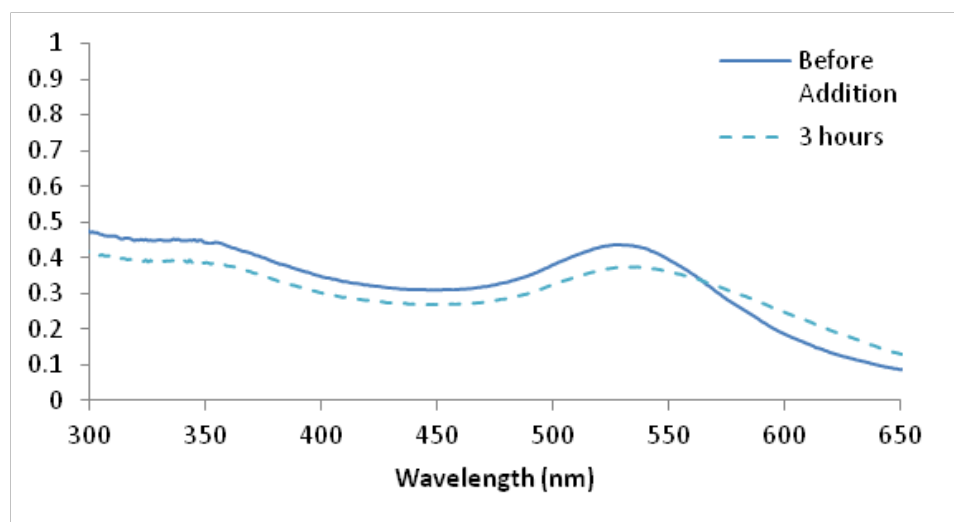


Figure S4: Change in UV-vis spectrum of **Au-1** after 3 hours upon addition of (2-chloroethyl)(methyl)sulphide (CEMS)

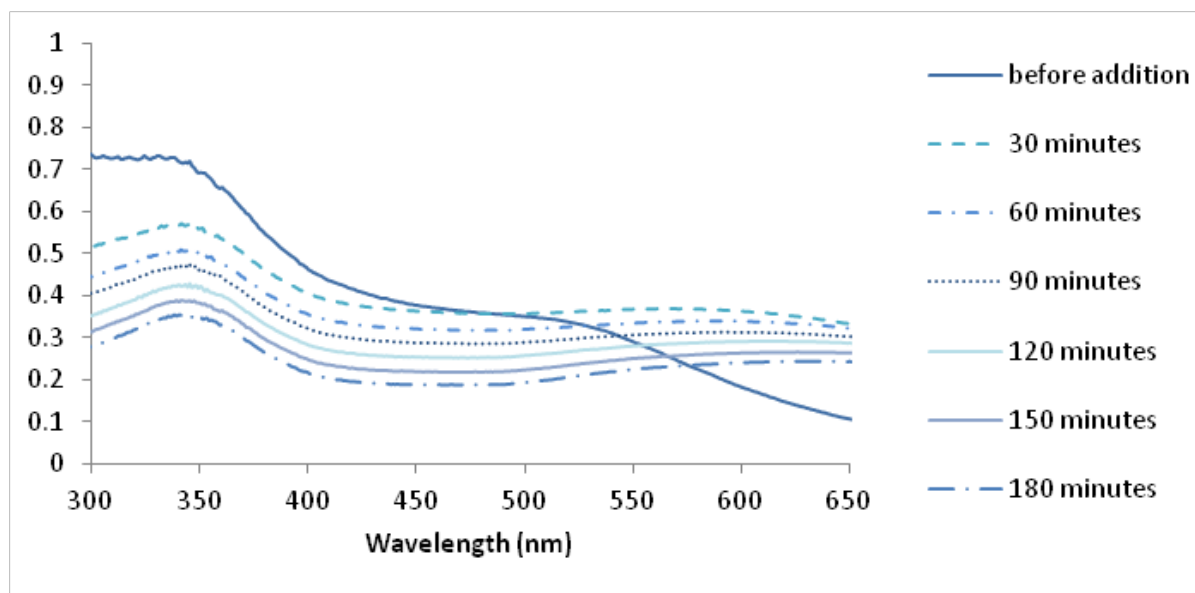


Figure S5: Change in UV-vis spectrum of **Au-2** upon addition of (2-chloroethyl)(methyl)sulphide (CEMS)

