

## Trace detection of tetrabromobisphenol A by SERS with DMAP-modified magnetic gold nanoclusters: Electronic Supplementary Information

Synthesis and characterization of magnetic gold nanoclusters (Figs. S1–S5) .....	S-1
SERS spectra of MGNCs exposed to adsorbates and trace analytes (Figs. S6–S8)....	S-6
Two-dimensional correlation analysis of SERS data.....	S-7
Raman spectroscopy of DMAP (Fig. S9, S10).....	S-8
Vibrational Raman modes of DMAP–Au (Fig. S11) .....	S-9

### General experimental details

All materials were obtained from commercial sources and used as received, unless otherwise noted. Deionized water was obtained from an ultrafiltration system (Milli-Q, Millipore) with a measured resistivity above 18 M $\Omega$ ·cm, and passed through a 0.22- $\mu$ m filter to remove particulate matter. CS<sub>2</sub> was used as supplied and stored with minimum exposure to air. Nanoparticles were characterized by transmission electron microscopy (TEM) using a Tecnai T20 (FEI) with a LaB<sub>6</sub> filament at 200 kV. Optical extinction spectra were measured using a Cary-50 spectrophotometer (Varian) with a 1-cm cell path length. X-ray diffraction (XRD) measurements were performed on dry powder samples with a Bruker D8-Focus diffractometer using Cu K $\alpha$  radiation (20 kW,  $\lambda$ =1.5406 Å). SERS spectra were acquired at an excitation wavelength of 785 nm using a custom-built Raman microscope, with a laser power of 20 mW at the sample and an exposure time of 100 seconds. SERS signals produced by specific adsorbates on MGNCs were confirmed by positive controls using nanoporous SERS substrates.<sup>21</sup>

### Synthesis and characterization of MGNCs and intermediate materials

*Step 1: co-precipitation of colloidal Fe<sub>3</sub>O<sub>4</sub>.* FeCl<sub>3</sub> (648 mg, 4 mmol) and FeCl<sub>2</sub>·4H<sub>2</sub>O (398 mg, 2 mmol) were dissolved in deaerated, deionized water (5 mL) and added dropwise to a 28 wt% solution of NH<sub>4</sub>OH (15 mL) over a period of 10 min, with the reaction flask immersed in an ultrasonic cleaning bath under an inert atmosphere. The reaction was agitated by vortex mixing for 2 min to produce a uniform dispersion of colloidal Fe<sub>3</sub>O<sub>4</sub>. A 1-mL aliquot of this dispersion was removed and precipitated with a handheld magnet, then redispersed in 5 mL deionized water. This cycle of precipitation and redispersion was repeated 4 times; the final concentration of colloidal Fe<sub>3</sub>O<sub>4</sub> was determined to be 25–30 mg/mL, based on an oven-dried sample.

**Step 2: PEGylation of colloidal  $Fe_3O_4$ .** A solution of methyl(polyethyleneglycol)-dithiocarbamate (mPEG-DTC) was prepared in situ by dissolving 5-kDa mPEG-NH<sub>2</sub> (20 mg, 4 mmol) in 1 mL of dry MeOH, followed by 1 equivalent of CS<sub>2</sub> (60  $\mu$ L, 4 mmol) and 0.4 equivalents of Et<sub>3</sub>N (50  $\mu$ L, 1.6 mmol). The reaction mixture was stirred for 45 min and monitored by UV-vis absorption for increases at 260 and 290 nm. An aliquot of the freshly prepared mPEG-DTC solution (1 mL) was then added to a suspension of colloidal  $Fe_3O_4$  (8 mg in 1 mL), then shaken by hand for 5 min and allowed to sit for 1 hour at room temperature. XRD analysis of a magnetically precipitated sample confirmed the presence of nanocrystalline  $Fe_3O_4$  (Figure S1).

