Supporting Information for

Chemical Modification of Single Wall Carbon Nanotubes with Tetrazine-tethered Gold Nanoparticles via a Diels-Alder Reaction

Jun Zhu,[a,b] Jonathan Hiltz,[b] R. Bruce Lennox,[b,*] Ralf Schirrmacher [a,*]

a. Montreal Neurological Institute & Hospital, McGill University, 3801 University Street, Montreal, QC H3A 2B4, Canada

b. Department of Chemistry and Centre for Self-Assembled Chemical Structures, McGill University, 801 Sherbrooke St. West, Montreal, QC H3A 2K6, Canada

* To whom all correspondence should be addressed:

ralf.schirrmacher@mcgill.ca; Fax: +1 514-340-7502; Tel: +1-514-398-1857

bruce.lennox@mcgill.ca; Fax: +1 514-398-3797; Tel: +1-514-398-5244

Experimental and method

Commercial Solvents and Reagents Used

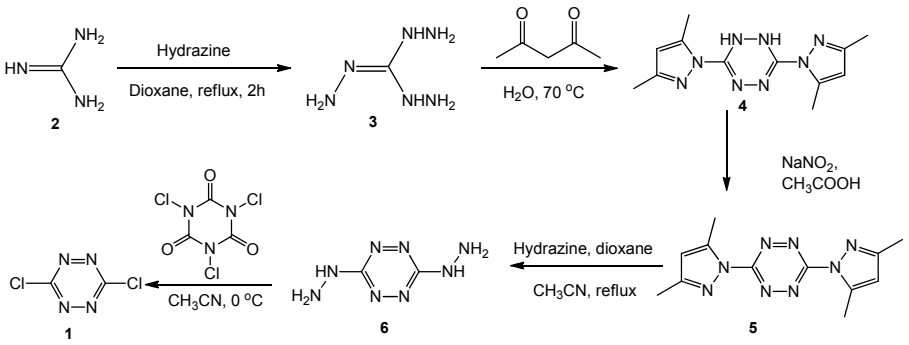
The compounds potassium tetrabromoaurate (III), hydrogen tetrachloroaurate(III), tetraoctylammoniun bromide, tetrabutylammonium borohydride, dodecanethiol, 11-mecaptoundecanol, guanidine hydrochloride, hydrazine monohydride, 2,4-pentanedione, sodium nitrite, trichloroisocyanuric were all purchased from Aldrich and used as received. Potassium carbonate (Caledon), chloroform-d_6 (Cambridge Isotope Laboratories) were also used as received. All solvents were purchased from Aldrich and used as received.

General Instrumentation

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on Mercury 400 (400MHz) in deuterated chloroform solutions and are reported in parts per million (ppm), with the residual

protonated solvent resonance used as a reference. HR-MS analyses were recorded at Department of Chemistry of McGill University. Infrared spectra were recorded on a Perkin Elmer ATR-FTIR spectrometer and are reported in wavenumbers (cm^{-1}). X-ray photoelectron spectroscopy was collected using a VG ESCALAB 220i-XL spectrometer employing a mono chromatic A1KR X-ray source and a hemispherical electrostatic analyzer. Raman scatting data was acquired from the dried films using a JY LabRamHR confocal Raman microscope. Transmission electron microscopy images and EDX spectrum were collected from a Philips CM200 TEM. X-ray photoelectron spectroscopy was collected using a VG ESCALAB 220i-XL spectrometer employing a mono chromatic A1KR X-ray source and a hemispherical electrostatic analyzer. XPS samples were prepared by dropcast of sample solutions on silicon wafer and scanned after dry.

Synthesis of s-dichlorotetrazine (1)



Dichlorotetrazine was synthesized following a slightly modified procedure developed by Hiskey.[i] The synthesis scheme is depicted above. Guanidine hydrochloride (**2**, 19.1 g, 0.20 mol) was suspended in 100 mL 1,4-dioxane, mixed with of hydrazine monohydride (34.0 g, 0.68 mol) under stirring and refluxed for 2 h. A white precipitate formed after cooling to room temperature. The product **3** was collected by filtration and purified by washing with 1,4-dioxane to give compounds **3** with quantitative yield. ^{13}C NMR (D_2O, 60MHz) δ (ppm): 160.90.

To a slurry of **3** (5g, 0.036mol) in 40 mL of water, 2,4-pentanedione (7.3g, 0.072mol) was added dropwise under stirring. Continue stirring the reactants overnight for completion of the

reaction. The mixture turned yellow and a precipitate formed over time. The precipitate was collected after filtration and washed with cold water to generate pure **4** with a yield of 90%. ^{1}H NMR ($CDCl_3$, 400MHz) (ppm): 8.06 (broad, 2H), 5.97 (s, 2H), 2.49 (s, 6H), 2.22 (s, 6H). ^{13}C NMR ($CDCl_3$, 60MHz) (ppm): 150.0, 145.9, 142.3, 109.9, 13.8, 13.5.

