Synthesis of bifunctional Au/Pt/Au core/shell nano-raspberries for in-situ SERS monitoring of platinum-catalyzed reactions

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Experimental section

Tetrachloroauric(III) acid ($HAuCl_4$), trisodium citrate, silver nitrate, hexachloroplatinic(IV) acid (H_2PtCl_6), 4-nitrothiophenol (4-NTP), and sodium borohydride were purchased from Sigma/Aldrich/Fluka and used without further purification. In all experiments ultrapure water (18.2 MΩ) was used.

Synthesis of Au/Pt/Au core/shell nano-raspberries: 50 mL of an aqueous 2.94×10^{-4} M $HAuCl_4$ solution was reduced by 1.25 mL of an aqueous 3.88×10^{-2} M citrate solution at boiling point (= reaction temperature for all NP preparation steps) under vigorous magnetic stirring for 20 min. Then 3 mL of an aqueous 5.88×10^{-3} M silver nitrate solution was added to the stirred solution dropwise, and, subsequently 750 µL of an aqueous 3.88×10^{-2} M citrate solution was added. After 1 hour, 80 µL of an aqueous 1.95×10^{-1} M H_2PtCl_6 solution was added and a dark mauve colloid was obtained. 15 mL of the product was centrifuged and washed with water two times and then resuspended in 30 mL water. 800 µL of an aqueous 5.88×10^{-3} M silver nitrate solution was added again at the same heating and stirring conditions as before, and subsequently 200 µL of an aqueous 3.88×10^{-2} M trisodium citrate solution were added. Again, the reaction mixture was left boiling for 1 hour. For the gold protuberance growing step, 100 µL of an aqueous 2.94×10^{-4} M $HAuCl_4$ and 100 µL of an aqueous 3.88×10^{-2} M citrate solutions were added simultaneously to the gold-platinum-silver trilayer nanoparticle suspension and the reaction was stopped after 20 min.

TEM/HRTEM including EDX measurements were performed with a JEOL JEM-2100 electron microscope operating with a LaB_6 cathode and an acceleration voltage of 200 kV. SEM measurements were carried out with a Zeiss Supra 50 electron microscope. EDX accessory (Oxford Inca x-sight 10 mm^2) from a Zeiss EVO MA10 electron microscope was used. SERS spectra were recorded on a Raman spectrometer from Princeton Instruments (Acton SP2500, 50 cm focal length, 1800 grooves/mm grating) with a laser excitation wavelength of 632.8 nm (HeNe laser). Extinction spectra were obtained on a Perkin Elmer UV/Vis absorption spectrometer (Lambda 35).

Non-negative matrix factorization (NMF)

Briefly, experimental data acquired from mixtures are decomposed into a linear combination of contributions from individual species (pure components). Only positive matrix entries are allowed since both Raman intensities as well as concentrations cannot assume negative values. First, all experimental SERS spectra are represented as column vectors and sorted by increasing $NaBH_4$ volume (left matrix in Figure S10). This experimental data matrix is then factorized (decomposed) into a product of two new matrices (right in Figure S10) with only positive entries.

As the only required piece of *a priori* knowledge, we assumed the presence of three components, based on the qualitative analysis of the experimental SERS spectra in Figure S8. The first matrix on the right side of the equation in Figure S10 contains the SERS spectra of the three pure components as column vectors, separately shown in Figure S10; they exhibit a very strong spectral overlap, which precluded several other forms of data evaluation such as univariate approaches. The second matrix on the right side in Figure S10 contains the relative contributions of each of the three species at a given $NaBH_4$ volume. The decomposition of the experimental data matrix therefore yields both the SERS spectra of the pure components and their relative contributions, as shown in the manuscript (Figure 4).