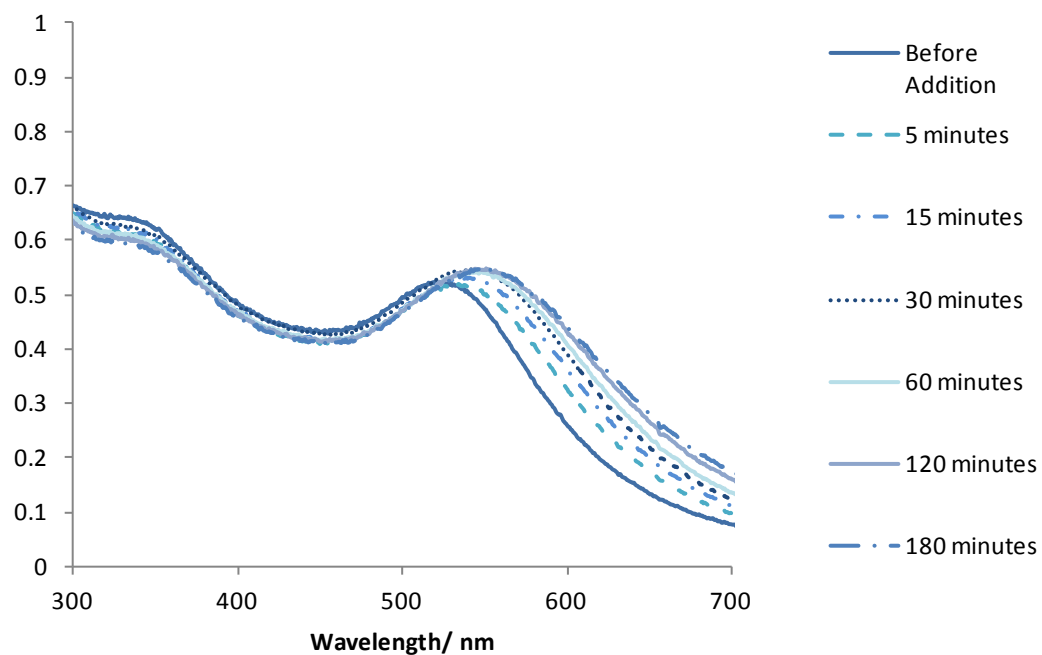


Figure S6: Change in UV-vis spectrum of **Au-1** upon addition of bis(2-chloroethyl)sulphide
(HD)

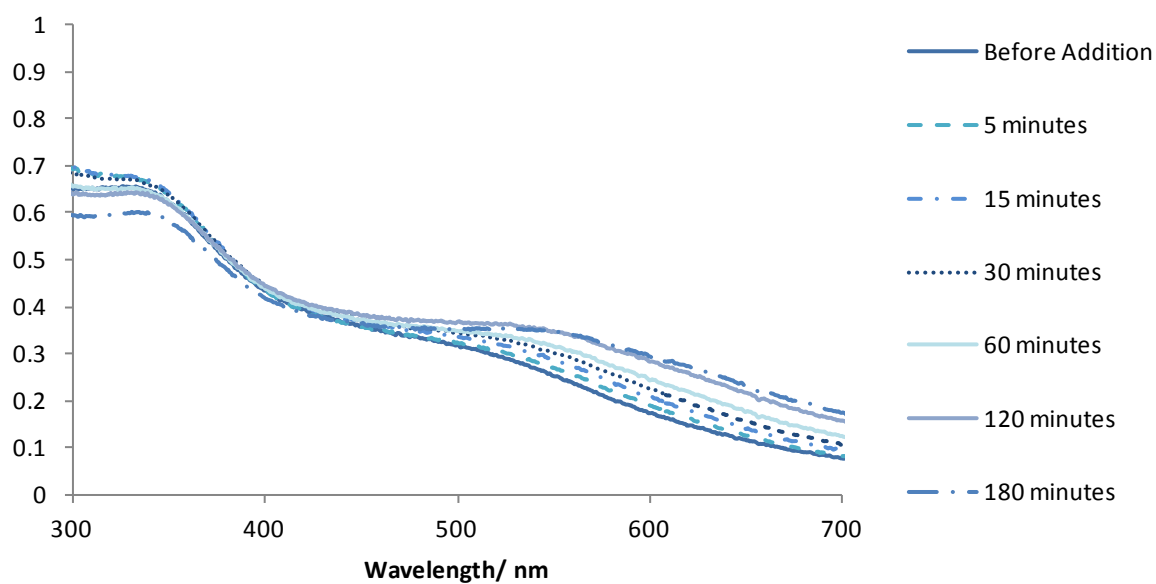


Figure S7: Change in UV-vis spectrum of **Au-2** upon addition of bis(2-chloroethyl)sulphide
(HD)

