

## Supporting Information

# A Nanoparticle-Gel Hybrid Material Designed with Bile acid Analogues.

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## 1) General procedure for the synthesis of bile acid derived thiols

**Method 1 :** To a clear solution of iodocholane (1 mmol) in DMF (5 mL), thiourea (3 mmol) was added and the mixture was stirred at r.t. for 24 h. To the reaction mixture 25 mL of 25 % NaOH was added, stirred for additional 2 h and diluted to 100mL with distilled water. The solution was neutralised with dil. HCl (5 %) and the product formed was filtered, washed quickly and dried. The crude product was purified by passing through a silica column using 5-10% EtOH/CHCl<sub>3</sub> as the eluent. The pure product was isolated as a white solid.

**Method 2 :** To a solution of bile acid derived disulphide (0.15 mmol) in THF/MeOH (10 mL) was added Zn-dust (10 mg) in one portion and 10% HCl (1.0 mL) and stirred for 4 h. The reaction mixture was filtered and concentrated under reduced pressure. The crude product was chromatographed over silica gel using 5-10% EtOAc/CHCl<sub>3</sub> as the eluent. The pure product was isolated as a white powder.

### 24-Nor-23-mercapto-3 $\alpha$ , 7 $\alpha$ , 12 $\alpha$ -trihydroxy-5 $\beta$ -cholane (1)

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ :** 0.698(s, 3H), 0.893 (s, 3H), 0.988(d, J = 6.3 Hz, 3H), 1.02 – 1.92 (steroidal CH, CH<sub>2</sub>), 2.24 (m, 1H), 2.45 (m, 1H), 2.63 (m, 1H), 3.45(m, 1H), 3.85 (br. s, 1H), 3.98 (br. s, 1H)

**<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ :** 12.45, 17.29, 21.99, 22.40, 23.19, 26.24, 26.24, 27.62, 28.05, 30.14, 34.59, 34.71, 34.95, 35.28, 39.40, 40.50, 41.40, 41.56, 41.61, 46.40, 47.05, 68.42, 71.80, 73.09

### 24-Nor-23-mercapto-3 $\alpha$ , 12 $\alpha$ -dihydroxy-5 $\beta$ -cholane (2)

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ :** 0.683 (s, 3H), 0.905 (s, 3H), 0.975 (d, J = 6.3 Hz, 3H), 1.02 – 1.88 (steroidal CH, CH<sub>2</sub>), 2.46 (m, 1H), 2.61 (m, 1H), 3.61 (m, 1H), 3.99 (t, 1H)

**<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz) δ:** 12.69, 17.25, 21.98, 23.11, 23.64, 26.09, 27.10, 27.56, 28.61, 30.37, 33.56, 34.07, 34.86, 35.19, 35.97, 36.34, 40.42, 42.02, 46.49, 47.30, 48.20, 71.66, 73.09.

**24-Nor-23-mercapto-3 $\alpha$ -hydroxy-5 $\beta$ -cholane (3)**

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz) δ:** 0.65 (s, 3H), 0.921(s, 3H), 0.94 (d, merged with 0.92, 3H), 0.96 – 1.98 (steroidal, CH, CH<sub>2</sub>), 2.45 (m, 1H), 2.63 (m, 1H), 2.79 (m, 1H), 3.65 (m, 1H)

**<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz) δ:** 12.01, 18.26, 20.78, 21.94, 23.34, 24.16, 26.38, 27.15, 28.28, 30.47, 34.53, 35.12, 35.30, 35.79, 36.36, 40.14, 40.39, 40.62, 42.044, 42.74, 56.02, 56.46, 71.84.

## **2) Synthesis of steroid capped Au nanoparticles**

### **i) General procedure for the preparation of steroid capped nanoparticles**

A solution containing 1 equivalent of  $\text{HAuCl}_4$  in methanol and 0.5 equivalent of steroid disulphide (or 1 equivalent of thiol with  $\text{S/Au} = 1$ ) was stirred for 1 h for thorough mixing. Sodium borohydride (5-6 times excess) in MeOH was added drop wise to the stirring mixture. The deep yellow colour of the gold chloride-steroid thiol mixture turned to dark brown immediately upon addition of borohydride. Stirring was continued for additional 2 h. After cooling the mixture  $< -15\text{ }^\circ\text{C}$  the particles settled at the bottom of the flask. The supernatant was removed by decantation.

### **ii) Purification/isolation of steroid capped gold nanoparticles**

The gold nanoparticles obtained were purified by precipitation. To a solution containing the Au nanoparticles in EtOH, hexane was added slowly and cooled in the freezer till the gold particles separated out. This procedure was repeated at least three times to get pure nanoparticles. The mixture was filtered and the particle on the filter paper was re-dissolved in 1:1 EtOH/chloroform. Finally, the solution was dried under vacuum.

### 3) Dispersability of steroid capped gold nanoparticles

**Table 1.** Dispersibility of the gold nanoparticles (1mg/mL) stabilized by steroidal thiols in various solvents listed at 27 °C.

