Supporting information for la051125q

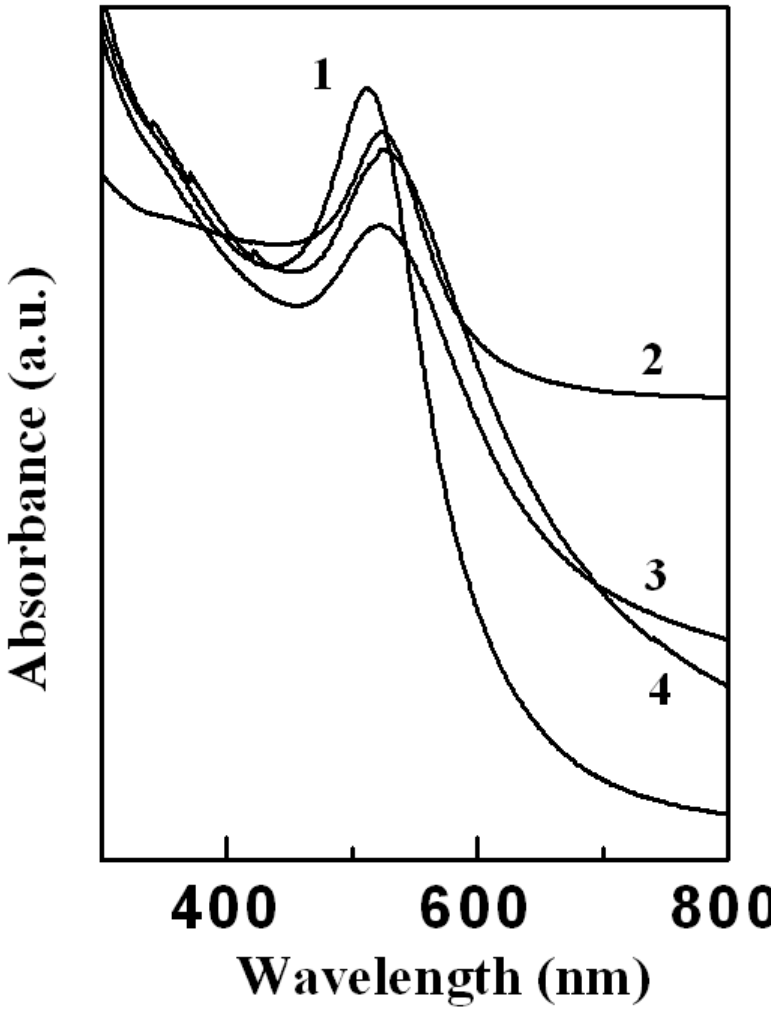


Fig. S1: UV-visible spectra of as-prepared gold nanoparticles in 1) aqueous medium and in chloroform phase transferred using 2) Benzyldimethylstearylammoniumchloride (BDSAC), 3) octadecylamine (ODA) 4) Dodecylamine (DDA).