Compounds **4** (2.32g, 0.008 mol) was suspended in 10 mL of DCM at 0 ºC in an ice bath. A $NaNO_2$ solution (1.64g, 0.024mol $NaNO_2$ in 35 mL of milliQ water) was added under stirring. To this mixture, 1.2 mL of acetic acid (0.020 mol) was added dropwise. The solution turns to clear pink with gas evolution. The reaction was continued for 4h and the red organic layer was collected. The upper aqueous layer was washed with 2 x 30 mL DCM until the organic layer remained clear colorless. The organic layer was combined and washed with 5% K_2CO_3, dried with $MgSO_4$, filtered and evaporated to give **5** as a red solid with a yield of 95%. ^{1}H NMR ($CDCl_3$, 400MHz) (ppm): 6.14 (s, 2H), 2.65 (s, 6H), 2.33 (s, 6H). ^{13}C NMR ($CDCl_3$, 60MHz) (ppm): 159.6, 154.3, 143.8, 14.7, 13.8.

Compound **5** (1.0 g, 3.7 mmol) was suspended in 20 mL of acetonitrile. 0.40 mL of hydrazine monohydrate (8.20 mmol) was added dropwise at room temperature. A precipitate starts forming during this procedure. Continue refluxing the mixture for 20 min. The dark red precipitate was collected after cooling to room temperature and washed with CH_3CN. The precipitate was re-suspended in 5 mL of anhydrous CH_3CN and cooled to 0 ºC in ice bath. 1.9 g of trichloroisocyanic acid (0.82 mmol) was dissolved in 5 mL of anhydrous CH_3CN and slowly added to the first slurry. Solution color turned from dark red to orange and a white precipitate formed during the addition of trichloroisocyanic acid. The solution was stirred at room temperature for additional 30 min. The clear orange clear layer was passed through a short silicone gel plug and the orange band was eluted with anhydrous CH_3CN. The solvent was removed in vacuum and 0.51 g of pure compound **1** was produced as orange crystals with a yield of 92%. The purity of **1** was characterized by GC-MS. ^{13}C NMR ($CDCl_3$, 60MHz) (ppm): 168.1.