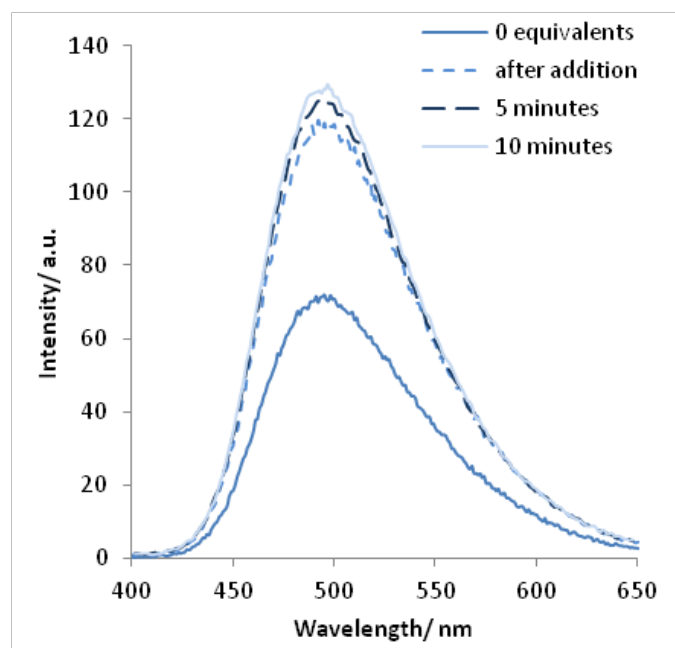


Figure S8: Change in emission intensity of **Au-1** upon addition of (2-chloroethyl)(methyl)sulphide (CEMS) ($\lambda_{ex} = 345$ nm)

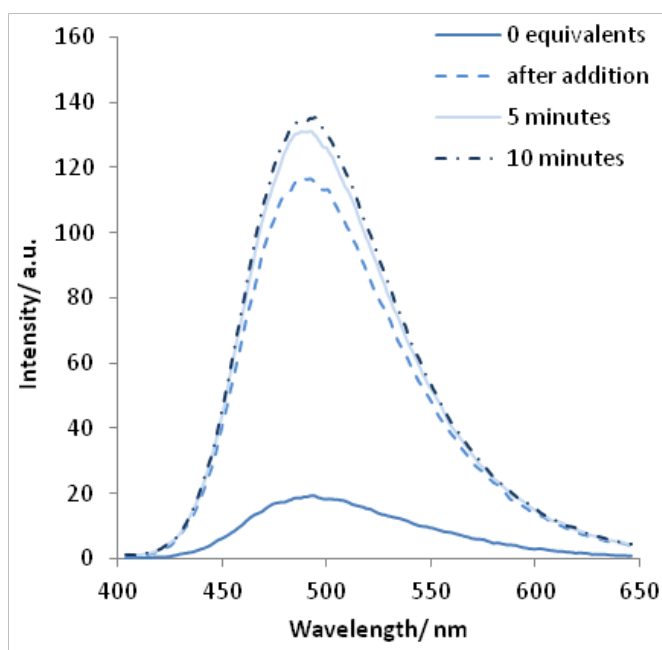


Figure S9: Change in emission intensity of **Au-2** upon addition of (2-chloroethyl)(methyl)sulphide (CEMS) ($\lambda_{ex} = 345$ nm)