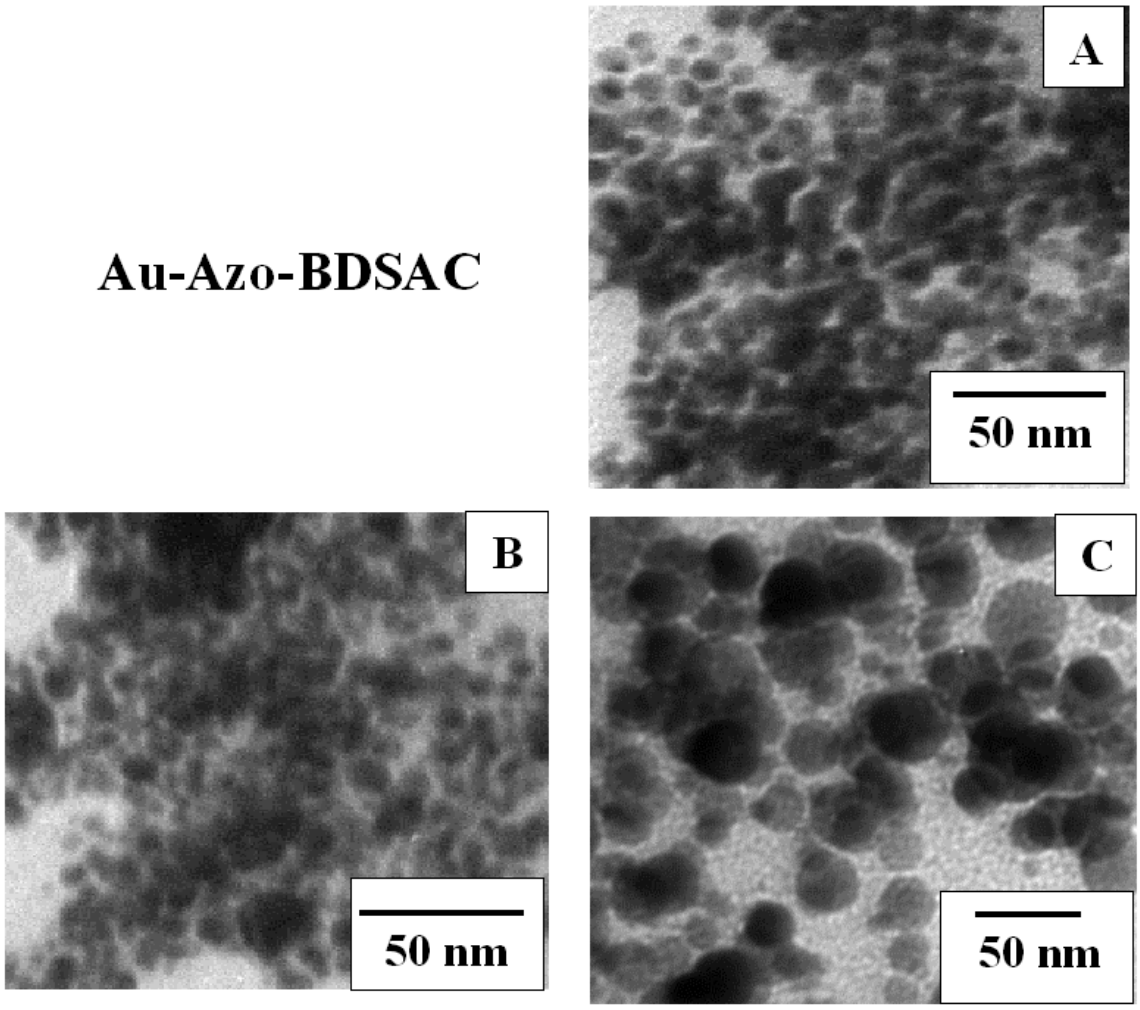


Fig. S2: TEM images of BDSAC capped nanoparticles A) immediately after the addition of linker molecule B) after irradiating the network with UV light and C) after the network has been irradiated with visible light.