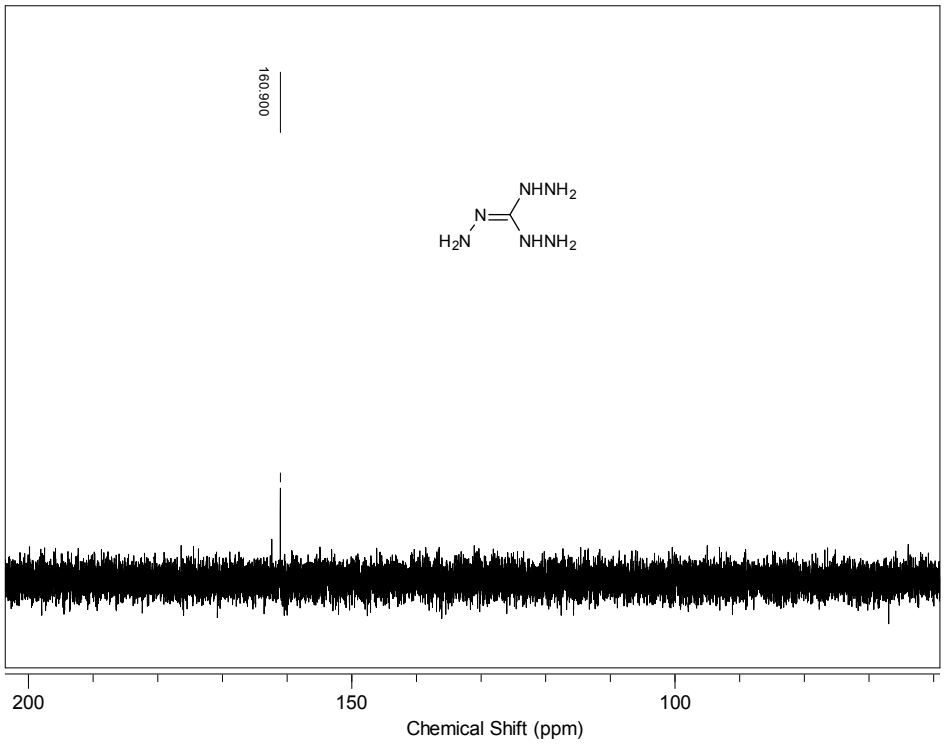


Figure S1. ^{13}C NMR of compounds 3

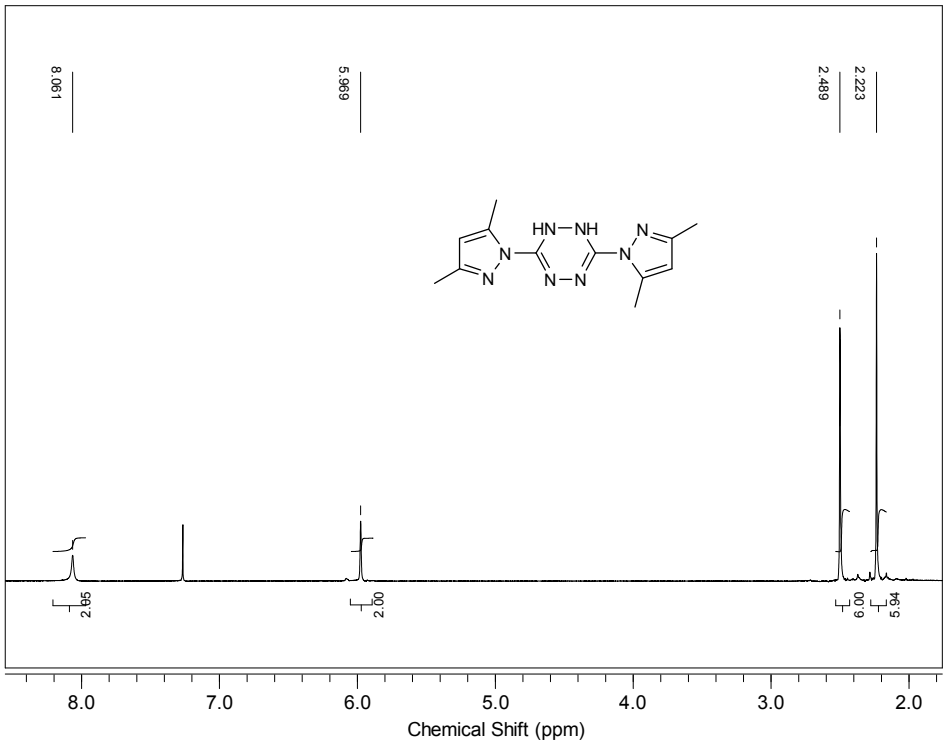


Figure S2. ^{1}H NMR of compounds 4

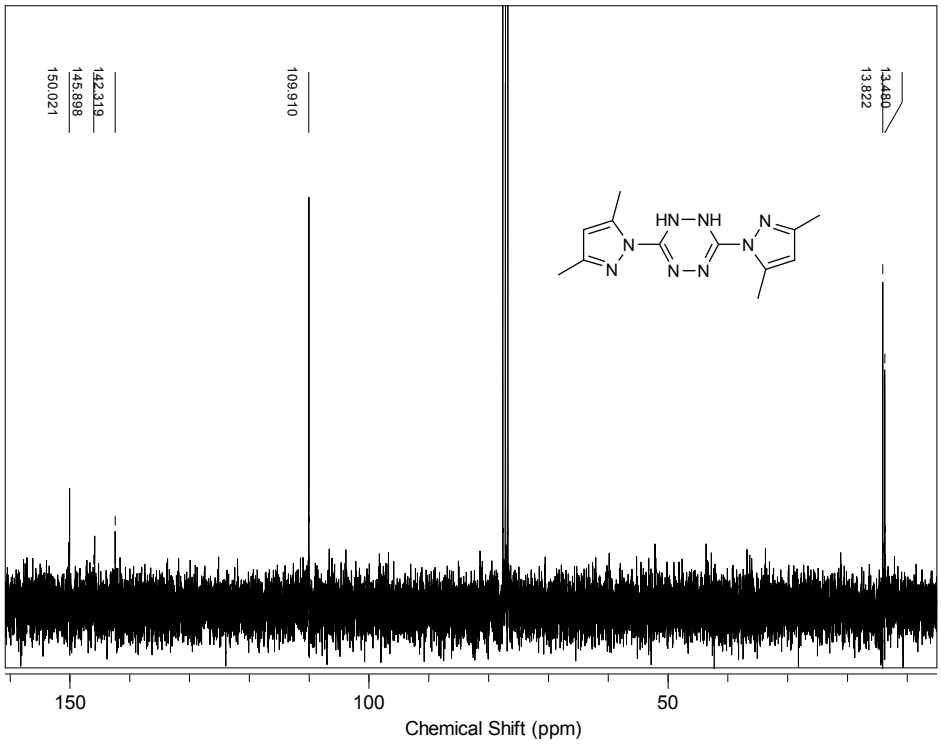


Figure S3. ^{13}C NMR of compounds 4

