ELECTRONIC SUPPLEMENTARY INFORMATION

Chemical Speciation of Heavy Metals by Surface-enhanced Raman Scattering Spectroscopy: Identification and Quantification of Inorganic- and Methyl-Mercury in Water

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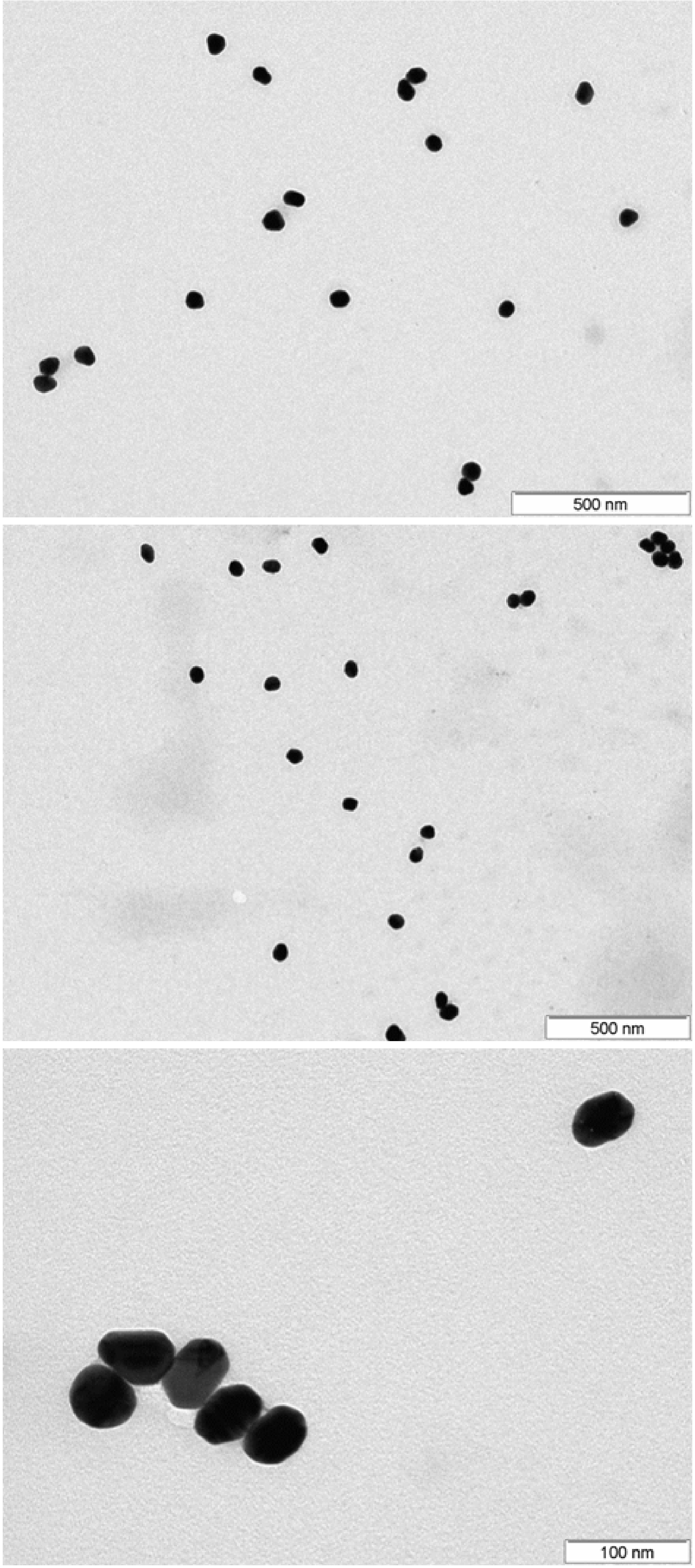

Figure S1. Representative TEM microscopies of AuNPs.