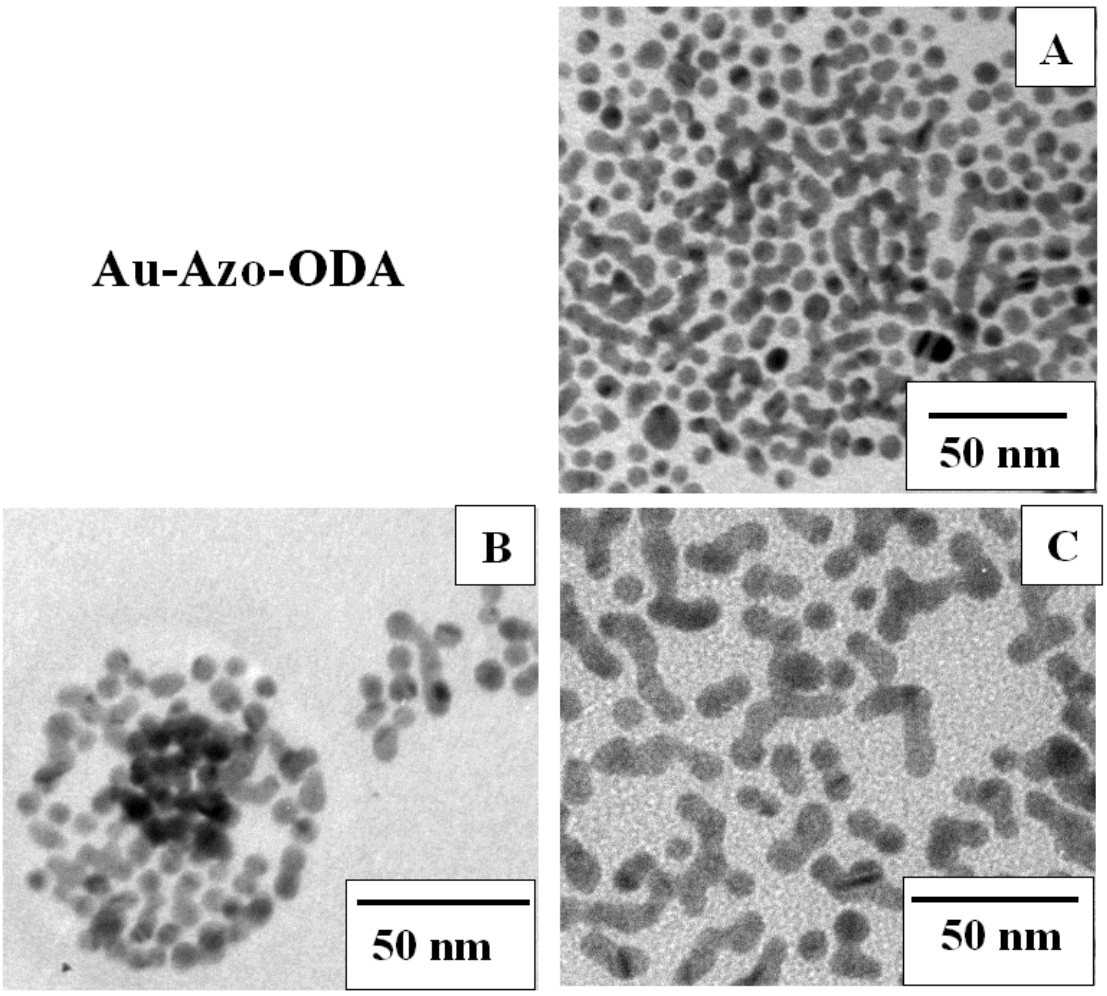


Fig. S3: TEM images of octadecyl amine capped nanoparticles A) immediately after the addition of linker molecule B) after irradiating the network with UV light and C) after the network has been irradiated with visible light.

