Dithiocarbamate Assembly on Gold: Supporting Information

Preparation of chemical reagents:

Spectrophotometric grade CS_2 (Sigma-Aldrich) was freshly distilled from CaH_2 just prior to use. Methanol and tetrahydrofuran were dispensed in an anhydrous state from a solvent purification system (MBraun). Dimethylamine, diethylamine, dibutylamine, didecylamine, diisopropylamine, piperidine, and morpholine (Aldrich) were used without further purification. In the case of dimethylamine, neat samples could be obtained by condensation at –78 ºC. Methamphetamine hydrochloride and nortriptylene hydrochloride (Sigma-Aldrich) were very kindly provided by Professor Eric Barker (Dept. of Medicinal Chemistry and Molecular Pharmacology, Purdue University). Bis(2-pyridylmethyl)amine was prepared by condensation of 2-pyridylmethylamine and 2-pyridinecarboxaldehyde (Aldrich) followed by reductive amination, and purified by silica gel chromatography.

Tetra(*N*-methyl)aminomethyl resorcinarene (TMAR) was prepared by modification of an earlier procedure described by Reinhoudt and coworkers (*J. Org. Chem.*, **1997**, *62*, 7148), in which methylamine was substituted directly onto the corresponding tetra(bromomethyl)cavitand. The tetrabromide was synthesized by modification of an earlier procedure (Balasubramanian et al., *Langmuir* **2002**, *18*, 3676; Supporting info.), in which tetra-*C*-methylcavitand was brominated using $NaBrO_3$ under the biphasic conditions reported by Ishii and coworkers (*J. Org. Chem.*, **1998**, *63*, 6023).

Smooth Au substrates:

Thin glass cover slips (Corning, 18×18 mm^2) were coated with a 10-nm Cr adhesive layer and 50-nm Au film by thermal evaporation, and used immediately after preparation. Samples for XPS analysis were comprised of Au films having a thickness of 100 nm.

Roughened Au substrates:

Au foil (0.1 mm, Alfa Aesar) was cut into 6 × 6 mm squares and annealed by propane torch for 2–3 min, sonicated for 10 min in deionized water, then roughened using a potentiostat (Princeton Applied Research 273A) in 0.1 M KCl. The parameters for electrochemical roughening were as follows: (i) initial potential (E1) of –0.3 V, (ii) a delay time (D1) of 30 sec; (iii) ramping the potential at a rate of 500 mV/sec to an upper limit (E2) of 1.2 V; (iv) a delay time (D2) of 1.3 sec, (v) decreasing the potential at a rate of 500 mV/sec to E1. The oxidation–reduction process was repeated for 25 cycles, in accord with the protocol of Weaver and coworkers (*J. Electroanal. Chem.* **1987**, *233*, 211). All voltages were referenced against a saturated calomel electrode (SCE).

Colloidal Au nanoparticles:

Aqueous suspensions of colloidal Au particles (British Biocell International, EM.GC40, ~10^{11} particles/mL) were treated with a mixed-bed ion-exchange resin (Amberlite MB-3, Mallinckrodt) for 30 minutes to minimize the presence of electrolyte in solution.

Preparation of dithiocarbamate-coated substrates:

For the preparation of dithiocarbamates **1**–**7**: A 10% solution of CS_2 in methanol or ethanol (1 mL) was treated dropwise with one molar equivalent of secondary amine dissolved in the same solvent (1 mL), followed by vortex mixing for 30 sec. The final concentration of CS_2/amine was 0.83 M. A freshly prepared Au substrate was introduced and soaked for variable periods, then rinsed twice in pure methanol and dried in air. 10 minutes was deemed to be sufficient for obtaining SERS spectra; saturation coverage was obtained after soaking for several hours (up to 12 hours in the case of **3** and **4**).

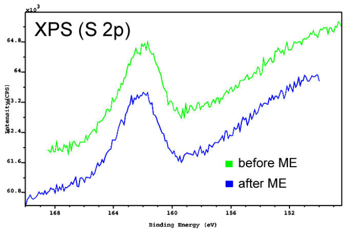
For the preparation of dithiocarbamates **8**–**10**: A 2% solution of CS_2 (0.1 mL) was mixed with one molar equivalent of secondary amine in methanol (0.1 mL), followed by vortex mixing. The final concentration of CS_2/amine was 0.17 M. In the case of dithiocarbamates **9** and **10**, one molar equivalent of NaOH was added to neutralize the HCl salt before mixing with CS_2.