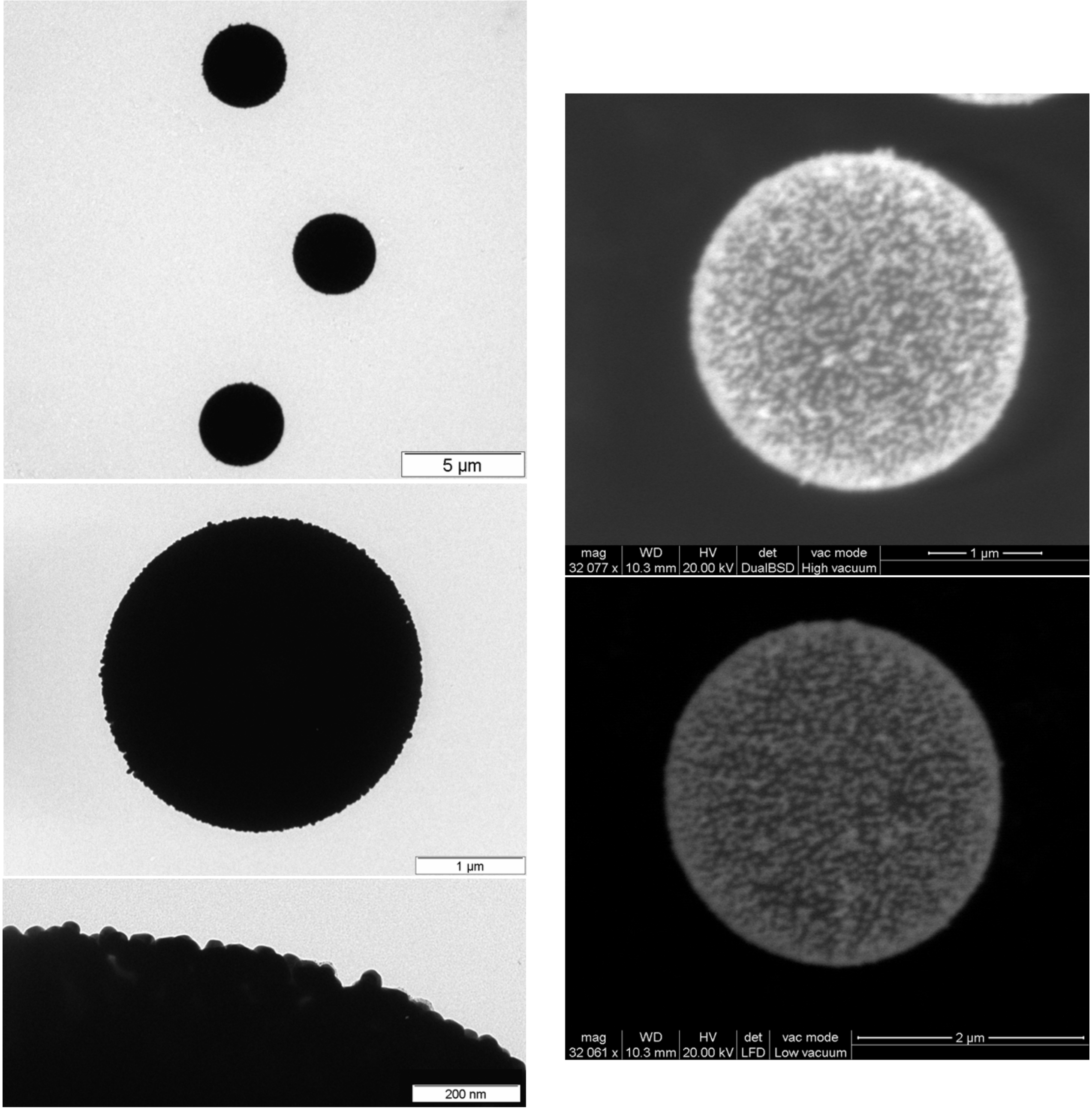

Figure S2. Representative TEM (left column) and ESEM (right column) microscopies of PS@Au beads.