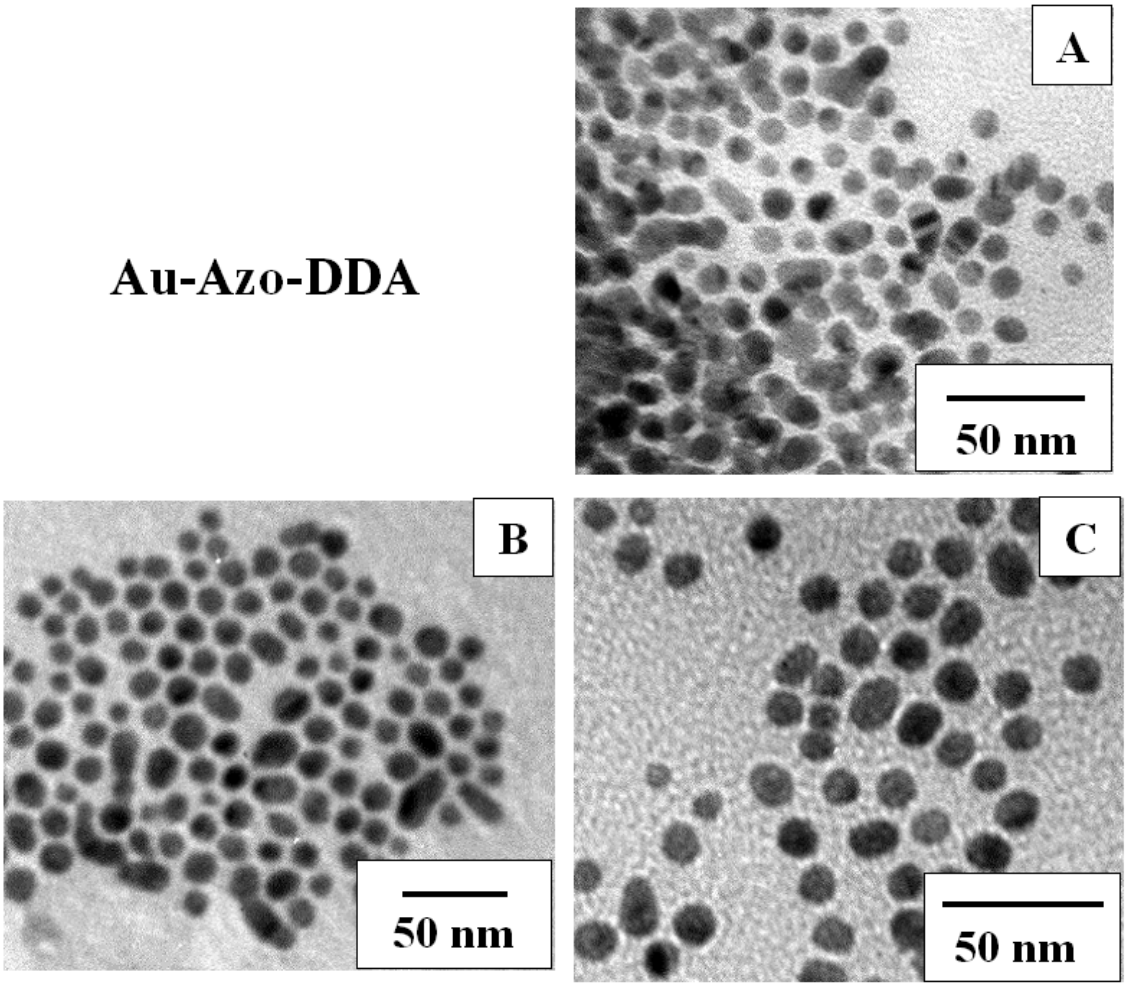


Fig. S4: TEM images of dodecyl amine capped nanoparticles A) immediately after the addition of linker molecule B) after irradiating the network with UV light and C) after the network has been irradiated with visible light.