Solvents	Stabilized by 3*	Stabilized by 2*	Stabilized by 1*
Hexane	ID	ID	ID
Toluene	ID	ID	ID
CHCl <sub>3</sub>	ID	ID	SD
EtOAc	ID	ID	ID
1:1 EtOAc/ CHCl <sub>3</sub>	ID	ID	SD
1:1 EtOH/EtOAc	D	D	SD
10% EtOH/CHCl <sub>3</sub>	D	D	D
EtOH	SD	D	D
90% MeOH/CHCl <sub>3</sub>	D	D	D
MeOH	SD	D	D
DMSO/DMF	D	D	D
Isopropanol	D	D	D
n-Butanol/t-BuOH	D	D	D
10% Water/EtOH or MeOH	ID	SD	SD
1:1 Water/EtOH	SD	SD	SD
Water	ID	ID	ID
20% AcOH/water	ID	SD	SD

Foot notes to table 1:

*\*ID–Not dispersible, D–Dispersible, SD–Sparingly dispersible*

#### 4) IR spectra of thiol and capped NPs.

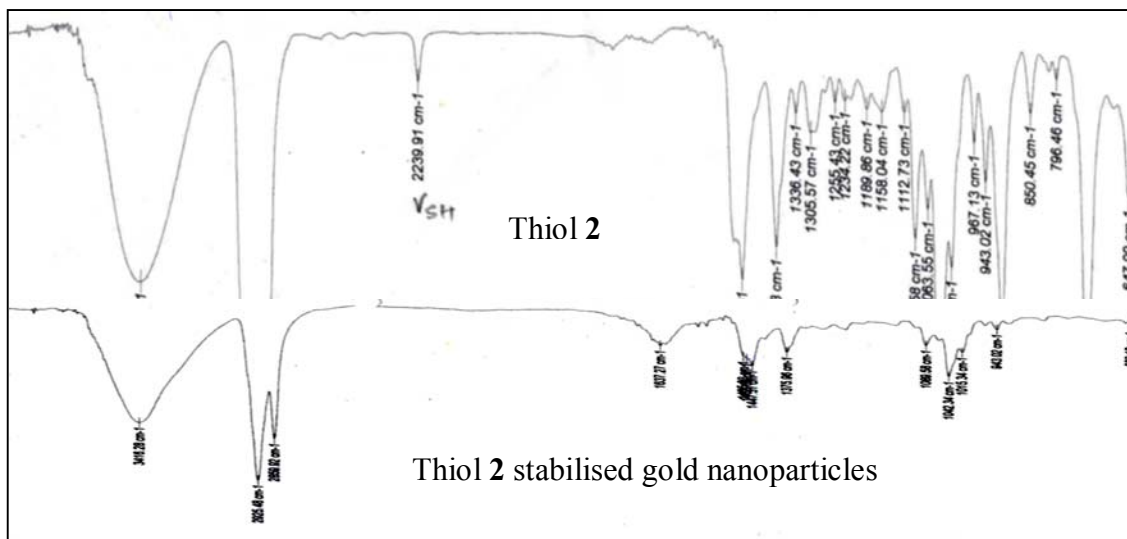


Figure 1: IR spectra (KBr) of thiol 2 (top) and 2.Au (bottom)