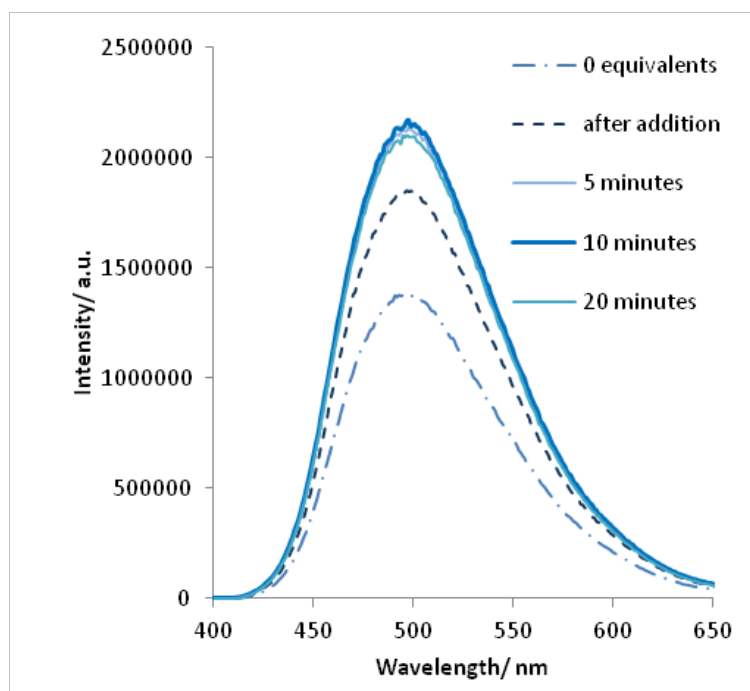


Figure S10: Change in emission intensity of **Au-1** upon addition of bis(2-chloroethyl)sulphide (HD) ($\lambda_{ex} = 345\text{ nm}$)

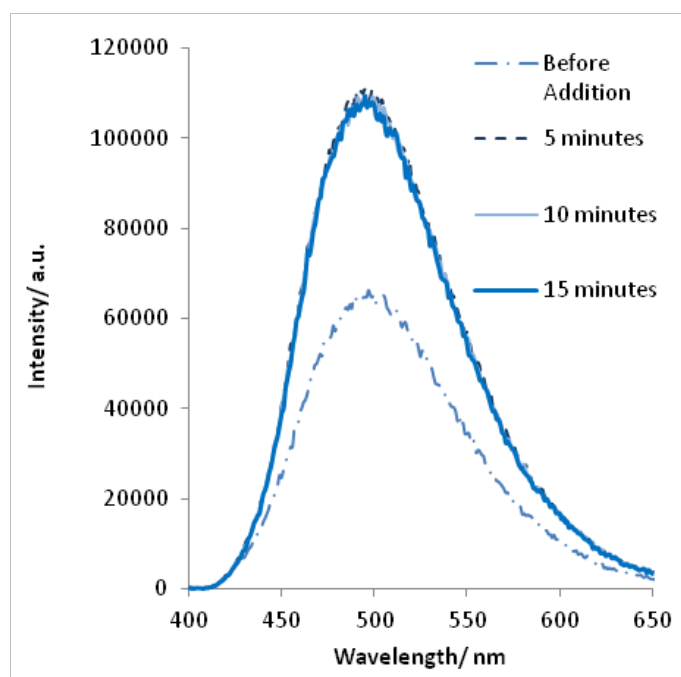


Figure S11: Change in emission intensity of **Au-2** upon addition of bis(2-chloroethyl)sulphide (HD) ($\lambda_{ex} = 345\text{ nm}$)

Quantitative Titrations

A 2.5 mL solution of GNPs (0.04 g/mL) was used. The emission intensity at 501 nm of the GNPs was monitored for seventeen titration points (for 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0 and 10.0 equivalents of analyte added). A chloroform solution of the analyte was added with 2 μ L corresponding to 0.2 molar equivalents of dansyl ligand. The emission intensity was allowed to stabilise for five minutes preceding the recording of the emission spectra. Association constants were calculated using the SPECFIT⁴ program assuming a 1:1 binding model.

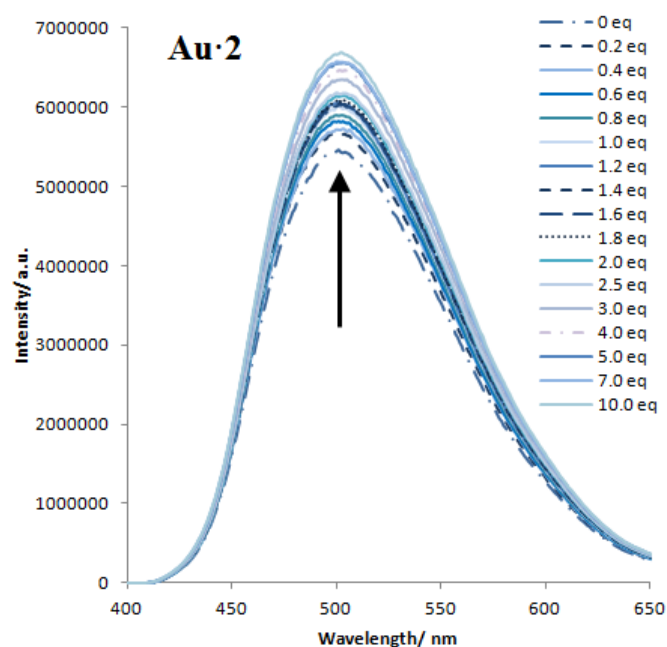


Figure S12: Change in emission intensity at 501 nm of **Au-2** upon titration of bis(2-chloroethyl)sulphide (HD) ($\lambda_{ex} = 345$ nm)