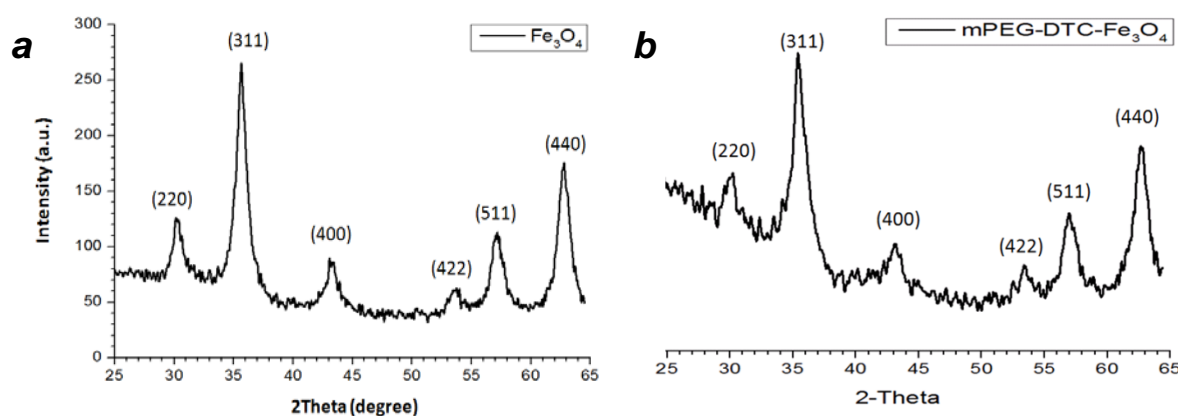


Figure S1. XRD spectrum of (a)  $Fe_3O_4$  particles and (b) mPEG-functionalized  $Fe_3O_4$  (JCPDS 75-0033).

**Step 3: preparation of MGNCs.** A suspension of mPEG-modified colloidal  $Fe_3O_4$  (1 mg in 0.25 mL) was incubated with 6.5 mM L-histidine (4 mg in 4 mL) adjusted to pH 5–6, and allowed to sit for 1 hour at room temperature, then added to 9 mM AuCl<sub>4</sub> adjusted to pH 9–10 (12.75 mL). This was equilibrated for 20 min prior to treatment with 20 mM *N*-methylhydroxylamine (5 mg in 3 mL), which was added in six portions every 10 min while shaken by hand. The color of the reaction mixture changed from pale brown to deep purplish-blue, and was allowed to sit for 24 hours for complete reduction. The MGNCs were collected by magnetic precipitation, then redispersed in deionized water (20 mL) in a sonication bath. The weight of crude MGNCs is approximately 5 mg.

**Step 4: removal of excess  $Fe_3O_4$ .** A 0.5 M solution of bis(2-hydroxyethyl)DTC was prepared by dissolving diethanolamine (105 mg, 1.0 mmol) in 1 mL of deaerated methanol, followed by CS<sub>2</sub> (30  $\mu$ L, 0.5 mmol) and stirring for 30–45 min at room temperature. DTC formation was confirmed by the formation of UV absorption peaks at 260 and 290 nm. An aqueous suspension of crude MGNCs (~2 mg in 8 mL) was treated with 0.5 M bis-HE-DTC in methanol (32  $\mu$ L) and shaken by hand. After 30 min,

the cleansed MGNCs were collected by magnetic precipitation and redispersed in 1 mL of water.

### **Preparation of DMAP-modified MGNCs for SERS analysis**

Cleansed (bis-HE-DTC treated) MGNCs in water (2 mg/mL) were magnetically precipitated and redispersed in an aqueous DMAP solution (1 nM, 1 mL). These were collected again and redispersed in deionized water to 2 mg/mL and left to sit for 1 hour. For TBBPA detection, DMAP-modified MGNCs (2 mg/mL) were magnetically precipitated and redispersed in an aqueous TBBPA solution (10–100 pM, 1 mL) and left to sit for 1 hour. For SERS analysis, a 0.3-mL aliquot (ca.  $6 \times 10^9$  particles) was subjected to magnetic precipitation, followed by removal of the supernatant. The particles in the retentate (60  $\mu$ L) were deposited onto a quartz substrate and dried in air for 15 min while exposed to a conical magnet, resulting in a final spot size of 1.5–2.0 mm.