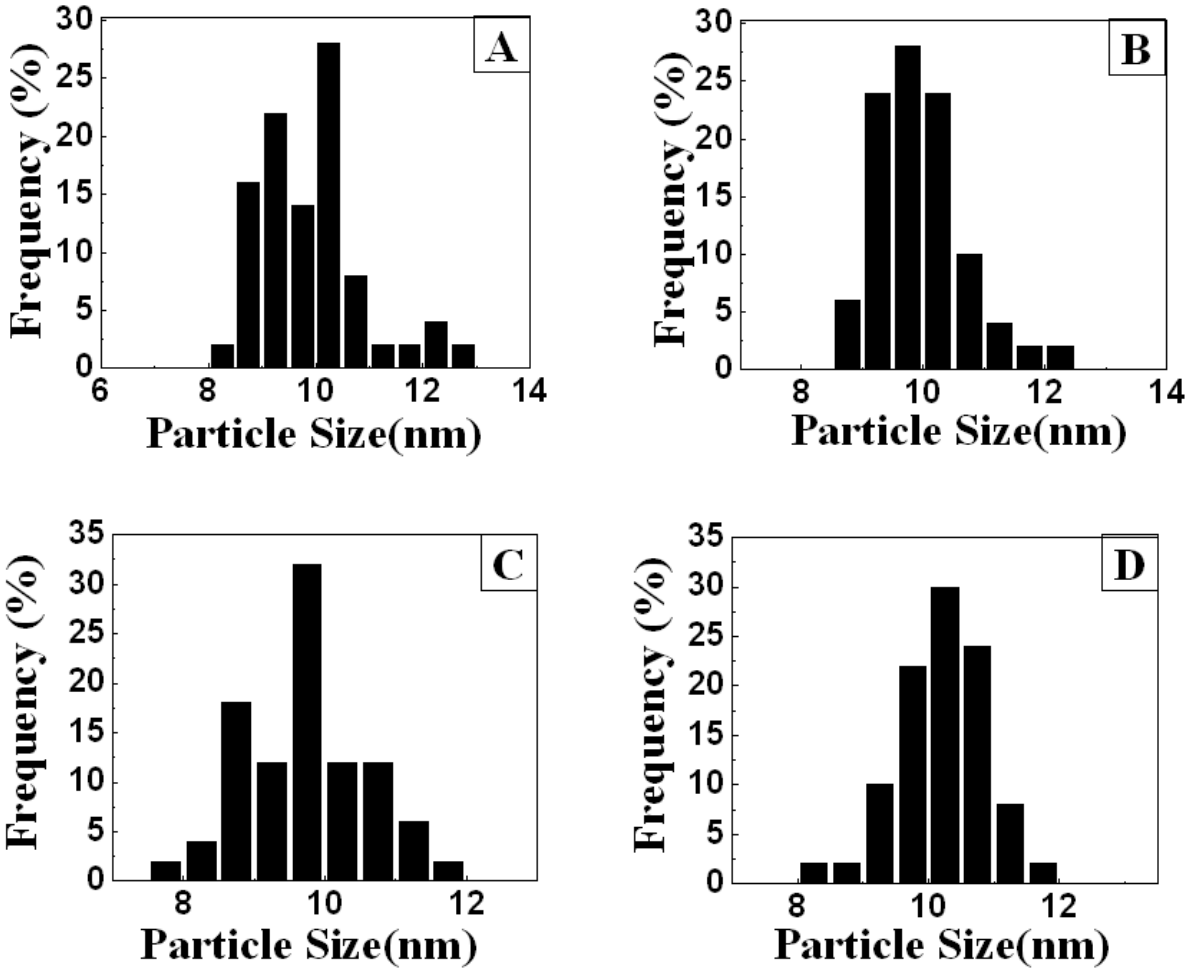
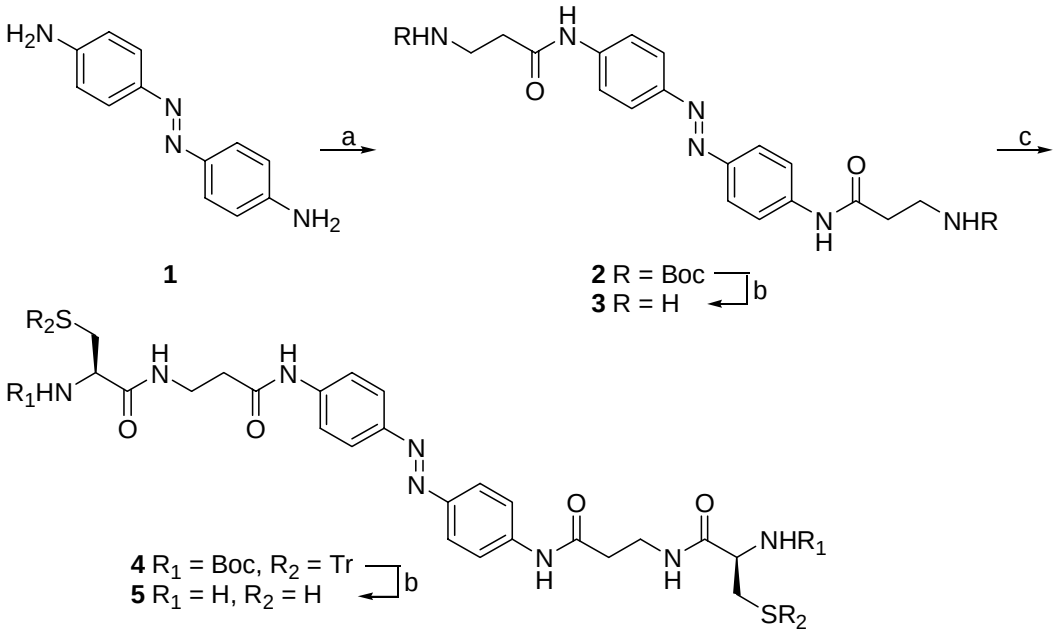


Fig. S5: Particle size distributions of dodecyl amine capped nanoparticles A) after phase transferring them to chloroform B) immediately after the addition of linker molecule C) after irradiating the network with UV light and D) after the network has been irradiated with visible light.

Synthesis of linker molecule:

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Unless otherwise reported all reactions were performed under nitrogen atmosphere. Removal of solvent *in vacuo* refers to distillation using a Buchi or Heidolph rotary evaporator attached to an efficient vacuum pump. Products obtained as solids or syrups were dried under high vacuum. Analytical thin-layer chromatography was performed on pre-coated silica plates (Merck F_{254}, 0.25 mm thickness); compounds were visualized by UV light or by staining with anisaldehyde spray. ^{1}H, ^{13}C NMR spectra were recorded on Bruker AV 200 (200 MHz for ^{1}H and 50 MHz for ^{13}C NMR) or Bruker MSL300 (300 MHz for ^{1}H and 75 MHz for ^{13}C NMR) spectrometers. Chemical shifts (δ_H) are quoted in ppm and are referenced to tetramethylsilane (internal). IR spectra were recorded on Schimadzu FT-IR spectrophotometer and elemental analysis was carried out on Thermo Finnigan Flash EA 1112 series analyzer.