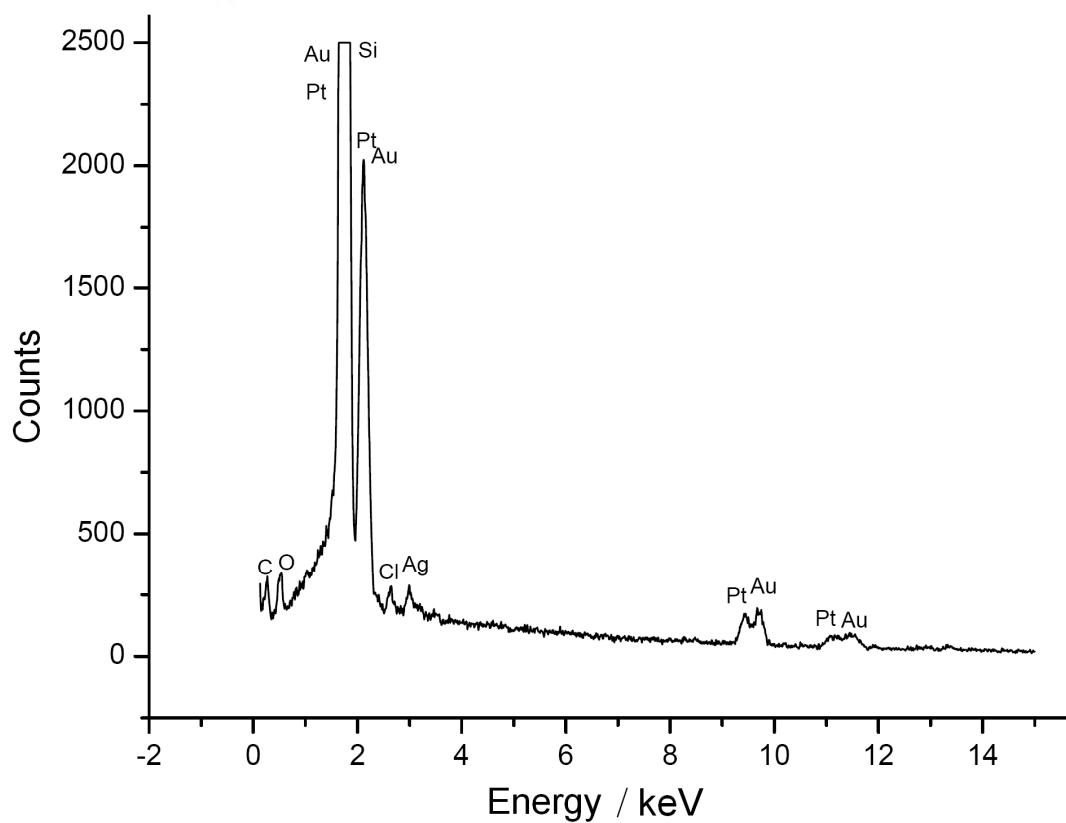
Figure S1. EDX spectrum of Au/Pt core/shell nanoparticles (NPs) recorded on a Si wafer. The Ag signal arises from AgCl, which precipitates during the galvanic replacement of Ag by Pt.
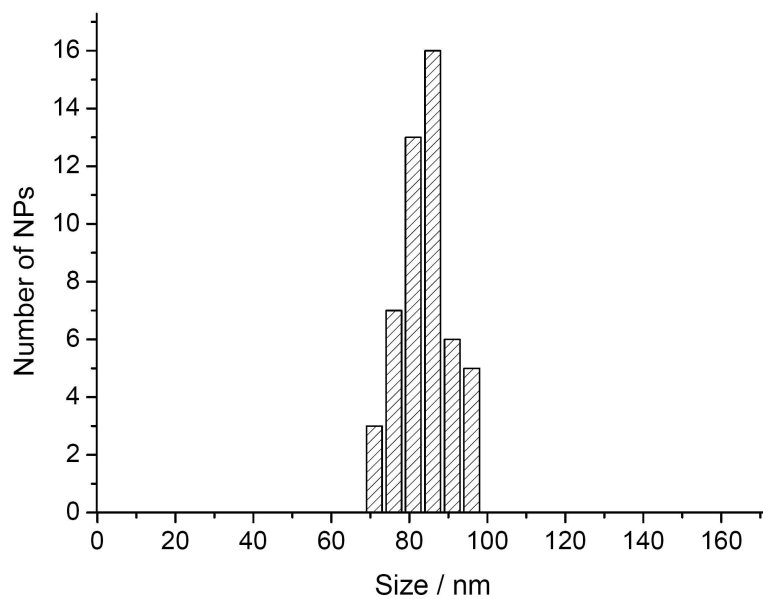
Figure S2. Size-histogram of Au/Pt/Au core/shell nano-raspberries based on TEM measurement. 50 randomly chosen nano-raspberries were analyzed. The diameter of each nano-raspberry was estimated by determining the longest distance between two points at the edge. The resulting average diameter is 86.7 nm, the standard deviation is 6.4 nm.