### **Materials characterization of MGNCs**

TEM images were acquired on a Tecnai T20 (FEI) operating at 200 kV, at 35kx magnification using a 1024x1024 digital CCD camera. Particle size analysis was performed by SigmaScan Pro (Figure S2). MGNCs were also characterized by selected-area electron diffraction, which revealed lattice planes for fcc-Au (Figure S3, Table S1). Optical extinction spectroscopy on dispersed MGNCs indicated a broad absorbance across the visible and NIR spectrum (Figure S4a). The dispersions were precipitated within several minutes by a handheld magnet (Figure S4b), but easily redispersed by light sonication or vortex mixing. Nanoparticle tracking analysis (NTA) was performed using a Nanosight LM-10 system (Malvern Instruments) with 405-nm laser excitation and particle-free water for serial dilutions; a typical MGNC sample contains ca.  $2 \times 10^{10}$  particles/mL, with an average particle size of 100 nm (Figure S5).

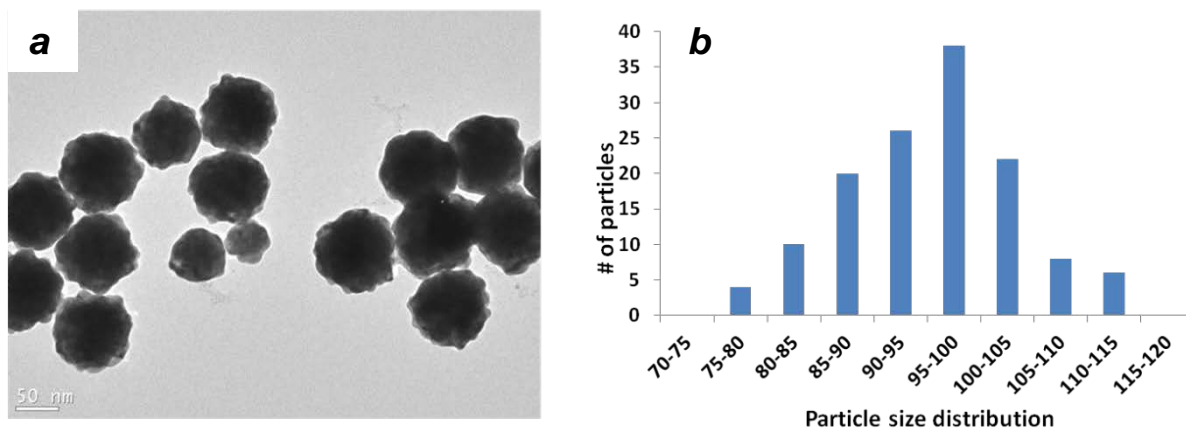


Figure S2. (a) TEM image of DE-DTC cleaned MGNC's; scale bar 50 nm. (b) Particle size distribution of MGNCs after step 4 ( $N=134$ ), with a median size of 95-100 nm.

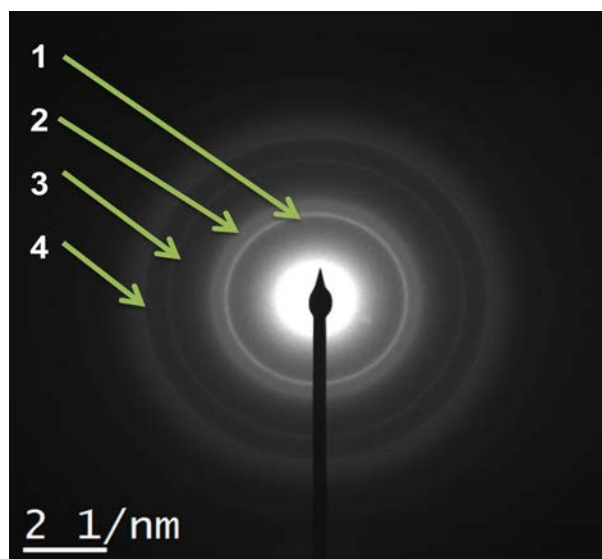


Figure S3. Selected-area electron diffraction analysis of cleansed MGNCs, indicative of bcc-Au.

Table S1. Selected area electron diffraction data for MGNCs (ref. = JCPDS 04-0784)

#	$d$ [ $\text{\AA}$ ] (expt.)	Intensity (expt)	$d$ [ $\text{\AA}$ ] (ref.)	Intensity (ref.)	$h$	$k$	$l$
1	2.337	127	2.355	100	1	1	1
2	2.035	49	2.039	52	2	0	0
3	1.426	50	1.442	32	2	2	0
4	1.216	40	1.230	36	3	1	1