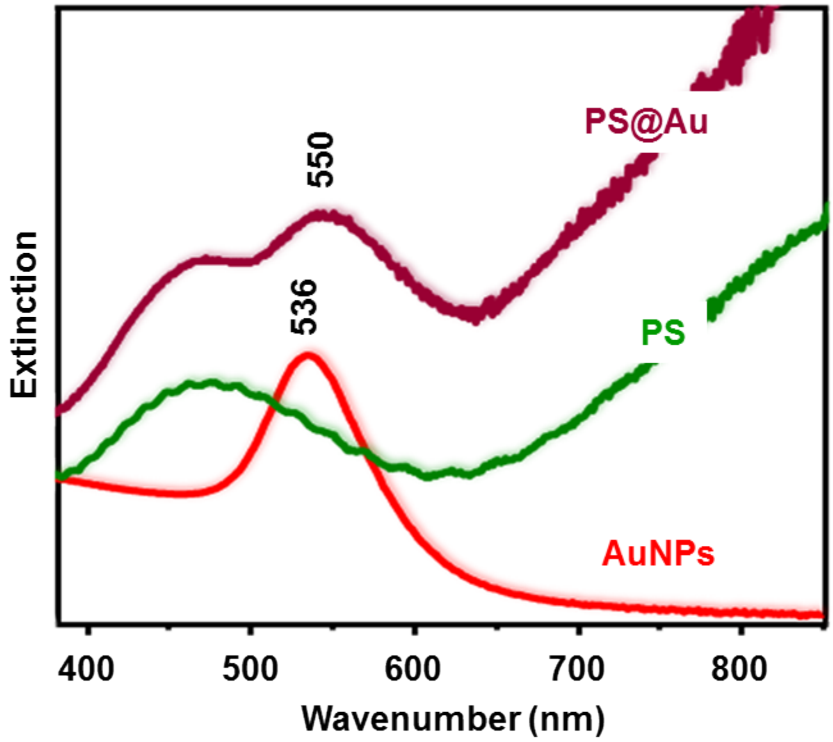

Figure S3. Optical extinction spectra of the PS@Au suspension, as well as those of its individual components (i.e. Au colloids and naked PS beads in suspension). The intensity of the extinction spectra was freely adjusted for the sake of comparison. Red-shift of the LSPR for monodispersed Au colloids at 536 nm takes place upon assembly onto the bead surfaces as a result of the plasmonic coupling of adjacent nanoparticles, as revealed by the broad feature centered around 550 nm in the PS@Au spectrum.

Table S1. Raman shifts (cm^{-1}) and Their Assignments in the SERS Spectrum of 4-mercaptopyridine on PS@Au beads in suspension. Assignments from refs [1-7].

Symmetry	**Assignment**	**SERS**
	ν(Hg-CH$_3$)	*526*
6a1	β(CC)/ν(CS)	702
10b1	γ(CH)	777
1a1	Ring breathing	1001
18a1	β(CH)	1040
12a1	Ring breathing/ν(CS)	1096
	β(Hg-CH$_3$)	*1167*
9a1	β(CH)	1220
3b2	β(CH)	1276
19b2	ν(C=C)/ν(C=N)	1465
19a1	ν(C=C)/ν(C=N)	1494
8b2	ν(C=C) with deprotonated nitrogen	1580
8a1	ν(C=C) with protonated nitrogen	1612

ν, stretching; β, bending; δ, in-plane deformation; γ, out-of-plane deformation.