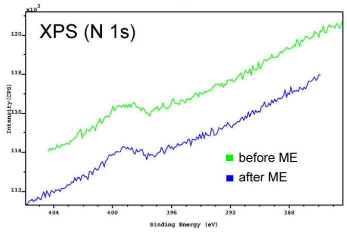
*Extraction of nanoparticles coated with dithiocarbamate **11**:*

An aqueous suspension of Au colloid treated with ion-exchange resin (1 mL) was mixed vigorously with a 1 mM solution of CS_2 in THF (1 mL). A 1 mM solution of TMAR in THF (1 mL) was added, and the solution was agitated vigorously by vortex mixing for another 5 minutes. Addition of CH_2Cl_2 (1 mL) resulted in phase separation, with extraction of the nanoparticles to the organic phase.

XPS data:

XPS spectra were obtained using a Kratos analytical ESCA system with monochromatic Al Kα radiation at 1486.6 eV and a fixed takeoff angle of 90º. Smooth Au substrates were saturated with dibutyl DTC **3** as described above. One substrate was then immersed in a 1 mM ethanolic solution of 2-mercaptoethanol (ME) for 24 hours at room temperature, then washed extensively with solvent.





Atomic concentration ratios:

	S/Au	N/Au	C/Au	O/Au	S/N ratio
DTC **3**	0.06	0.028	0.52	0.021	2.14
DTC **3**, after ME treatment	0.045	0.021	0.40	0.037	2.14

We note that while the S/N ratio remains unchanged after ME treatment, the S/Au and N/Au ratios both decreased by 25%. There are two possible reasons: i) the Au substrate was oversaturated with DTC **3** prior to ME treatment, supporting more than one monolayer, or ii) some chemisorbed DTC was displaced by ME, which in turn was desorbed after extensive washing. Additional studies are in progress to validate one of these possibilities.

Contact angle measurements:

Smooth Au substrates were exposed to solutions of CS_2 and secondary amine as described above, then washed several times with deionized water and dried in air. Contact angle measurements were taken at room temperature by depositing a 0.5-µL droplet of deionized water onto the substrate, which was characterized under stationary conditions using an automated goniometer (Rame-Hart, Model 500). All measurements were performed in triplicate.

Table S1. Contact Angle Measurements on Dithiocarbamate (DTC)-Coated Surfaces

Substrate	Mean Angle (θ_{av}), degrees	Left Angle, degrees	Right Angle, degrees	Drop Height, mm	Drop Width, mm
Bare Au	81.7±0.5	82.1±0.9	81.3±1.1	0.67±0.01	2.49±0.04
DTC **1**[a]	60.1±1.8	60.5±1.8	59.8±2.2	0.40±0.04	3.06±0.18
dimethylamine[b]	72.9±2.1	71.7±3.0	74.0±1.4	0.46±0.03	3.04±0.07
DTC **1**, following C12SH treatment[c]	76.7±0.4	77.1±0.9	76.3±0.9	0.58±0.04	2.59±0.02
dimethylamine, following C12SH treatment[c]	97.3±2.1	97.1±1.9	97.5±2.3	0.85±0.06	2.13±0.03
dodecanethiol[c]	111.4±1.2	111.3±0.9	111.4±1.4	1.06±0.02	1.91±0.08
DTC **2**[a]	68.1±1.5	68.1±1.0	68.1±2.6	0.48±0.03	2.71±0.22
DTC **2**, following C12SH treatment[c]	81.8±0.5	81.7±0.8	81.9±0.5	0.62±0.09	2.52±0.09
DTC **3**[d]	107.0±0.7	106.8±1.2	107.2±0.8	0.99±0.07	1.96±0.07
DTC **3**, following 2-mercaptoethanol treatment[c]	104.4±0.8	104.3±0.6	104.5±1.1	0.97±0.07	2.05±0.12
DTC **4**[d]	108.0±2.8	107.3±3.3	108.6±2.9	0.92±0.07	2.01±0.09
DTC **4**, following 2-mercaptoethanol treatment[c]	101.7±1.3	101.3±1.1	102.2±1.7	0.87±0.04	2.10±0.08

[a] Substrates were immersed in methanolic solutions for 1 hour. [b] Substrates were immersed in THF solutions. [c] Substrates were exposed to a 1 mM solution of alkanethiol in ethanol for 24 hours. [d] Substrates were immersed in methanolic solutions for 12 hours.