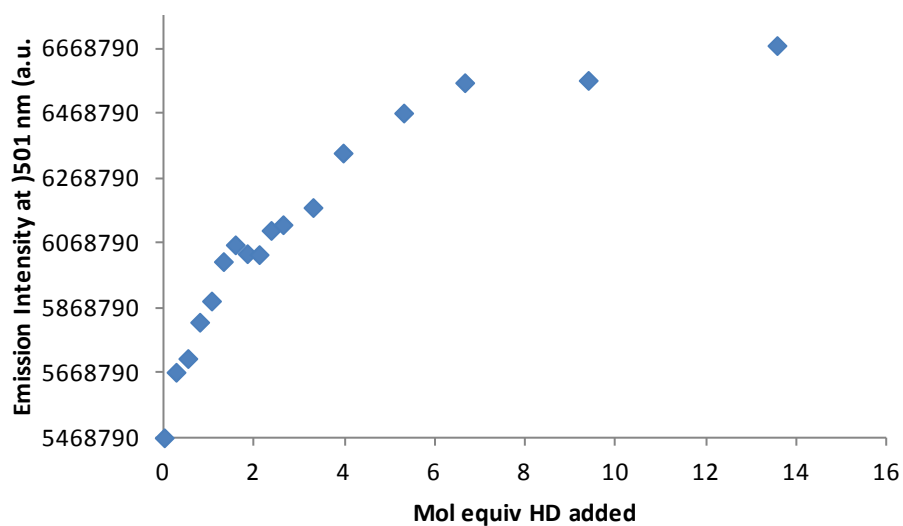


Figure S13: Corrected binding curve for the change in emission intensity at 501 nm of **Au·2** upon titration of bis(2-chloroethyl)sulphide (HD) ($\lambda_{ex} = 345$ nm)

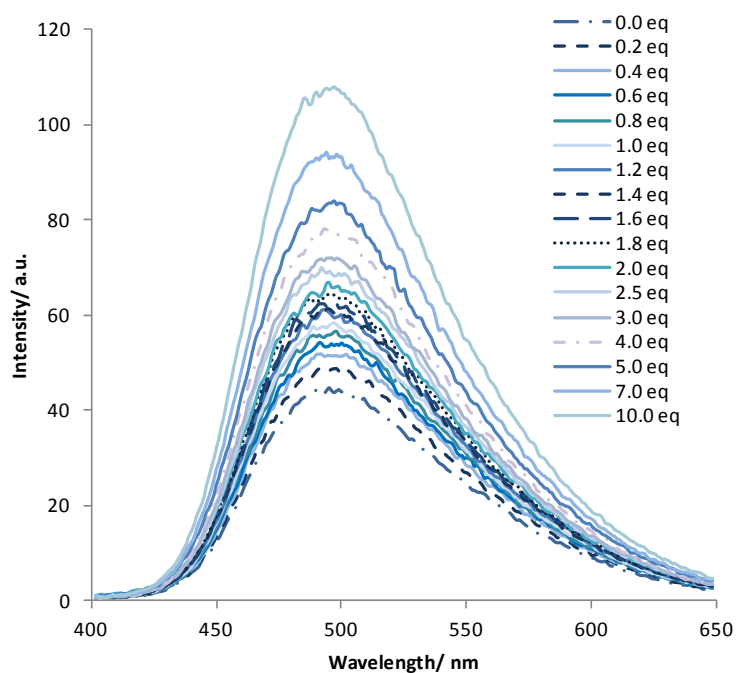


Figure S14: Change in emission intensity at 501 nm of **Au·2** upon titration of (2-chloroethyl)(methyl)sulphide (CEMS) ($\lambda_{ex} = 345$ nm)