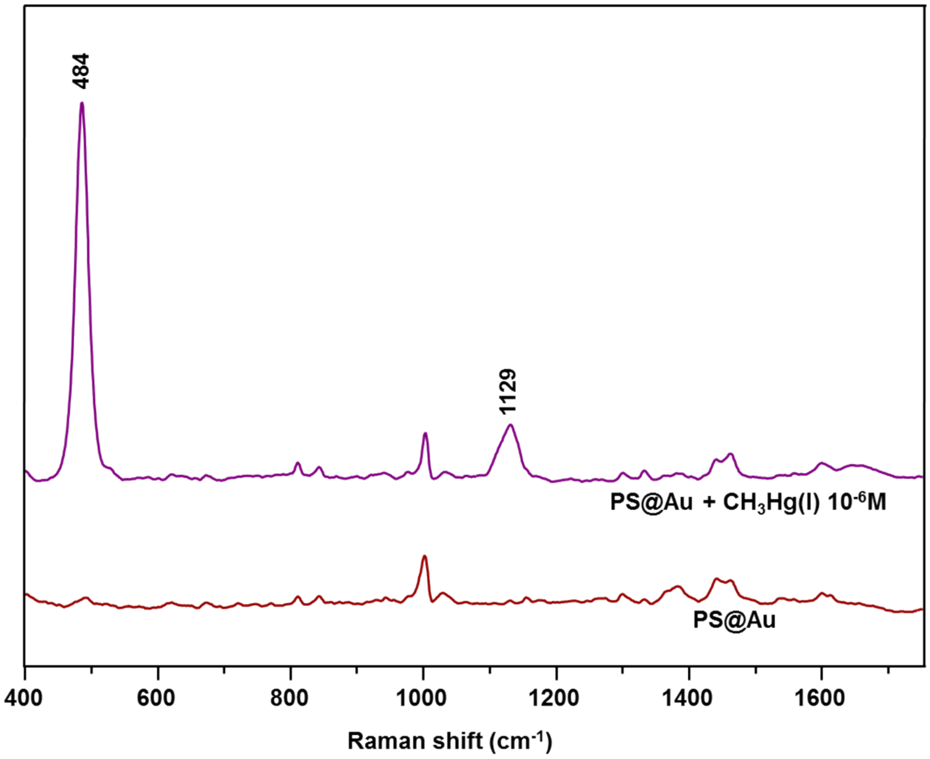

Figure S4. SERS spectra of the naked PS@Au beads before and after the addition of CH_3HgCl 10^{-6} M solution (final concentration of beads in solution = 16 µg/mL). The Raman background of the plastic container was subtracted to each spectrum (residual weak narrow bands at ca. 808 and 841 cm^{-1} ascribed to the plastic may still appear in some spectra). Measurements were obtained using 785 nm excitation and a long working distance objective (100% laser power, 1 accumulation, 10s exposure time).