Figure S3. HR-TEM image of a single Ag-coated Au/Pt core/shell NP. The Ag deposition leads to the formation of a thin and discontinuous layer on the platinum surface.

Figure S4. 3D model of a nano-raspberry (a) based on the experimental HR-TEM image in Figure 2C, and geometric model together with formulas (b) for estimating the surface area. n: number of Au protuberances on the nano-raspberry; r: radius of the Au protuberance; h: height of the Au protuberance; R: radius the Au-Pt core-shell NP; h_{Pt}: auxiliary quantity for calculating the Pt surface area lost due to Au protuberance. For $n = 18$, $\theta = 60°$, $r = 8.4$ nm, $R = 27.1$ nm, $h = 15.6$ nm, $h_{pt} = 0.3$ nm, the entire surface area $A = A_{Au} + A_{pt}$ is $\sim 2.3 \times 10^{-14}$ m^2, with $A_{Au} \sim 1.5 \times 10^{-14}$ m^2 and A_{pt} $\sim 8.3 \times 10^{-15}$ m^2.
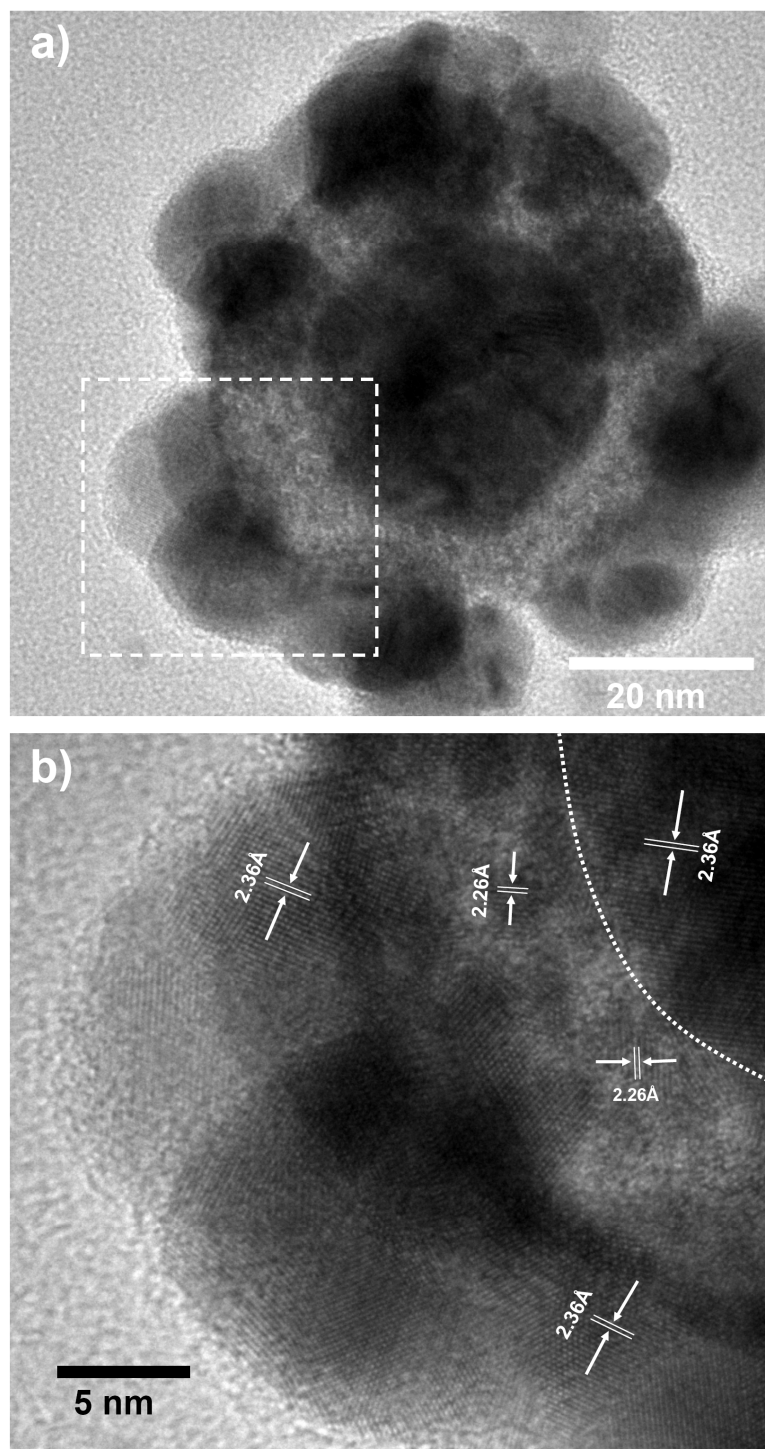
Figure S5. HR-TEM images of a single Au/Pt/Au core/shell nano-raspberry (a) and at higher magnification in (b). At higher magnification, the crystallographic planes of cubic face-centered Au (d=2.36 Å) and Pt (d=2.26 Å) can be observed.
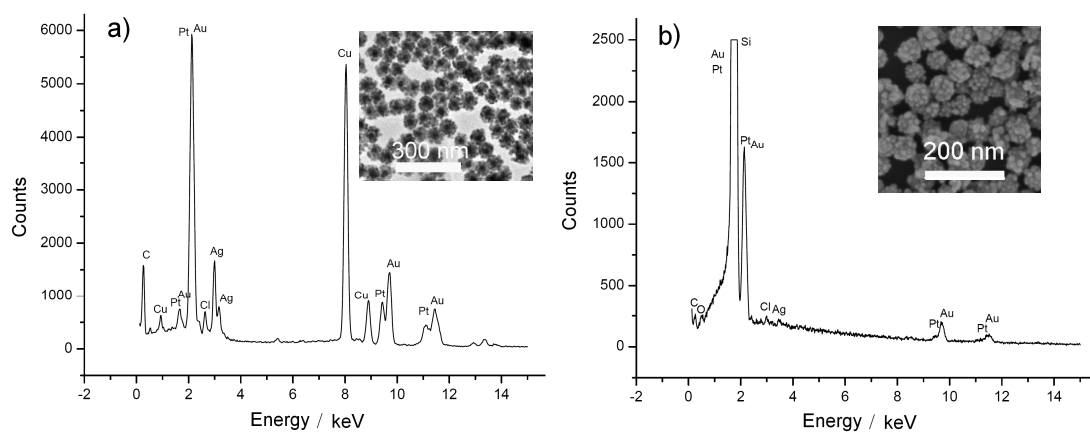
Figure S6. EDX spectra of Au/Pt/Au nano-raspberries obtained by using accessories from TEM (a) and SEM (b). Samples for the measurements are supported by a copper grid coated with an ultra-thin carbon film (TEM) and a silicon wafer (SEM), respectively. The Ag signal is assigned to AgCl, which precipitates during the galvanic replacement.