Synthesis Scheme



Reagents. a) Boc.β-ala.OH, HBTU, DIPEA, HoBT, CH_2Cl_2, 0 ^{o}C – rt, 2 h, 65 %; b) 20 % Trifluoroacetic acid in CH_2Cl_2, CH_2Cl_2, 30 min, rt, 97 %; c) Boc.Cys(Tr).OH, HBTU, DIPEA, HoBT, CH_2Cl_2, 0 ^{o}C – rt, 2 h, 75 %.

*Synthesis of compound **2***:

A solution of Boc.β-ala.OH (1.0 g, 5.29 mmol), *O*-(1H-Benzotriazol-1-yl-)-*N*,*N*,*N'*,*N'*-tetramethyluronium hexafluorophosphate (HBTU) (2.4 g, 6.34 mmol), HoBT (0.9 g, 6.34 mmol) in anhydrous N,N-dimethylformamide (40 mL) was cooled to 0 ^{o}C, added diisopropylethyl amine (1.09 ml, 6.34 mmol) and stirred for 10 min. and 1,4-diaminoazobenzene (0.6 g, 2.65 mmol) was introduced *via* a syringe under nitrogen atmosphere. The resulting solution was heated to room temperature and stirred for 2 h. At the end of reaction (judged by TLC), water (50 mL) was added and extracted with ethyl acetate (3 x 50 mL), combined organic layers were dried over anhydrous sodium sulphate and concentrated *in vacuo*. The resulting crude residue was purified by conventional silica gel column chromatography using ethyl acetate-petroleum ether (60-80 ^{o}C) to obtain compound **2** (1.0 g, 65 %).

m.p. = 197 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$ /$DMSOd_6$):1.43 (s, 9 H), 2.61 (t, 2 H, *J* = 5.84 Hz), 3.45 (t, 2 H, *J* = 5.84 Hz), 4.77 (bs, 1 H), 6.73 (d, 2 H, *J* = 8.64 Hz), 7.71-7.77 (d, 2 H, *J* = 8.60 Hz), 9.77 (s, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$ / $DMSOd_6$): 27.6, 35.9, 36.4, 78.1, 113.4, 119.0, 122.0, 124.1, 139.5, 143.6, 147.9, 150.1, 155.3, 169.7; DEPT (50 MHz, $CDCl_3$ / $DMSOd_6$): 27.6, 35.8 (negative), 36.3 (negative), 113.4, 119.0, 122.0, 124.1; Anal. Calcd. for $C_{28}H_{38}N_6O_6$: C. 60.63 %, H. 6.91 %, N. 15.15 %. Found: C. 60.91 %, H. 6.64 %, N.15.55 %; IR (Nujol, cm^{-1}): 3395, 2924, 1672, 1592, 1502.

*Synthesis of compound **3***:

20 % Trifluoroacetic acid in CH_2Cl_2 (1 mL per mmol of **2**) was added to a solution of compound **2** in CH_2Cl_2 and stirred at room temperature for 30 min. Resulting reddish brown solution was concentrated under reduced pressure, the residue was redissolved in ethyl acetate and neutralized with excess triethyl amine (till the color of the solution changes to yellow). The reaction mixture was concentrated *in vacuo*, thoroughly dried under high vacuum for 4 h and directly used in the next peptide coupling reaction.