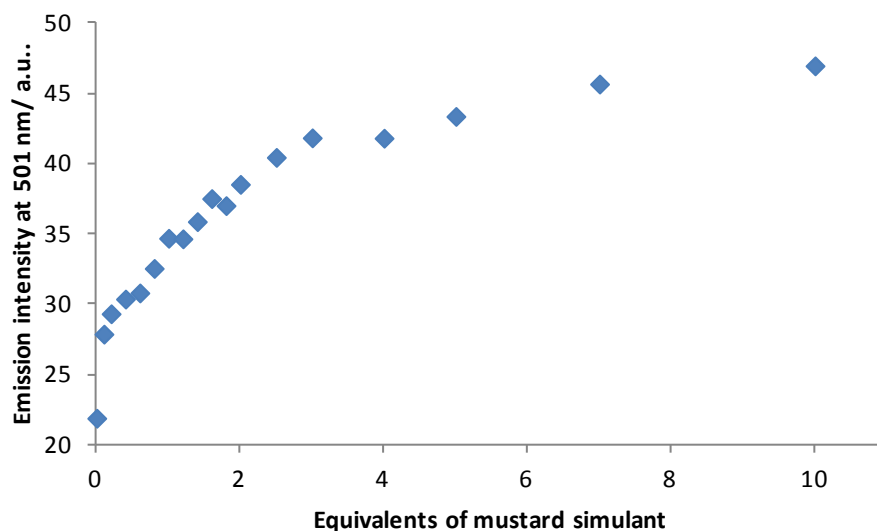


Figure S15: Corrected binding curve for the change in emission intensity at 501 nm of **Au-2** upon titration of (2-chloroethyl)(methyl)sulphide (CEMS) ($\lambda_{ex} = 345$ nm)

Qualitative Control Experiments

A solution of GNPs (0.04 g/mL) was used. 50 μ L of analyte was added to a 2.5 mL solution of the GNPs and the fluorescence spectra monitored directly after addition and at five intervals thereafter.

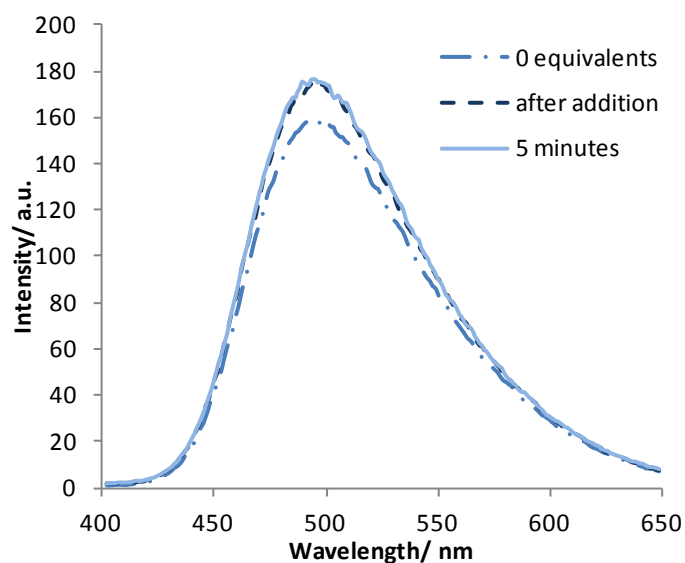


Figure S16: Change in emission intensity of **Au-1** upon addition of octan-1-ol ($\lambda_{ex} = 345$ nm)

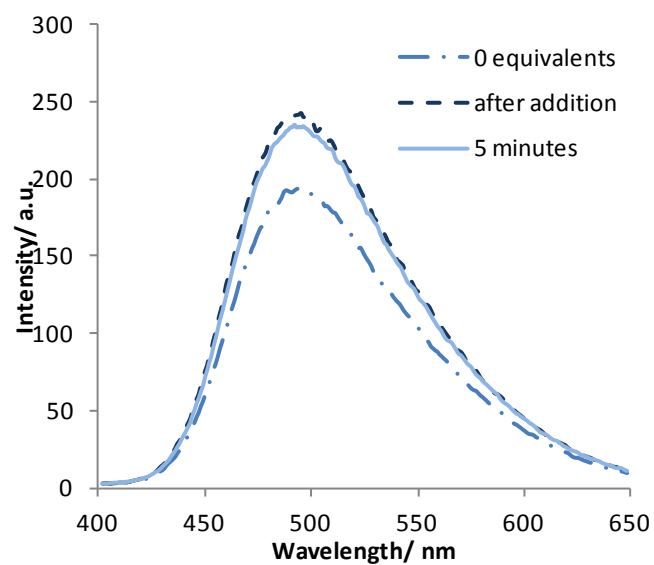


Figure S17: Change in emission intensity of **Au-2** upon addition of octan-1-ol ($\lambda_{ex} = 345$ nm)