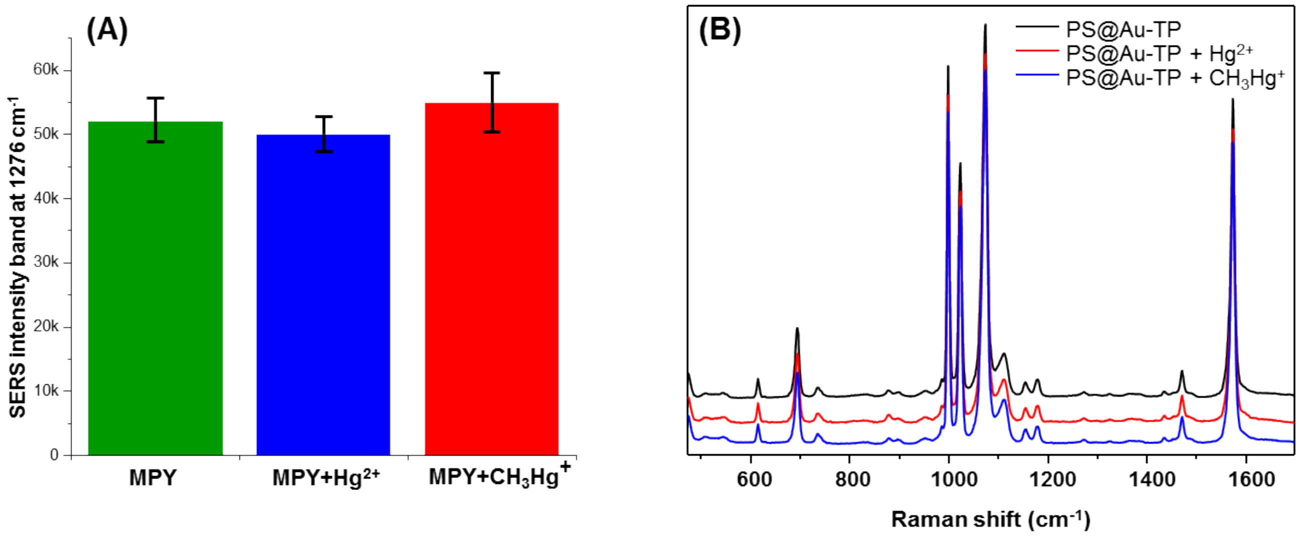

Figure S5. (A) Intensity of the MPY band at 1276 cm^{-1} before and after the exposure to $HgCl_2$ 1ppm and CH_3HgCl 1ppm. Dilution factors were applied to the values. Error bars are equal to three standard deviations (N = 3). (B) SERS spectrum of thiophenol (TP) on PS@Au before and after the exposure to $HgCl_2$ 1 ppm and CH_3HgCl 1ppm. Beads concentration in the samples was 0.8 µg/mL.

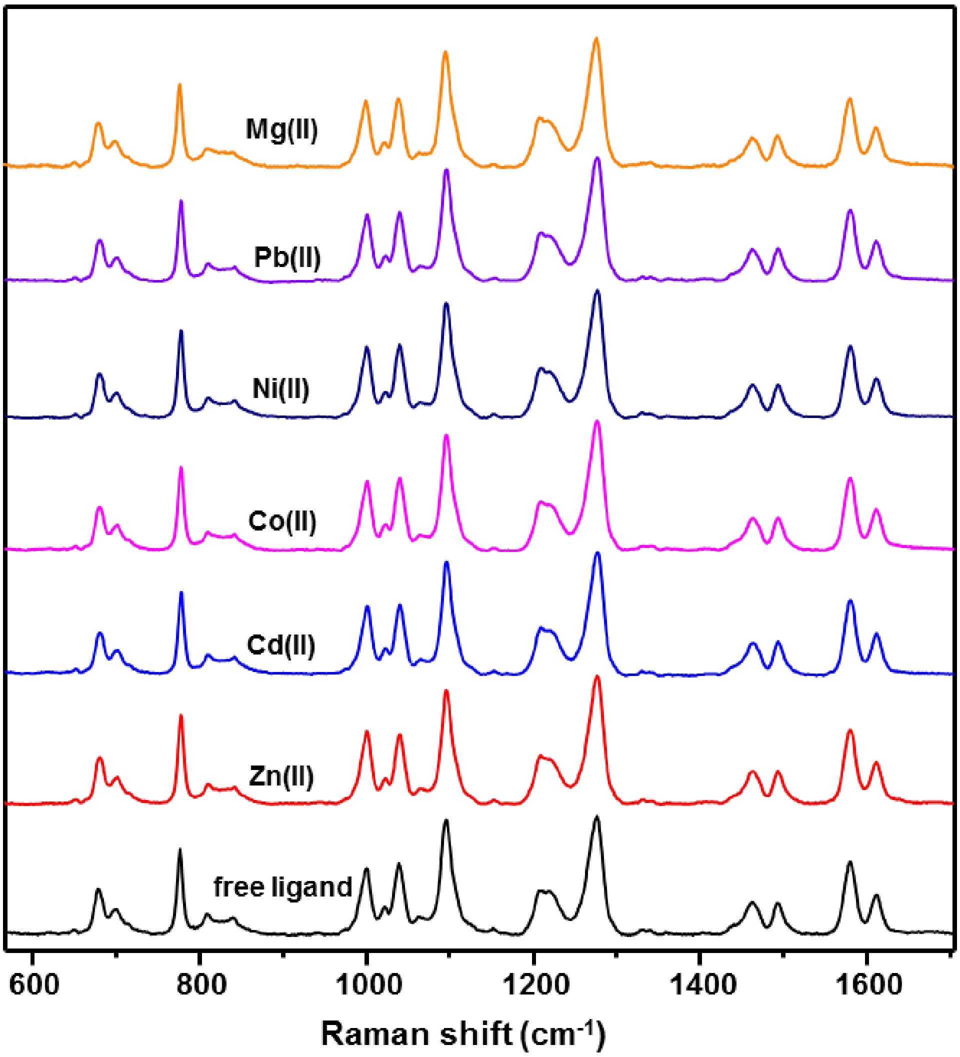

Figure S6. Normalized SERS spectra of MPY on PS@Au beads before and after the exposure to 10^{-6} M solutions of $ZnCl_2$, $CdCl_2$, $CoCl_2$, $Ni(NO_3)_2$, $PbCl_2$ and $MgSO_4$. Final concentration of beads in solution = 0.8 µg/mL. SERS spectra are normalized to the ring breathing band at 1096 cm^{-1}. Measurements were obtained using 785 nm excitation and a long working distance objective (100% laser power, 1 accumulation, 10s exposure time).