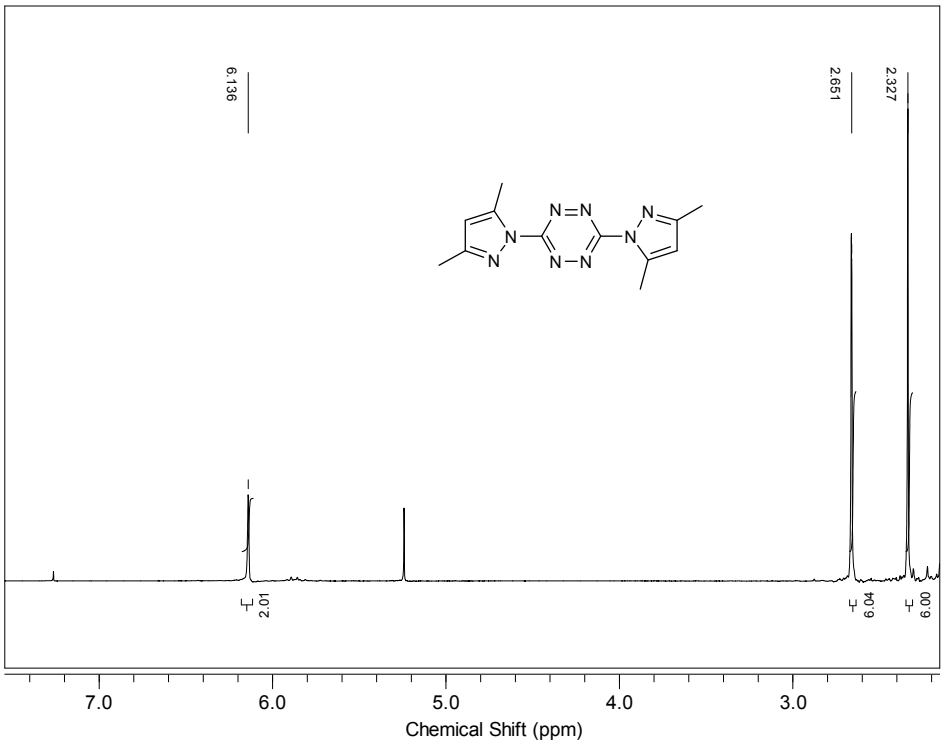


Figure S4. ^{1}H NMR of compounds 5

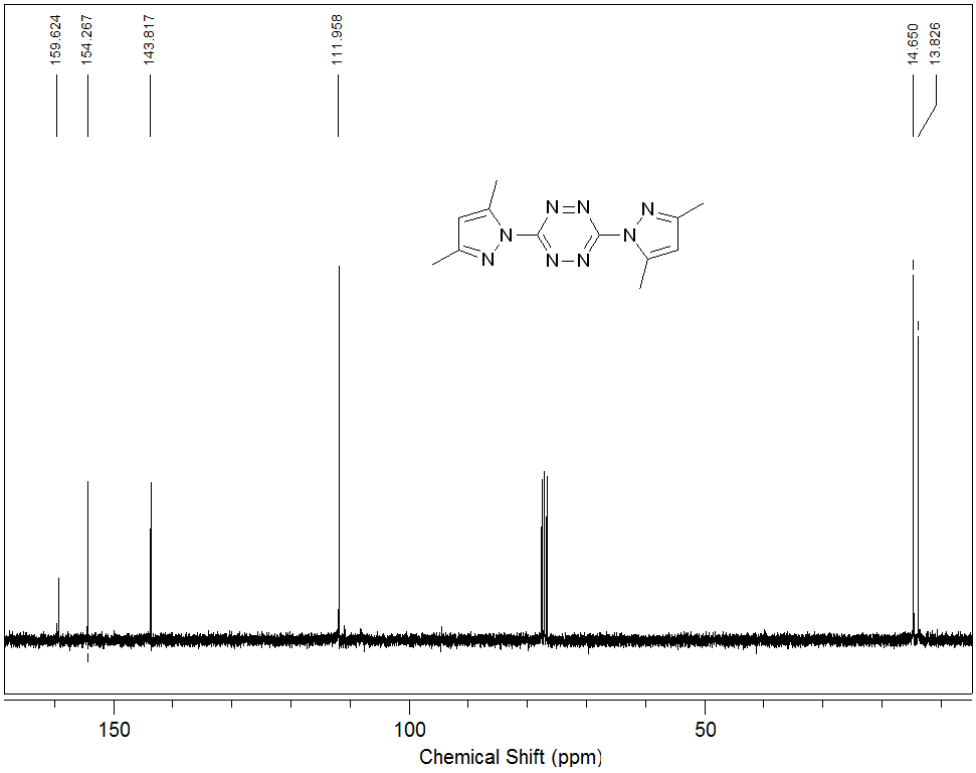


Figure S5. ^{13}C NMR of compounds 5

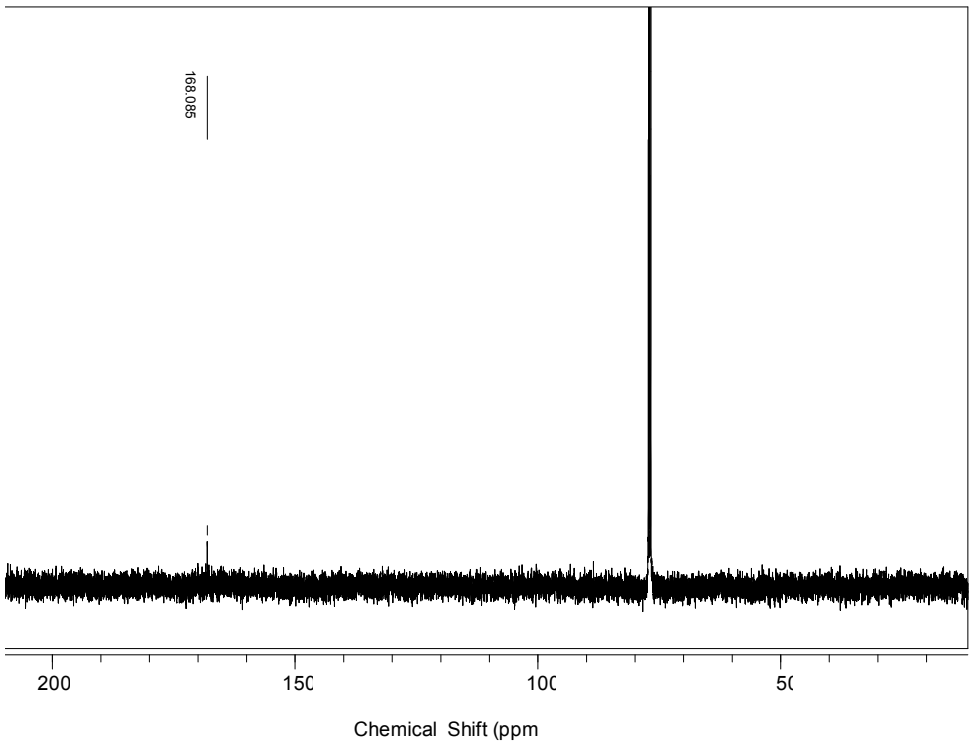


Figure S6. ^{13}C NMR of compounds of dichlorotetrazine (1)