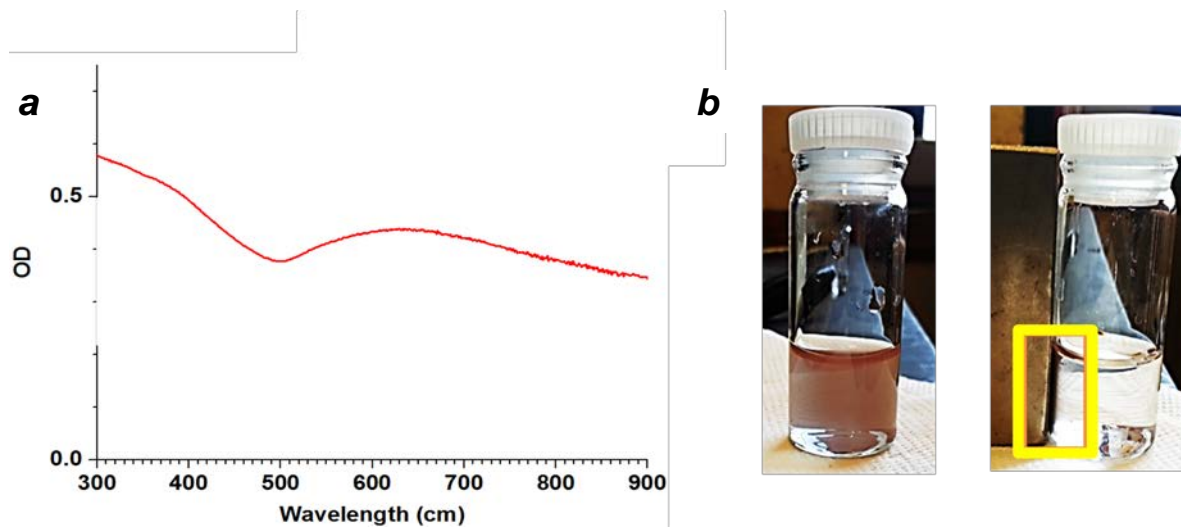


Figure S4. (a) UV/Vis spectra of the DE-DTC cleaned MGNC's. (b) MGNCs before and after magnetic precipitation.

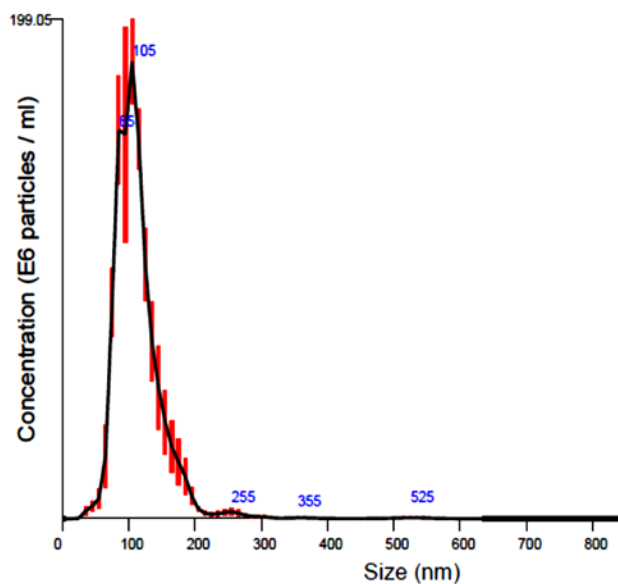


Figure S5. Nanoparticle tracking analysis of cleansed (bis-HE-DTC treated) MGNCs in water, diluted to  $10^9$  particles/mL; mode peak corresponds to a hydrodynamic diameter ( $d_h$ ) of 103 nm.