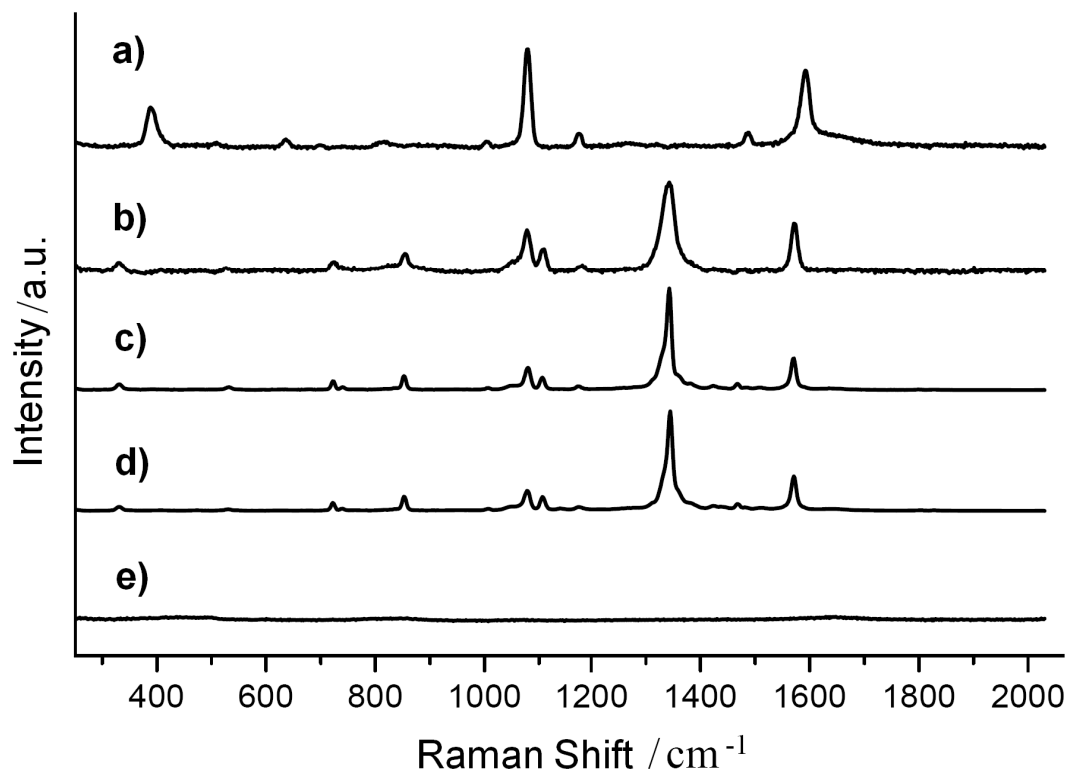
Figure S7. SERS spectra of 4-NTP-coated Au/Pt/Au core/shell nano-raspberries with (a) and without (b) the presence of sodium borohydride. SERS spectra of 4-NTP-coated Au nanospheres (80 nm) with (c) and without (d) sodium borohydride. SERS spectrum from a negative control experiment using 4-NTP-coated Au/Pt core/shell NPs (e), i.e. without Au protuberances. The SERS spectrum a) is recorded immediately after the addition of sodium borohydride, while spectrum c) is recorded 20 hours after the addition of sodium borohydride.
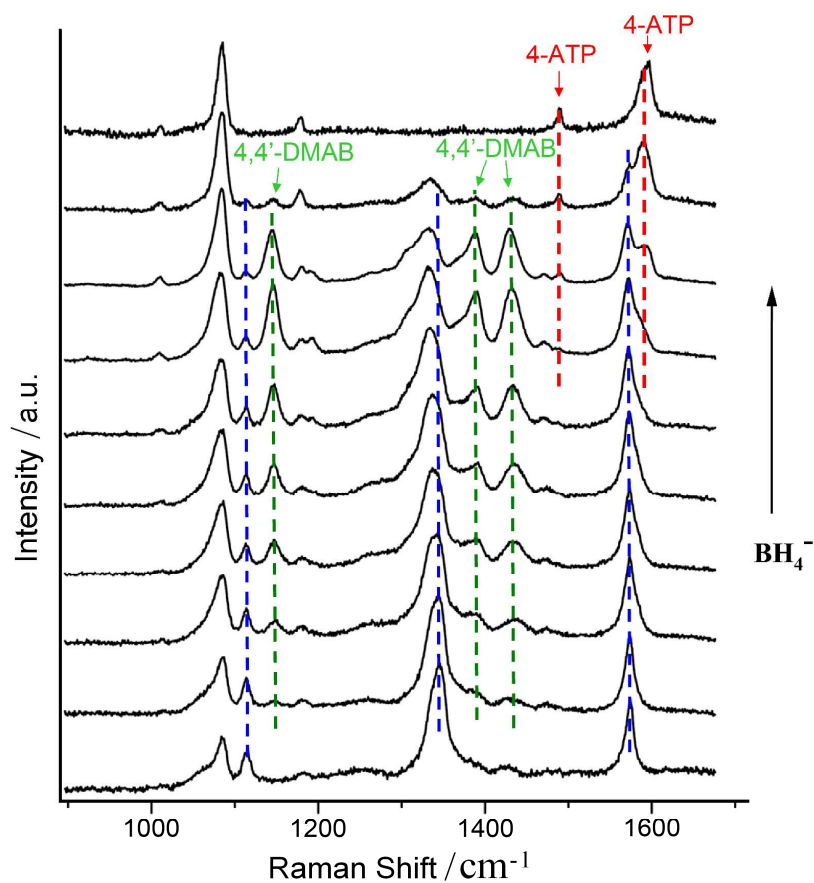
Figure S8. Raw SERS spectra recorded upon addition of different amounts of the reducing reagent NaBH₄. From bottom to top: volumes of 0, 2.5, 5.0, 7.5, 10.0, 12.0, 14.0, 16.0, 18.0 and 20.0 µL of a 10 mM sodium borohydride solution were added to 600 µL 4-NTP modified Au/Pt/Au core/shell nano-raspberries.