#### 5) <sup>1</sup>H-NMR of the thiol derived from bile acid and thiol capped Au NPs.

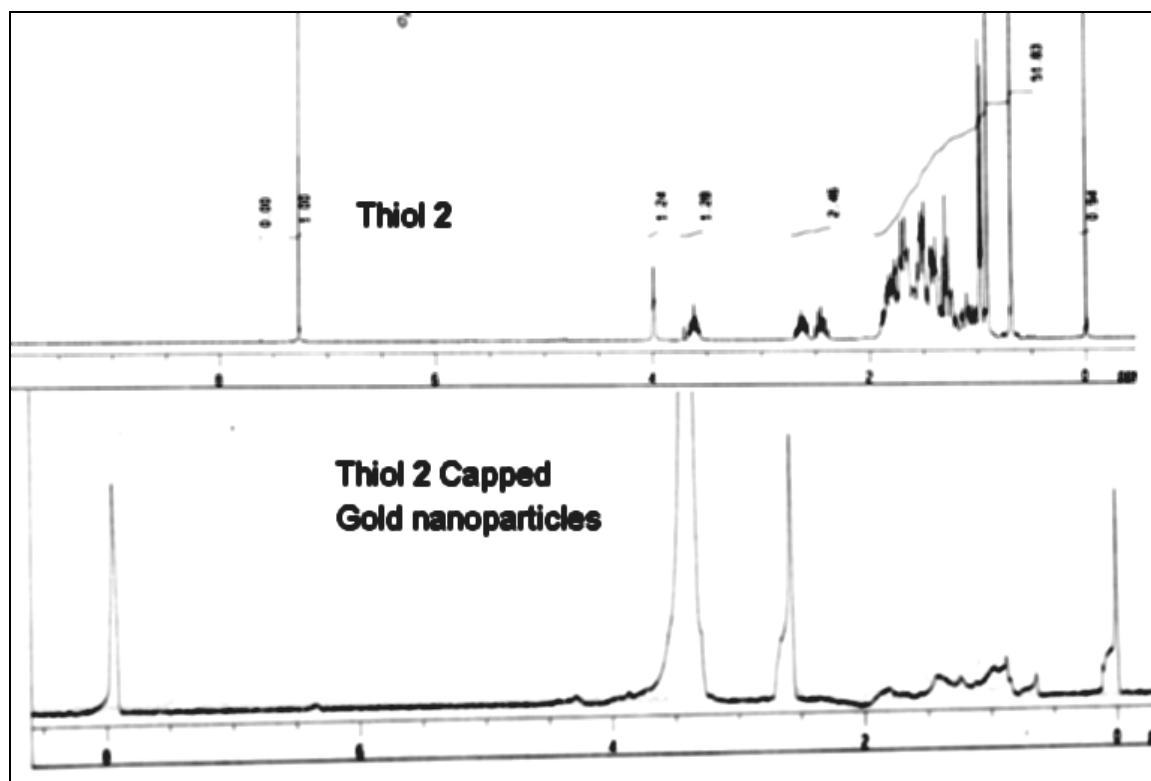
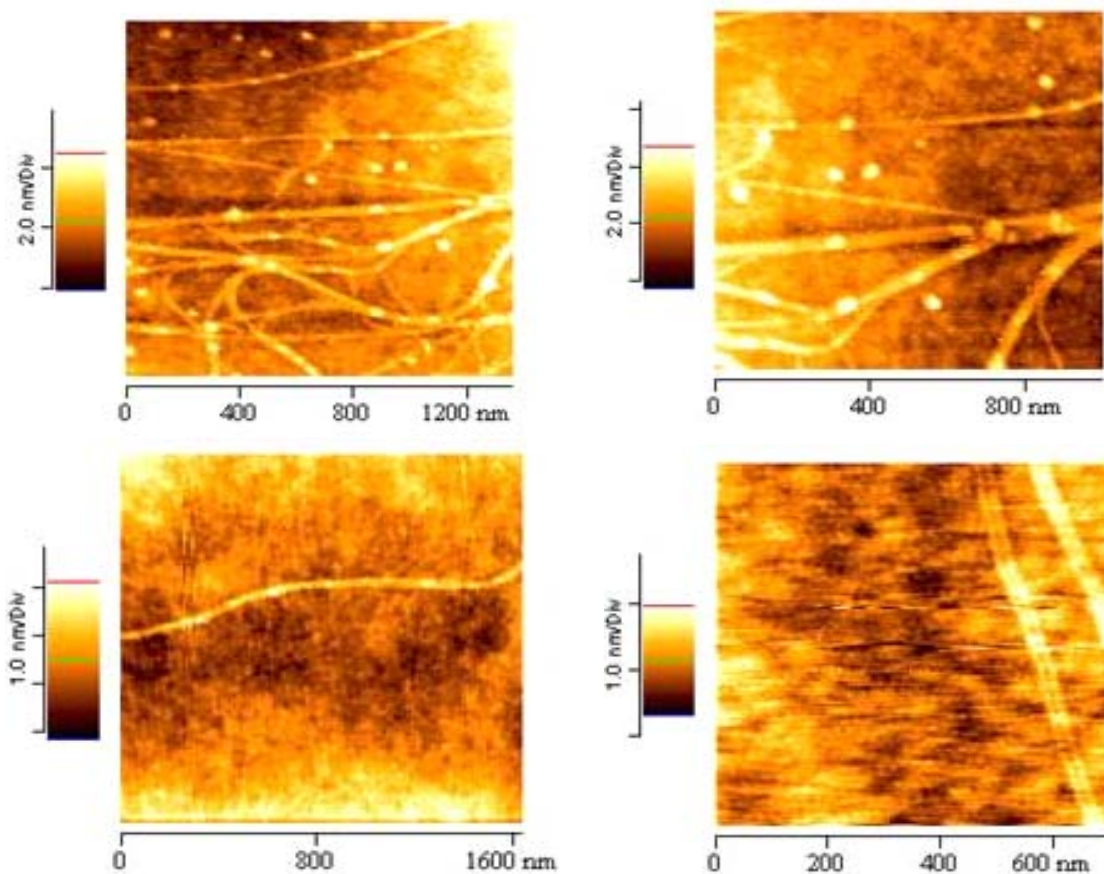


Figure 2: 300 MHz <sup>1</sup>H-NMR spectrum of thiol 2 in CDCl<sub>3</sub> (top) and thiol 2 capped Au nanoparticles in 1:1 CDCl<sub>3</sub>/DMSO-d<sub>6</sub> (bottom).

## 6) AFM imaging of the Nanoparticle-Gel hybrid material.

For obtaining AFM images of the composite material, samples were spin coated over mica substrate prior to use. The material surface was scanned using ultrasharp cantiliver ( $R_c < 10$  nm, force constant  $\sim 40$  N/m and resonant frequency  $\sim 325$  kHz).



**Figure 3:** AFM images of nanoparticle-gel composite material (0.05 mg AuNPs stabilized by thiol **1** dispersed in 1 mL of gel **4**, 2 mg of **4** in 20% AcOH/H<sub>2</sub>O) scanned at various levels of magnification.