## SERS spectra of MGNCs (unprocessed)

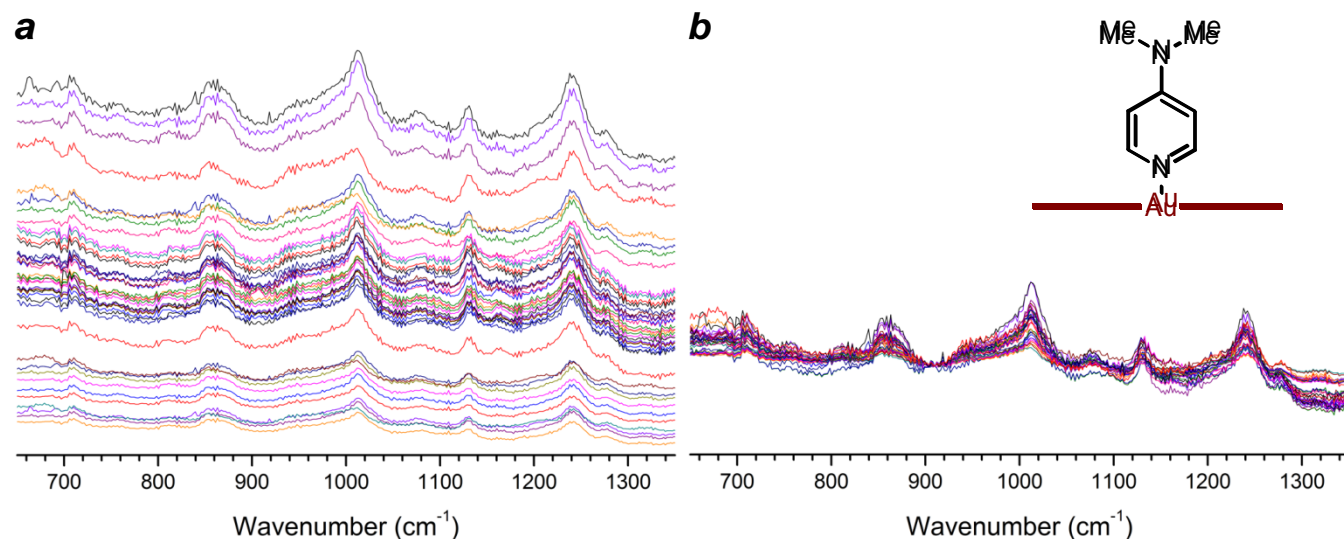


Figure S6. MGNCs after 1 hour exposure to 1 nM DMAP (44 spectra collected from 6 different samples). MGNCs (2 mg/mL) were magnetically precipitated and redispersed in deionized water, then magnetically deposited onto quartz substrates and dried in air prior to SERS analysis. (a) Unprocessed SERS spectra ( $\lambda_{\text{ex}} = 785 \text{ nm}$ , 100 sec exposure, 20 mW at the sample). (b) Collapsed SERS spectra with common intensity value at  $900 \text{ cm}^{-1}$ .