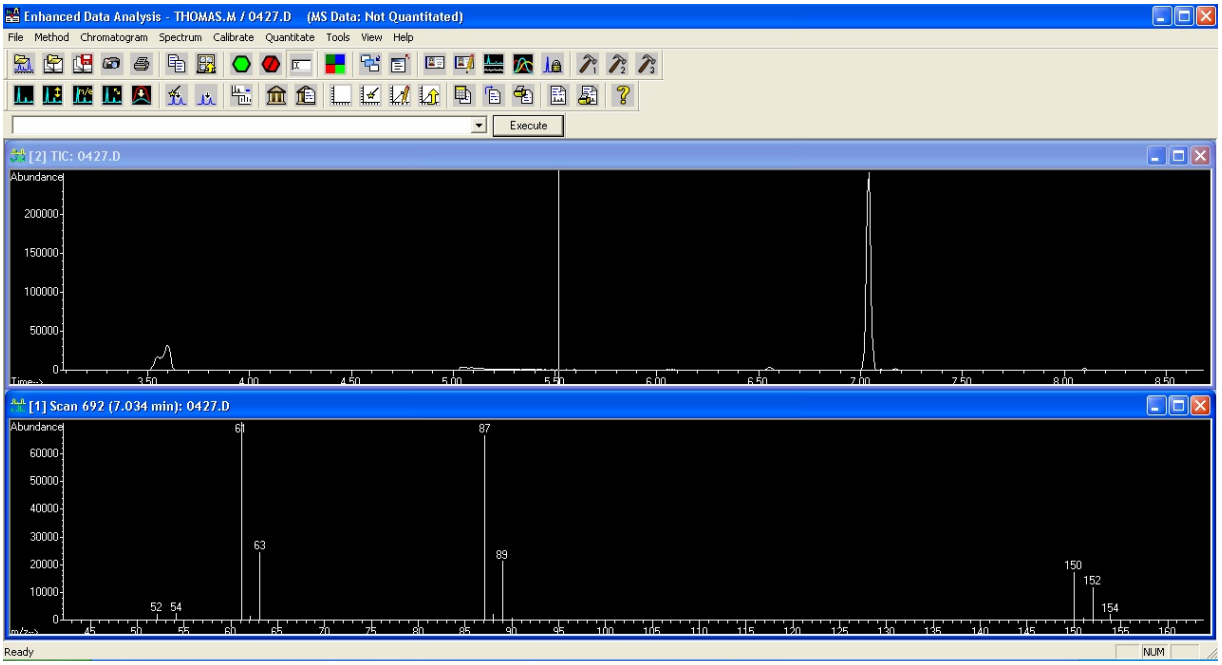


Figure S7. GC/MS spectroscopy of dichlorotetrazine 1.

Synthesis of mecaptoundecanol protected AuNP (MUD-AuNP)

Following the procedures of Brust and Murray,[ii, iii] hydrogen tetrachloroaurate (III) trihydrate (0.20 g, 0.51 mmol) was dissolved in 18 mL milli-Q water (resulting in a bright yellow solution) and then mixed with tetraoctylammonium bromide (1.53 g, 2.79 mmol) in 50 mL toluene (a clear and colorless solution is formed). The contents were stirred vigorously for 30 minutes at room temperature in order to facilitate the phase transfer of the hydrogen tetrachloroaurate (III) trihydrate into the toluene layer, which resulted in the organic layer turning to a dark orange color and the aqueous layer becoming clear and colorless. After phase transfer the aqueous layer was removed and the organic layer was cooled to 0°C in ice bath. Dodecanethiol (0.10 g, 0.12 mL, 0.51 mmol) was added to the solution via a volumetric pipette and allowed to stir for ten minutes. A fresh solution of sodium borohydride (0.22 g, 5.80 mmol) in 16 mL water was then added to the rapidly stirring toluene solution over 5 seconds. The solution darkened instantly and was allowed to warm to room temperature overnight (~18 hours) under stirring. After that the aqueous layer was removed and the toluene layer washed with 3 x 20 mL distilled water and dried over $MgSO_4$. The toluene layer was then isolated by gravity

filtration and evaporated to dryness. The resulting mixture of AuNP and tetraoctylammonium bromide was suspended in 100 mL of 95 % ethanol and placed in the freezer overnight during which the C_{12}-AuNP precipitated from solution. When the AuNP had precipitated the supernatant was decanted, and the precipitate dissolved in benzene and concentrated resulting in the formation of a film in the round bottom flask. This film was washed repeatedly with 10 x 15 mL of 95% ethanol and acetonitrile, resulting in pure dodecanethiolate protected base AuNP as confirmed by ^{1}H NMR spectroscopy.

The 100 mg of base C12-AuNP was mixed with 30mg of 11-mecaptododecanol in 20 mL of toluene and 2 mL methanol for 1 h under Ar. The solvent was removed by rotary evaporation. The resulting MUD-AuNP was purified by washing with ethanol and acetonitrile until pure as characterized by ^{1}H-NMR spectroscopy.

Synthesis of tetrazine terminated AuNP (1-AuNP)

MUD-AuNP (50 mg) and 3,6-dichlorotetraine (6 mg, 0.04 mmol) were dissolved in 10 mL of anhydrous DCM and degassed with argon. 5.54 µL of triethyleneamine was added to the solution and stirred for 2 h. The mixture was then concentrated and the resulting tetrazine-AuNP were washed with acetonitrile for 5 times. The purity of the resulting tetrazine-AuNP was confirmed by ^{1}H NMR spectroscopy.[iv] The 1-AuNP have a size of 1.9 ± 0.3 nm.