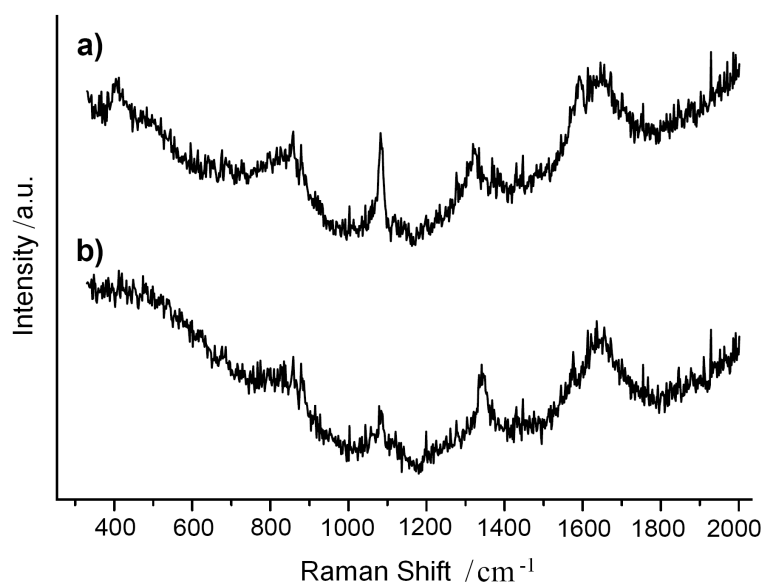
Figure S9. Raw SERS spectra of a 1:1 mixture containing Au and Pt NPs coated with 4-NTP after (a) and before (b) the reduction by using 20 μL of a 10 mM sodium borohydride solution (for 600 μL nanoparticle suspension). The catalytic reaction is not completed even upon addition of the highest $NaBH_4$ volume, indicating that quantitative monitoring by using the Au/Pt mixture is not possible, in contrast to the integrated Au/Pt/Au system (Figure S8).
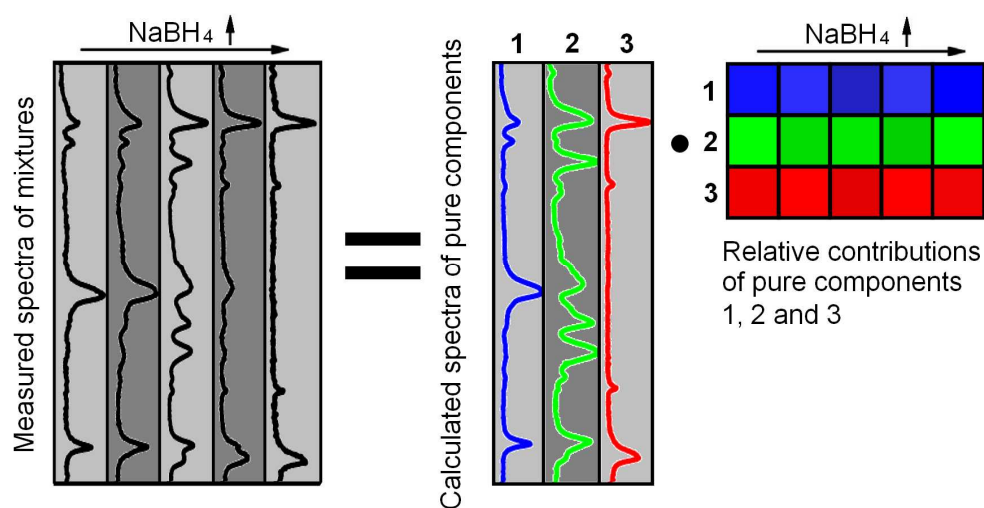
Figure S10. Decomposition of SERS spectra from mixtures into the relative contributions of the pure components by non-negative matrix factorization (NMF): **1** = 4-NTP, **2** = 4,4'-DMAB, and **3** = 4-ATP.