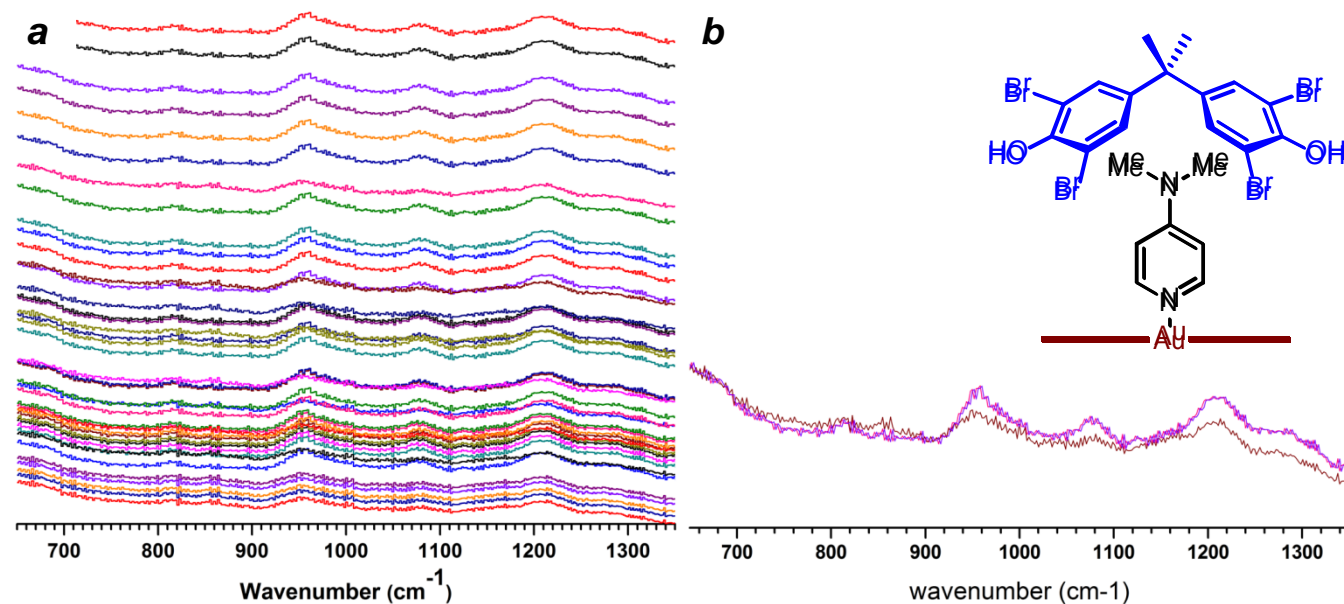


Figure S7. DMAP-modified MGNCs after 1 hour exposure to 100 pM TBBPA (42 spectra collected from 5 different samples). DMAP-MGNCs (2 mg/mL) were magnetically deposited onto quartz substrates and dried in air prior to SERS analysis. (a) Unprocessed SERS spectra ( $\lambda_{\text{ex}} = 785 \text{ nm}$ , 100 sec exposure, 20 mW at the sample). (b) Collapsed SERS spectra (amplified 2X) with common intensity value at  $900 \text{ cm}^{-1}$ .

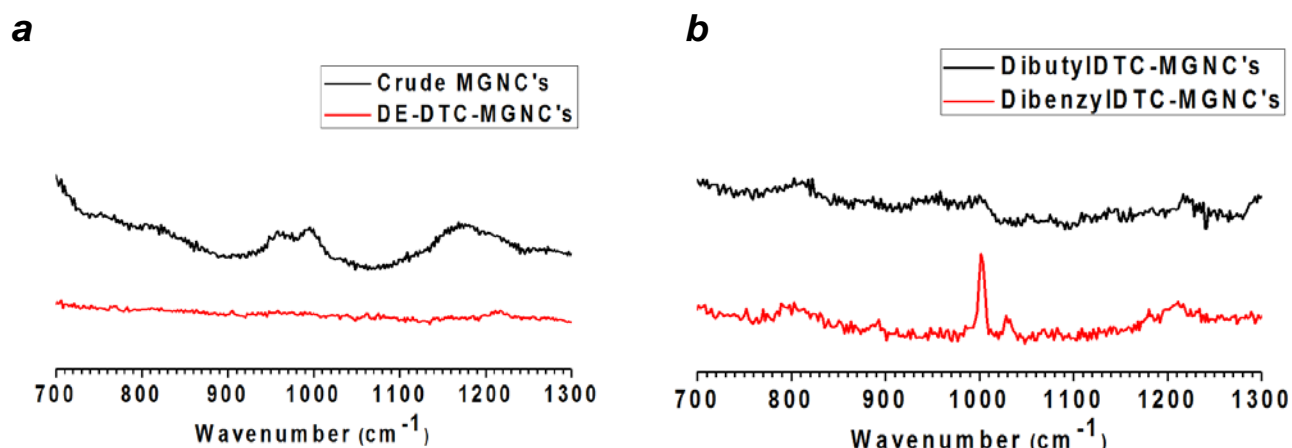


Figure S8. MGNCs after 1 hour exposure to various adsorbates: (a) Crude MGNCs (step 3; black) and MGNCs cleansed with bis-HE-DTC (step 4; red); (b) MGNCs treated with 2 mM *N,N*-dibutyl-DTC (black) and 2 mM *N,N*-dibenzyl-DTC (red). Treatment of cleansed MGNCs with 1 nM TBBPA did not produce any detectable signals, with Raman spectra essentially identical to that shown in (a).

### Two-dimensional correlation analysis

All calculations were performed using the statistical analysis packaged provided by OriginPro 8. SERS spectral data was processed without normalization, but each spectrum was calibrated to a common intensity value at 900 cm<sup>-1</sup> to minimize the effects of background counts (see Figs. S2B, S3B). Individual spectra were correlated against an intensity-averaged SERS spectrum of DMAP adsorbed on MGNCs (mean of 44 independent measurements), precipitated from a 1 nM DMAP solution.