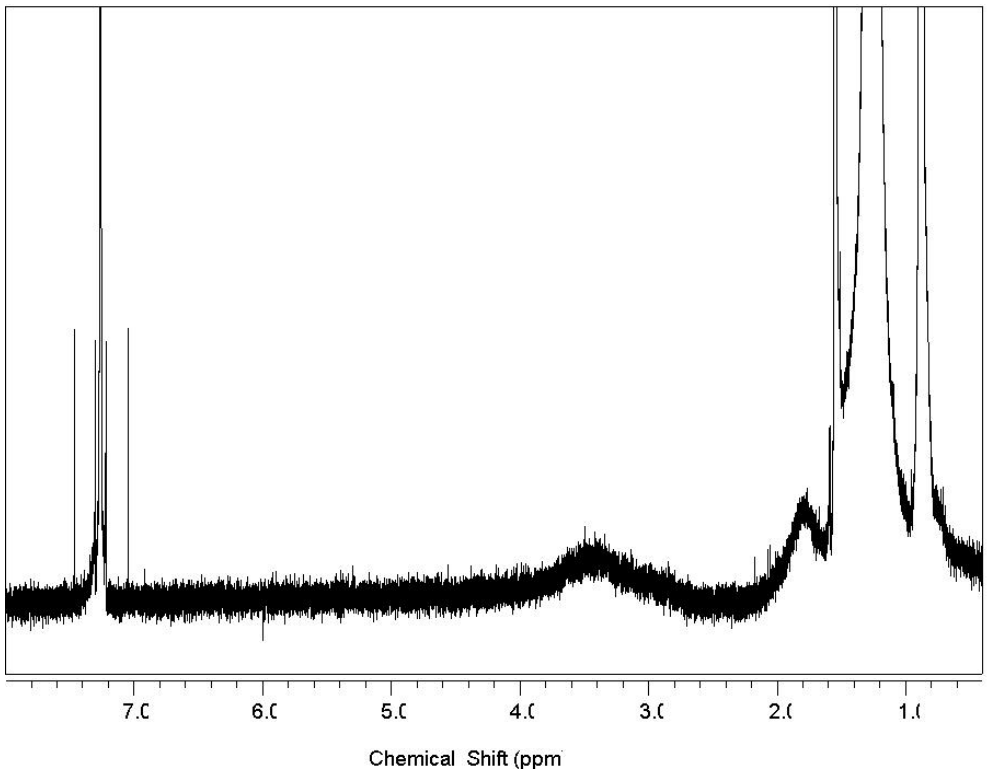


Figure S8. ^{1}H NMR of MUD-AuNP.

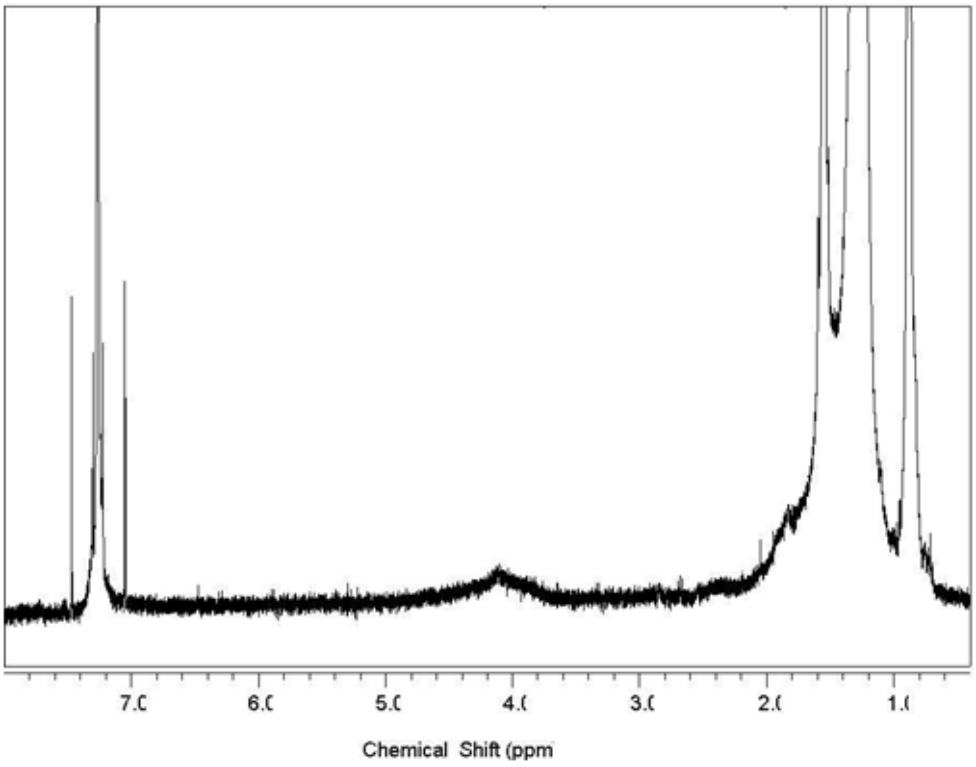


Figure S9. ^{1}H NMR of Tetrazine-AuNP.

The Diels-Alder reaction between tetrazine-AuNP and SWCNT

SWCNT (5.0 mg) was dispersed in 5 mL of anhydrous THF under sonication under Ar. A tetrazine-AuNP stock solution was prepared by dissolving 1 mg of tetrazine-AuNP in 5 mL of anhydrous THF for future use.