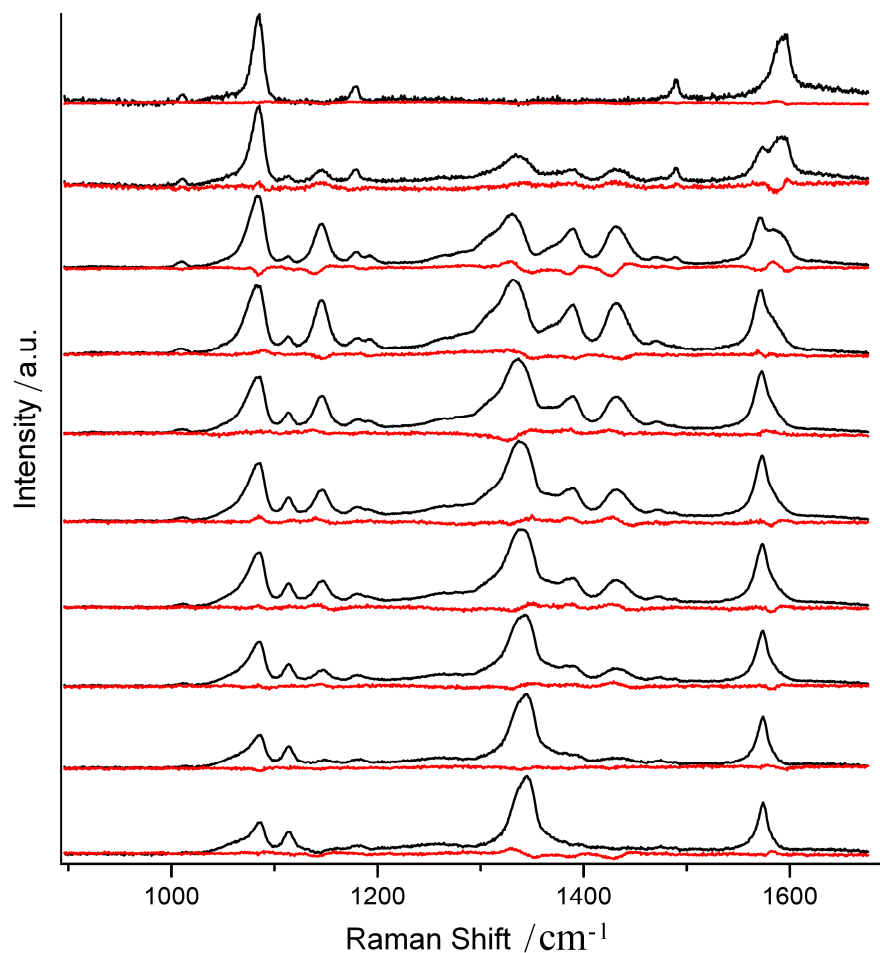
Figure S11. Reconstructed SERS spectra (black) were calculated as linear combinations of three pure component spectra (4-NTP, 4,4'-DMAB, and 4-ATP) as determined by NMF. The deviations of the reconstructed data (black) from the experimental spectra (cf. Figure S8) are shown as SERS difference spectra (red).