Correlations were performed with data points corresponding to major Raman bands of DMAP adsorbed on Au. Several bands were dampened upon exposure to TBBPA (*A*: 840–890 cm<sup>-1</sup>; *B*: 970–1040 cm<sup>-1</sup>; *C*: 1120–1140 cm<sup>-1</sup>; *D*: 1210–1260 cm<sup>-1</sup>), and were assigned as X1 (94 data points). Two bands showed modest increases upon TBBPA exposure (*B'*: 930–980 cm<sup>-1</sup>; *D'*: 1180–1240 cm<sup>-1</sup>) and were assigned as X2 (56 data points). Raman band *C'* (1060–1100 cm<sup>-1</sup>) appeared to be unaffected by TBBPA exposure, and was not included in the correlation analysis.

Pearson coefficients for X1 and X2 were used to evaluate differences in SERS signals produced by DMAP-modified MGNCs isolated from water (DMAP only) and MGNCs exposed to trace levels of analyte (DMAP + TBBPA). {X1,X2} datasets were presented in a two-dimensional scatter plot to illustrate the large difference in SERS signatures, as well as the reproducibility of individual readings.

### Raman spectroscopy of DMAP: Experimental versus simulated spectra

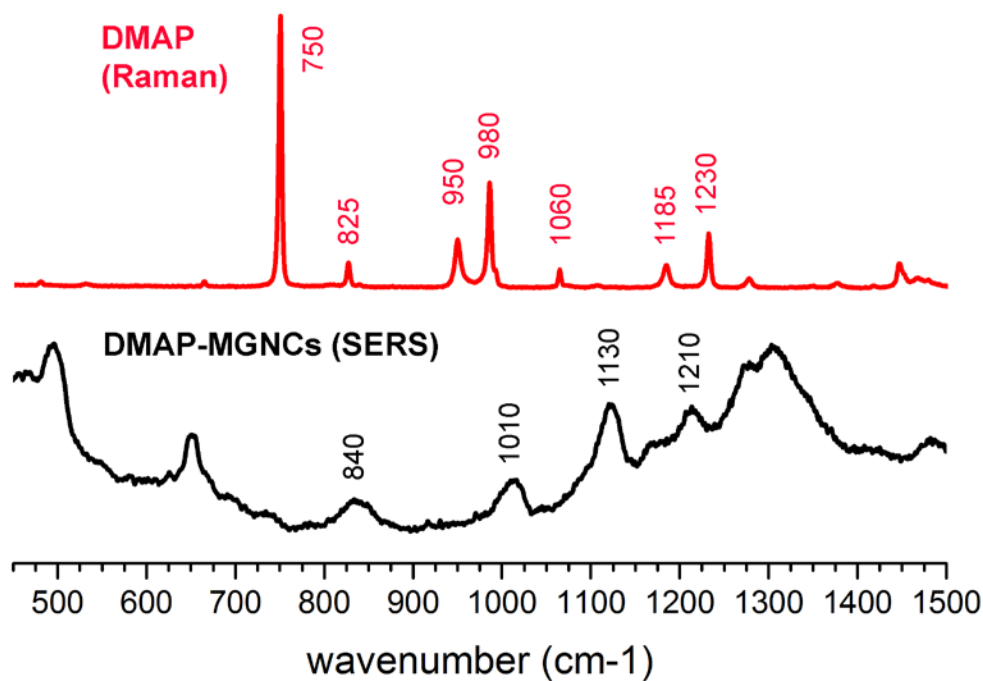


Figure S9. *Top*, Raman spectrum of neat (crystalline) DMAP. *Bottom*, SERS spectrum of DMAP-coated MGNCs.

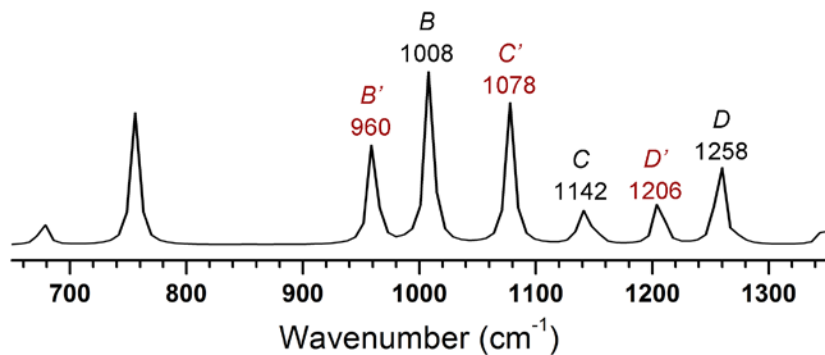


Figure S10. Simulated Raman spectrum of DMAP coordinated to Au using Gaussian05, with geometry optimization using the B3LYP method and LANL2DZ basis set.