(a) Low AuNP loading AuNP-SWCNT

50 uL of the tetrazine-AuNP (0.01 mg) stock solution was mixed with 1.0 mL of SWCNT suspension under Ar for 2 h. The solution was then centrifuged (5 min, 12,000 rpm) to form a pellet in the bottom and the upper black supernatant was removed. The resulting AuNP-SWCNT complex was re-suspended in THF, sonicated for 5 min and centrifuged again, and the upper layer solution was discarded. This procedure was repeated with THF, DCM, toluene, and acetonitrile for 10 times until the supernatant turned to clear colorless. The pure AuNP-SWCNT was then suspended in dry THF for further characterization. The success of this Diels-Alder reaction of tetrazine-AuNP with SWCNT was confirmed by TEM, XPS, and Raman spectroscopy.

(b) High AuNP loading AuNP-SWCNT

0.50 mL of the tetrazine-AuNP (0.1 mg) stock solution was mixed with 1.0 mL of SWCNT suspension under Ar for 2 h. The resulting high AuNP loaded AuNP-SWCNT was purified via the same centrifuge, washing procedure and further characterize by TEM, XPS, and Raman spectroscopy.

Raman spectroscopy study of SWCNT and AuNP-SWCNT

SWCNT and AuNP-SWCNT samples were suspended in THF and then drop casted onto cleaned glass slides. Raman scattering data was acquired from the dried films using a JY LabRamHR confocal Raman microscope. The sample was excited using a HeNe laser at 633nm through a 100x microscope objective, with a nominal power at the source of approximately 17mW. The spectra were obtained using an 1800 line/cm grating with an integration time of 1 minute, and were collected 5 times. The spectra were collected in the range of 400 to 2000 cm^{-1}. Background correction was performed on the data using Labspec software.

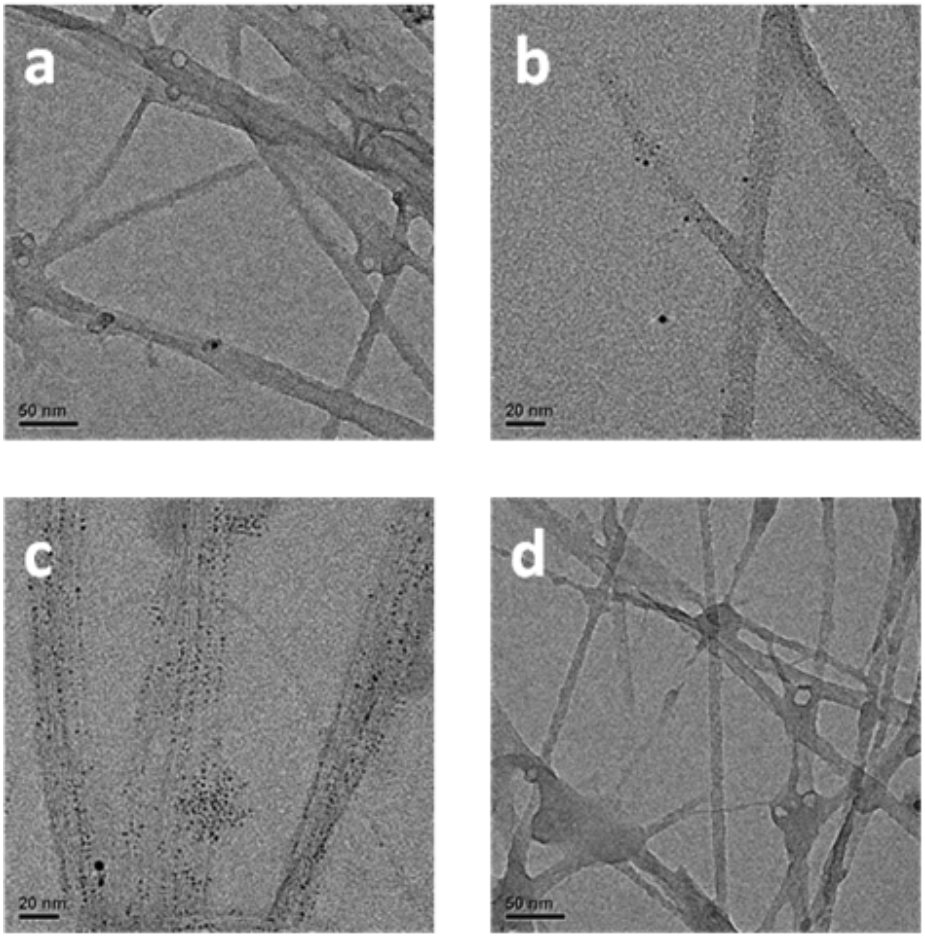


Figure S10. Transmission Electron Microscopy (TEM) images of (a) SWCNT, (b) low loading AuNP-SWCNT, (c) high loading AuNP-SWCNT, and (d) control (MUD-AuNP+SWCNT). In large scale.