Additional SERS spectra of dithiocarbamates on roughened Au surfaces:

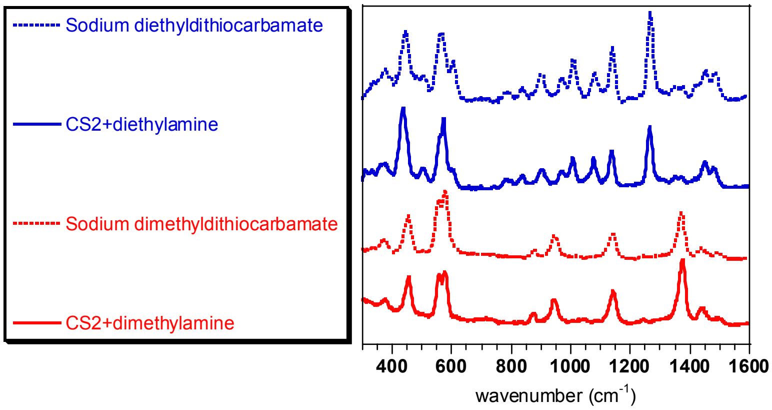


Figure S1. SERS spectra of dimethyl DTC (**1**) and diethyl DTC (**2**) on roughened Au substrates, formed *in situ* (solid line) and deposited as sodium dithiocarbamate salts (dashed line).

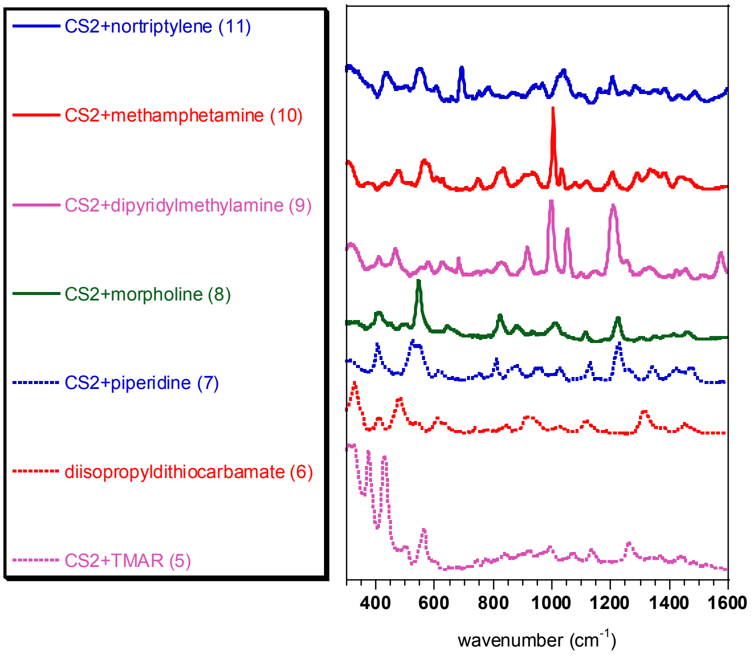


Figure S2. SERS spectra of DTC ligands **5** through **11** (in ascending order). Spectra were obtained using a dispersive Raman microscope with a 20X objective lens (N.A.=0.4), at an excitation wavelength of 785 nm and an exposure time of 30 seconds.

Calculated Raman spectra of dithiocarbamates on roughened Au surfaces:

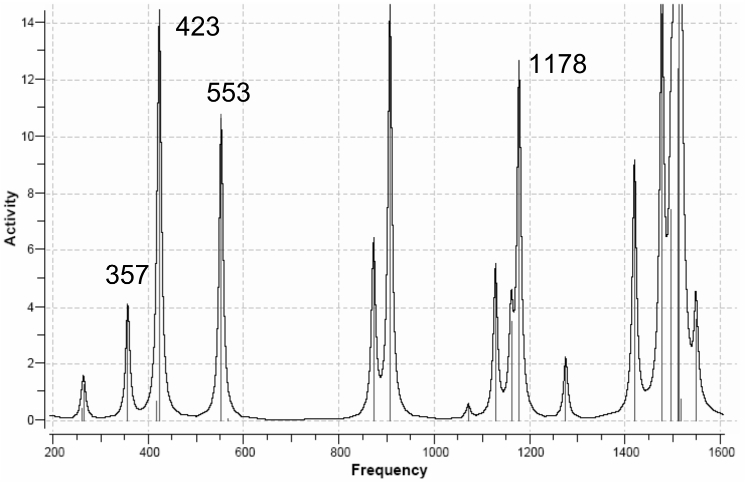


Figure S3. DFT calculation of Raman vibrational spectrum of DTC ligand **1** on Au_1, using the B3LYP method and LANL2DZ basis set (Gaussian04). C–S bending at 357 cm^{-1}; Symmetrical C–S stretching coupled with N–CH_3 scissoring at 423 cm^{-1} (**I**) and 553 cm^{-1} (**II**); (sp^2)C–N stretching coupled with N–CH_3 rocking at 1178 cm^{-1}.

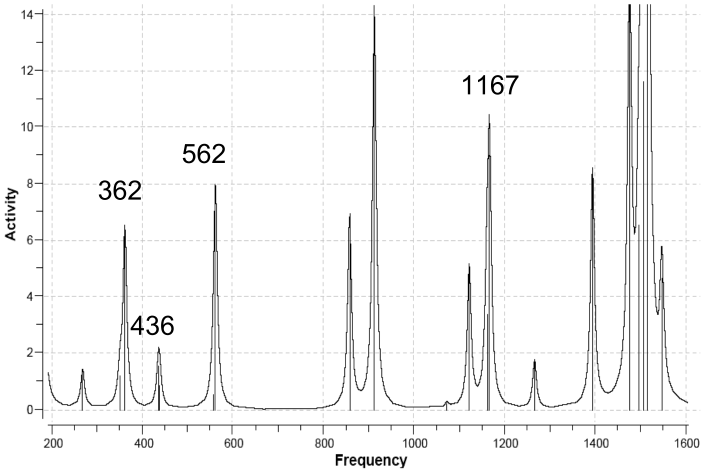


Figure S4. DFT calculation of Raman vibrational spectrum of DTC ligand **1** on Au_3, using the B3LYP method and LANL2DZ basis set (Gaussian04). C–S bending at 362 cm^{-1}; Symmetrical C–S stretching coupled with N–CH_3 scissoring at 436 cm^{-1} (**I**) and 562 cm^{-1} (**II**); (sp^2)C–N stretching coupled with N–CH_3 rocking at 1167 cm^{-1}.

Movies of vibrational modes **I** and **II** for **1** on Au_3 are available in MPEG format.
See: DimethylDTC_Mode_I_436.MPG, DimethylDTC_Mode_II_562.MPG.

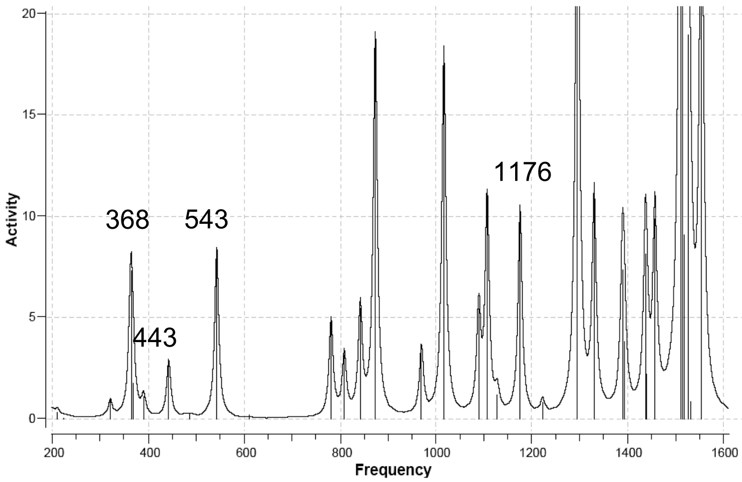


Figure S5. DFT calculation of Raman vibrational spectrum of DTC ligand **2** on Au_3, using the B3LYP method and LANL2DZ basis set (Gaussian04). Symmetrical C–S stretching coupled with N–CH_3 scissoring modes at 443 cm^{-1} (**I**) and 543 cm^{-1} (**II**); (*sp^2*)C–N stretching coupled with N–CH_3 wagging modes at 1176 cm^{-1}.

Movies of vibrational modes **I** and **II** for **2** on Au_3 are available in MPEG format.
See: DiethylDTC_Mode_I_443.MPG, DiethylDTC_Mode_II_543.MPG.