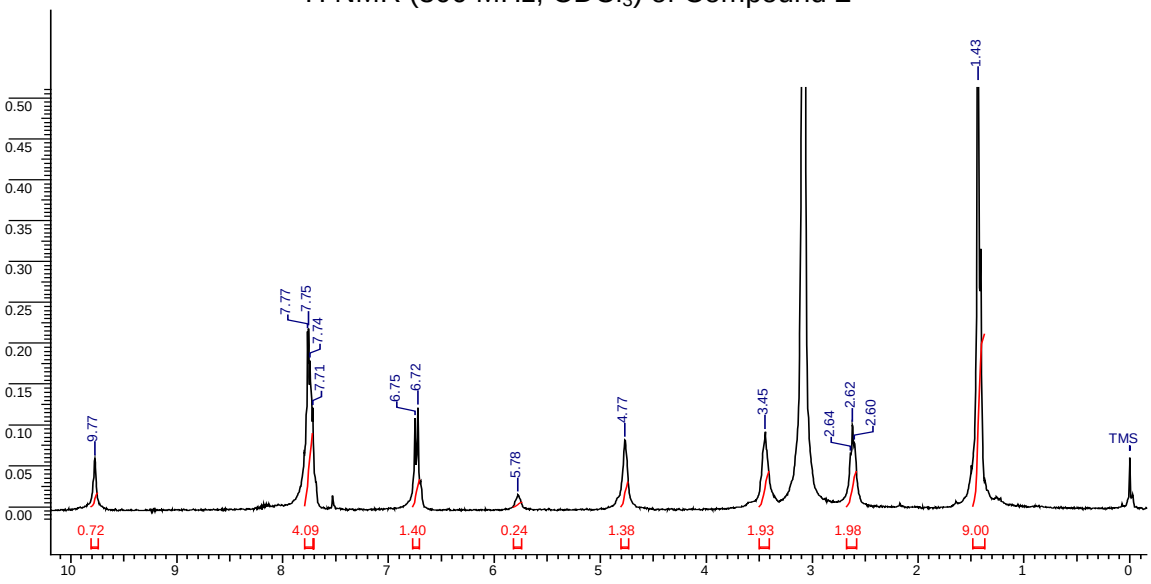
*Synthesis of compounds **4** and **5***:

To a solution of Boc.Cys(Tr).OH (0.5 g, 1.08 mmol), HBTU (0.5 g, 1.3 mmol) and HoBT (0.2 g, 1.3 mmol) in 10 ml of anhydrous DMF, diisopropylethyl amine (0.225 ml,1.3 mmol) was added at 0 ^{o}C and stirred for 10 minutes. Compound **3** (0.2 g, 0.54 mmol) in DMF (10 mL) was introduced at 0 ^{o}C and stirred for 2 hours at room temperature. At the end of the reaction, 20 mL of water was added and extracted with ethyl acetate (3 x 25 mL), combined organic layers were washed with brine solution and dried over anhydrous sodium sulphate and concentrated *in vacuo.* The crude residue was purified by silica gel column chromatography using ethyl acetate and light petroleum ether (1:4) to yield compound **4** as a yellowish orange solid (0.5 g, 75 %). Boc deprotection was carried-out by aforementioned method to obtain compound **5** in quantitative yield that was directly used to anchor gold nanoparticles.

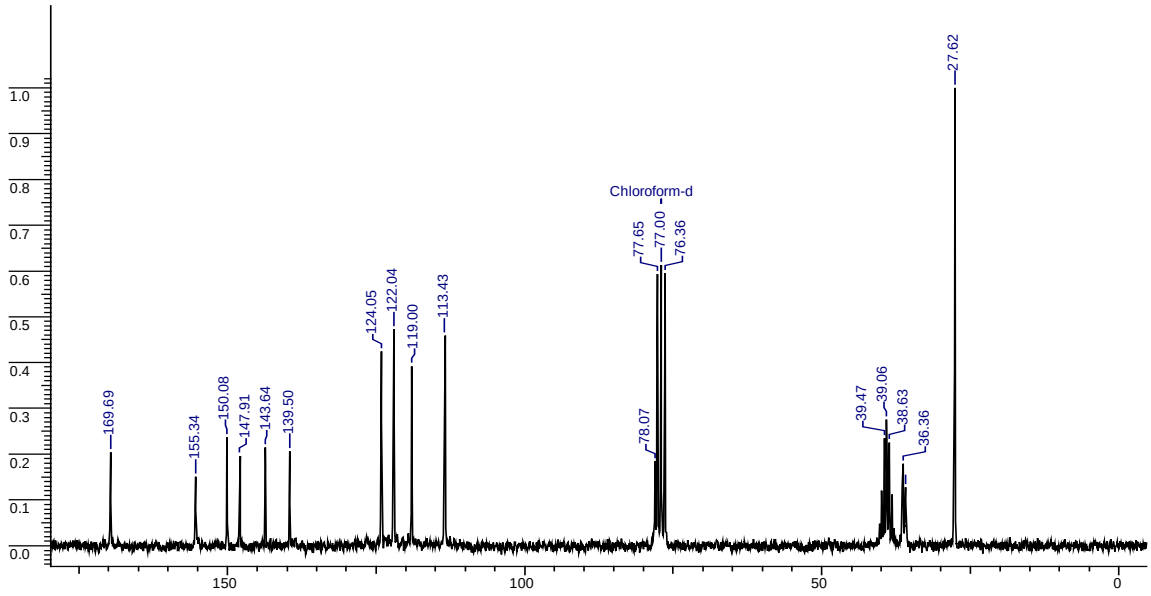
m.p. = 133 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$): 1.36 (s, 9 H), 2.50 (m, 3 H), 2.71 (m, 1 H), 3.4-3.70 (m, 3 H), 4.87 (d, 1 H, *J* = 7.3 Hz), 6.56 (m, 1 H), 6.73 (d, 1 H, *J* = 8.56 Hz), 7.10-7.42 (m, 15 H), 7.66 (d, 1 H, *J* = 8.56 Hz), 7.80 (d, 2 H, *J* = 8.56 Hz), 8.44 (bs, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): 28.2, 33.7, 35.7, 37.0, 54.0, 67.2, 80.5, 114.6, 119.8, 123.2, 124.5, 126.9, 128.0, 129.4, 139.7, 144.2, 145.5, 149.1, 149.4, 153.4, 169.8, 171.3; DEPT (125 MHz, $CDCl_3$): 28.2, 33.7 (negative), 35.7 (negative), 37.1 (negative), 53.9,