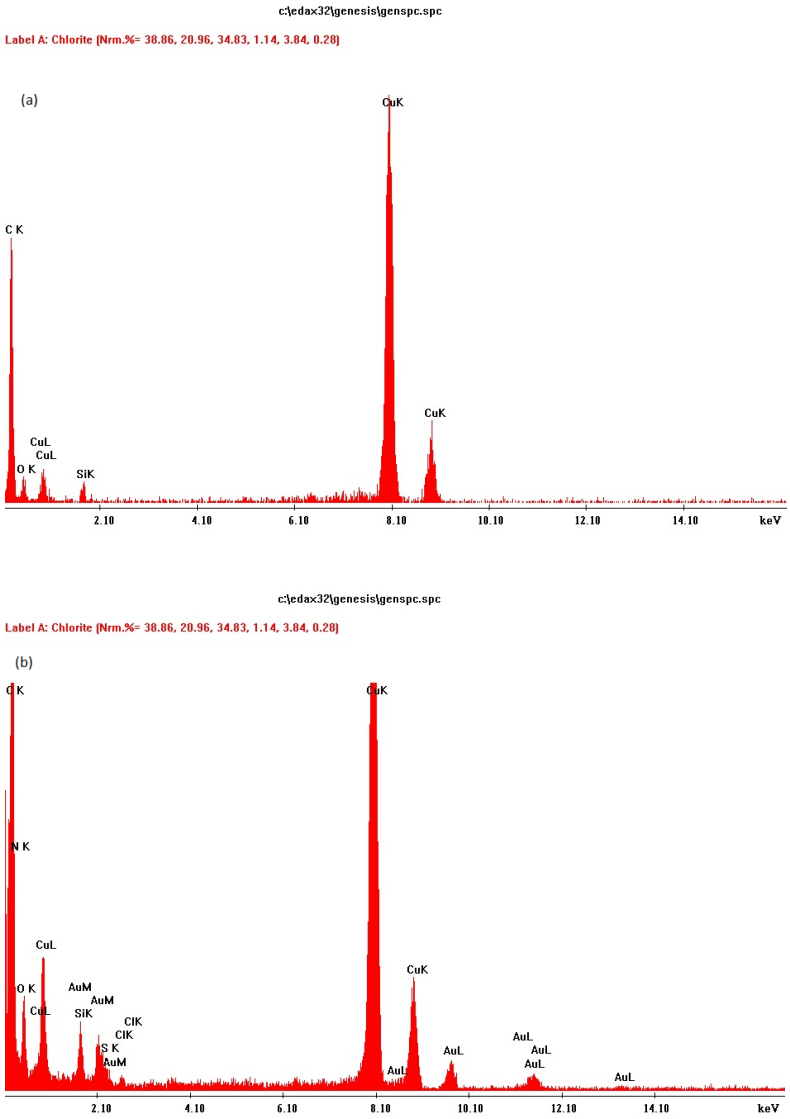


Figure S11. EDX of (a) SWCNT and (b) high loading AuNP-SWCNT

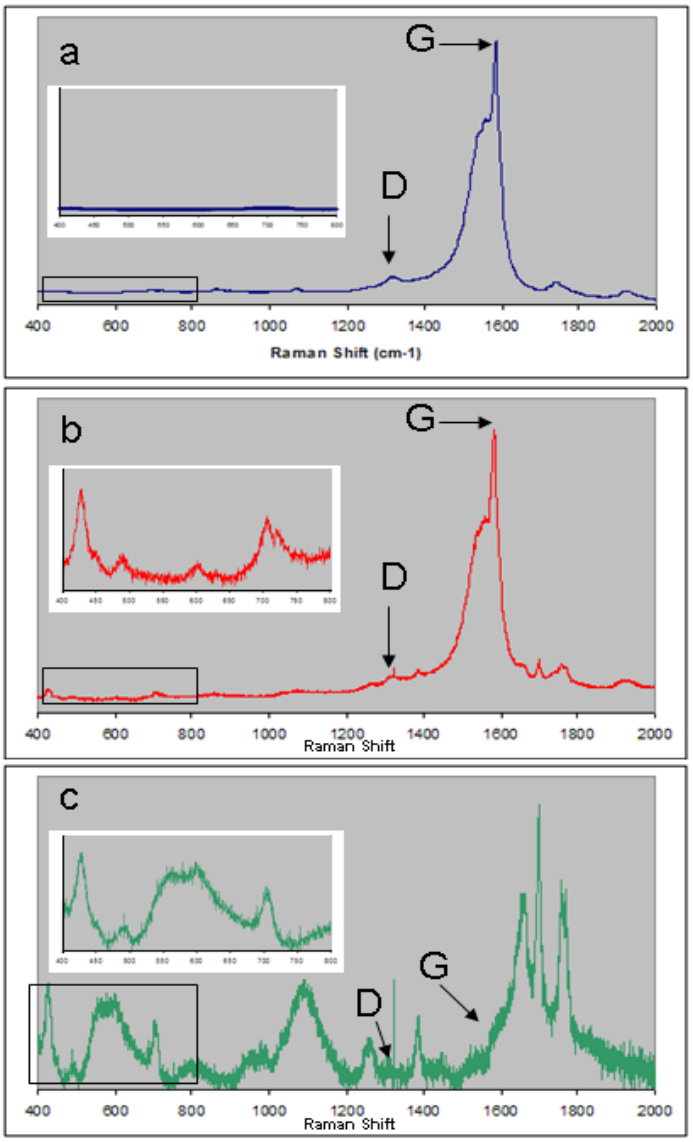


Figure S12. Raman spectra of (a) SWCNT, (b) low **1**-AuNP loading AuNP-SWCNT, and (c) high **1**-AuNP loading AuNP-SWCNT. The features are clearly shown in the inserted zoom-in spectra of the 400-800 cm^{-1} region. Raman peaks were assigned follow references.[v,vi,vii]

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