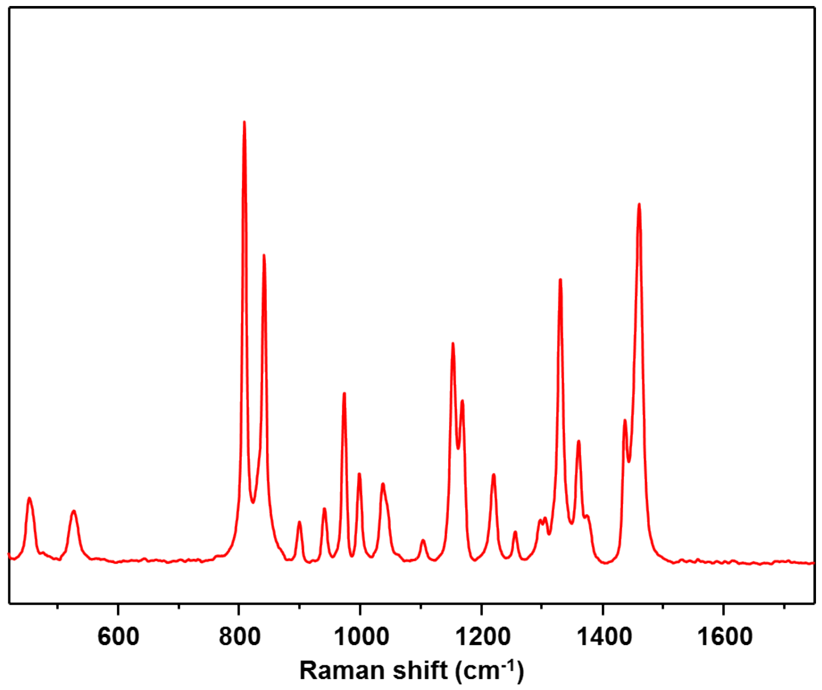

Figure S7. Normal Raman spectrum of the plastic container.

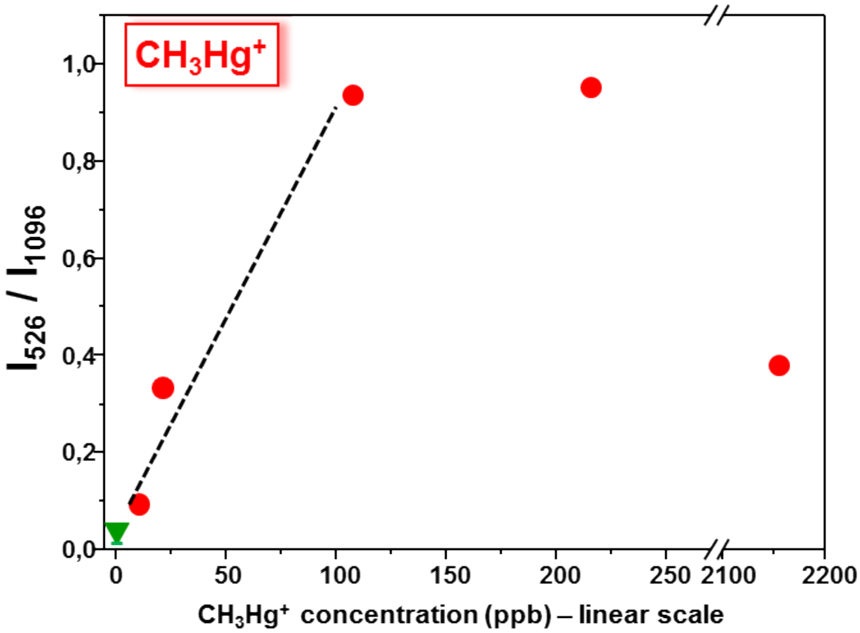

Figure S8. Intensity ratio, I_{526}/I_{1096}, of the ν(Hg-CH_3) band at 526 cm^{-1} and the MPY ring breathing band at 1096 cm^{-1} as a function of CH_3Hg^+ concentration (linear scale; bead concentration in the metal solutions equals to 16 µg/mL).