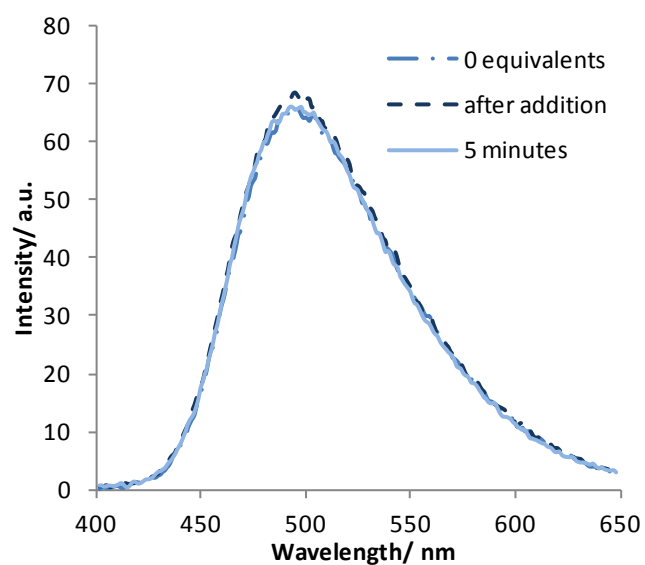


Figure S18: Change in emission intensity of **Au-1** upon addition of dibutylether (λ_{ex}
 $= 345$ nm)

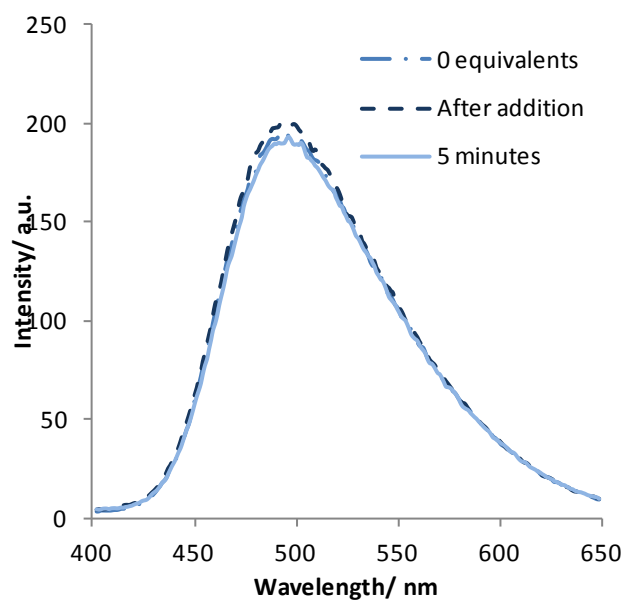


Figure S19: Change in emission intensity of **Au-2** upon addition of dibutylether

$$(\lambda_{ex} = 345 \text{ nm})$$

¹H NMR Experiments

3.5 mg of **Au-1** was dissolved in 500 μL of CDCl_3 and the ¹H NMR spectrum recorded. Ten equivalents of CEMS was added and the spectra recorded after 30 minutes.