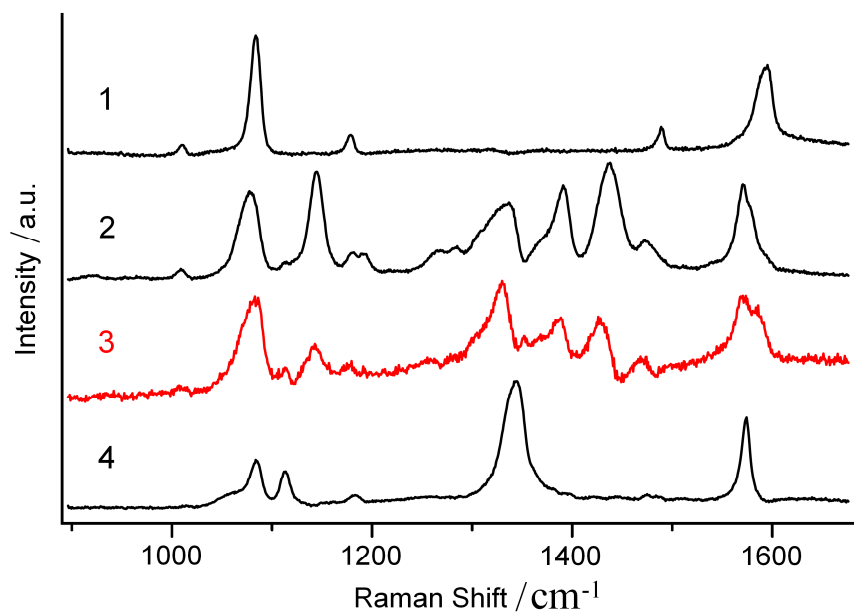
Figure S12. NMF-calculated SERS spectra for the *a priori* assumption of four components. In principle, NMF allows to determine the spectra of unknown species from the experimental spectra of mixtures. However, in this particular case, spectrum **3** exhibits a bad signal-to-noise ratio (SNR) compared with spectra **1**, **2**, and **4** and, more importantly, similar features as in spectrum **2** (which can be assigned to the azo intermediate 4,4'-DMAB). Based on these two criteria – much lower SNR compared with the other pure component spectra **1**, **2** and **4** as well as the large similiarity with spectrum **2** – the assumption of only three molecular species (pure components) seems reasonable (Figure 4a).
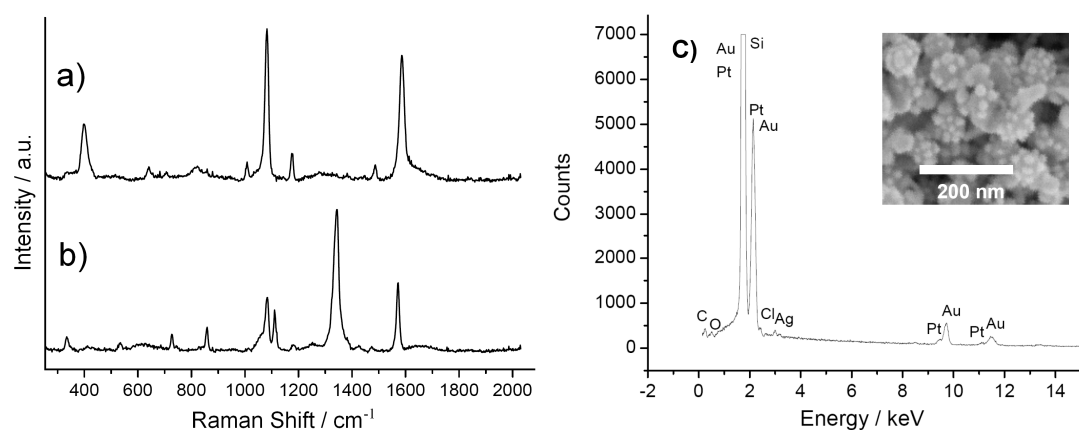
Figure S13. SERS spectra of the 4-NTP-coated Au/Pt/Au core/shell nano-raspberries after (a) and before (b) the reduction by sodium borohydride, recorded in aqueous solution at an elevated reaction temperature (90 °C). The SEM and EDX data (c) of nano-raspberries heated to 90 °C confirms the preservation of both their structure and elemental composition.