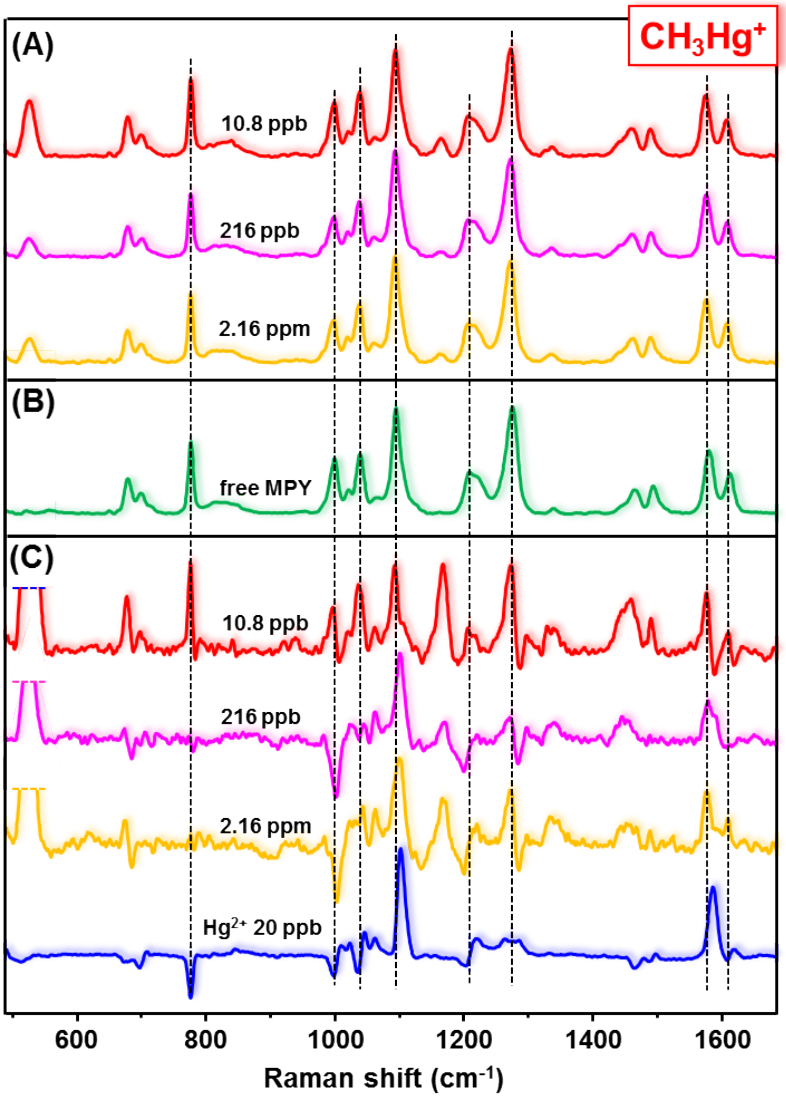

Figure S9. SERS spectra of MPY on (A) PS@Au beads after the exposure to CH_3HgCl solutions of different concentrations and on (B) PS@Au. SERS spectra are normalized to the ring breathing band at 1096 cm^{-1}. Final concentration of beads in solution = 0.8 µg/mL. (C) Difference SERS spectra obtained by subtracting the SERS spectrum of MPY in (B) to each spectrum in (A). Additionally, the difference spectrum for Hg^{2+} 20 ppb is included for further comparison. Measurements were obtained using 785 nm excitation and a long working distance objective (100% laser power, 1 accumulation, 10s exposure time).

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