114.6, 119.8, 123.2, 124.9, 126.9, 128.0, 129.4; Anal. Calcd. for $C_{72}H_{76}N_8O_8S_2$: C. 69.43 %, H. 6.15 %, N. 9.00 %, S. 5.15 %. Found: C. 69.86 %, H. 5.89 %, N. 9.33 %, S. 5.35 %; IR (Nujol, cm^{-1}): 3639, 2925, 1672, 1596, 1460, 1377.

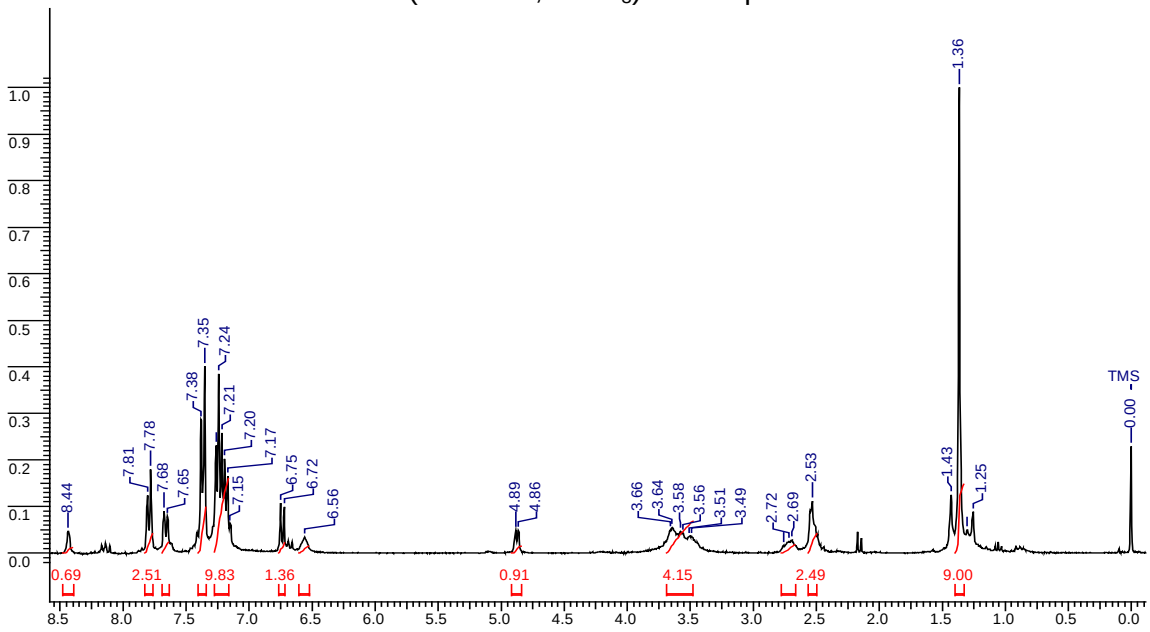
^1H NMR (300 MHz, $CDCl_3$) of Compound **2**



^{13}C NMR (50 MHz, $CDCl_3$) of Compound **2**



^{1}H NMR (300 MHz, $CDCl_3$) of Compound **4**



^{13}C NMR (125 MHz, $CDCl_3$) of Compound **4**