## DFT calculations of DMAP+Au: Vibrational Raman modes

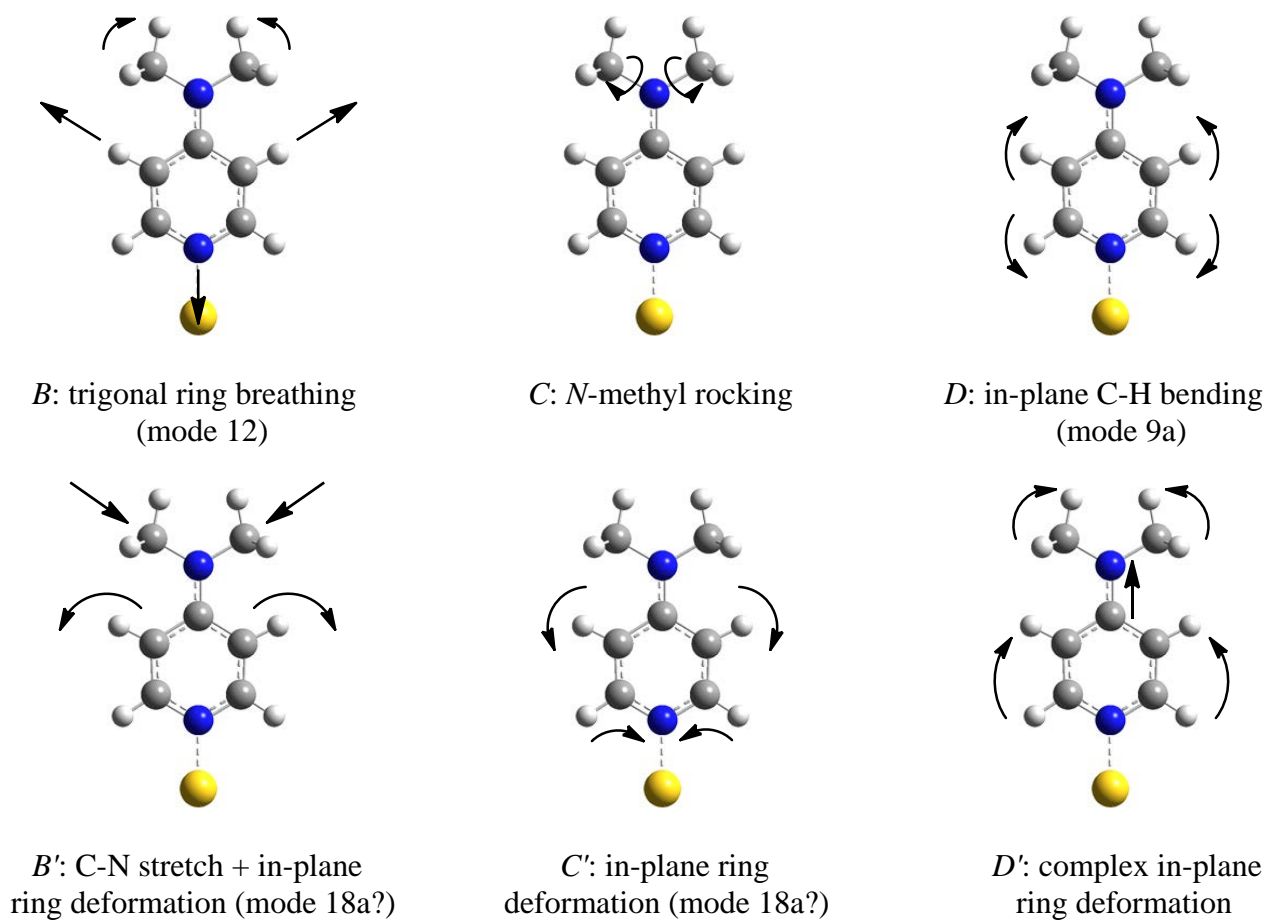


Figure S11. Raman vibrational modes assigned to TBBPA-sensitive bands (*B–D*) and TBBPA-insensitive bands (*B'–D'*). Wilson notations provided in parentheses.