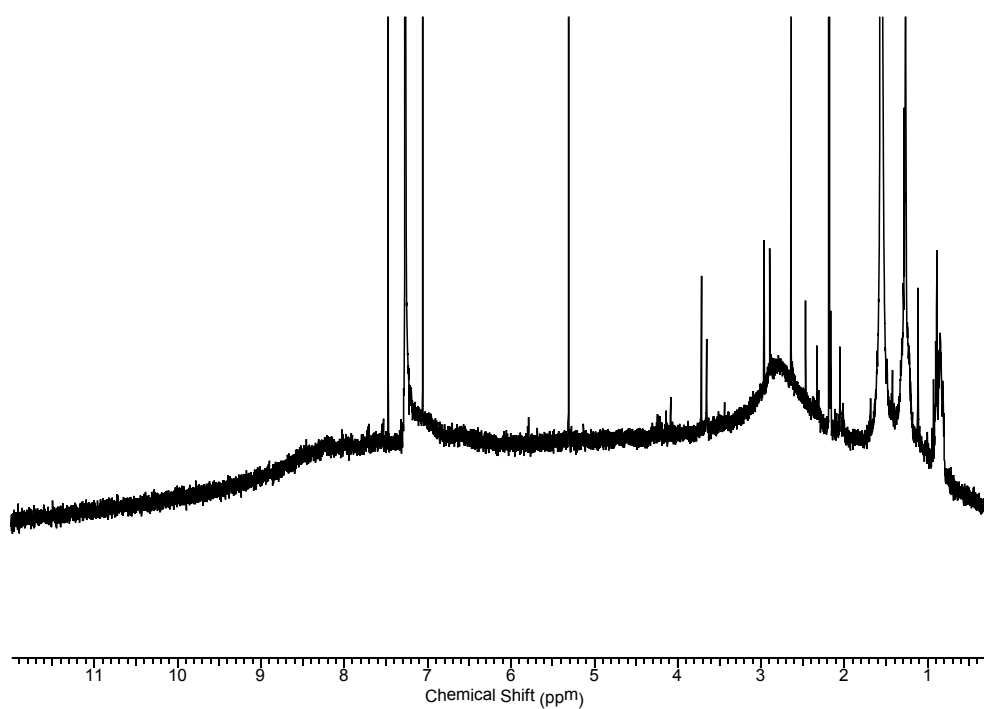


Figure S20: ^1H NMR spectra of **Au·I** (CDCl_3 , 500 MHz, 298 K)

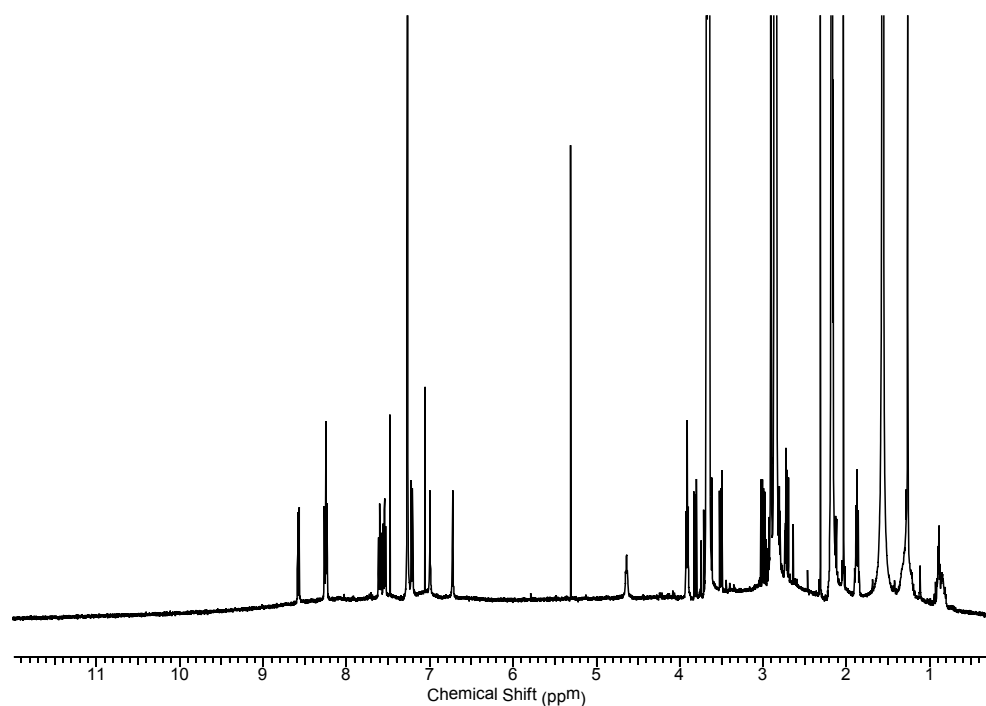


Figure S21: ^1H NMR spectra of **Au·I** 30 minutes after exposure to ten equivalents of CEMS
(CDCl_3 , 500 MHz, 298 K)

References

1. J. Cosier & A.M. Glazer, J. Appl. Cryst., 1986, 19, 105-107.
2. L. Palatinus & G. Chapuis, J. Appl. Cryst., 2007, 40, 786-790.
3. P.W. Betteridge, J.R. Carruthers, R.I. Cooper, K. Prout & D.J. Watkin, J. Appl. Cryst., 2003, 36, 1487.
4. SPECFIT, 2.02; Spectrum Software Associates Chapel Hill, NC, USA.