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Supporting Information

Isolating and Probing the Hot Spot Formed between Two Silver Nanocubes

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Instrumentation

The SERS spectra were recorded using a Renishaw inVia confocal Raman spectrometer coupled to a Leica microscope with 50✕ objective in backscattering geometry. The 514 nm wavelength was generated with an argon laser and used with a holographic notch filter with a grating of 1200 lines per milimiter. The backscattered Raman signals were collected on a thermoelectrically cooled (-60 $^{\mathrm{o}}$C) CCD detector. The scattering spectra were recorded in the range of 800-2000 cm^{-1}, in one acquisition, 30 s accumulations, and 0.7 mW at the sample. In the spectra, the broad band at 900-1000 cm^{-1} can be attributed to the Si substrate and was used in this work as a reference for intensity normalization. SEM images were taken using an FEI field-emission microscope (Nova NanoSEM 230) operated at an accelerating voltage of 15 kV. TEM images were recorded on a FEI Tecnai-G^{2} microscope operated at 120 kV. HRTEM images were recorded on a JEOL 2100F microscope operated at 200 kV. Samples for TEM and HRTEM studies were prepared by drying a drop of the suspension of Ag nanocubes on a piece of carbon-coated copper grid (Ted Pella, Redding, CA).

Calculation of the Enhancement Factors (EF)

We employed the peak at 1582 cm^{-1} to estimate the EF through the following equation:

$$EF = (I_{sers} \times N_{bulk}) / (I_{bulk} \times N_{sers}) \qquad (1)$$

where I_{sers} and I_{bulk} are the intensities of the same band for the SERS and bulk spectra, N_{bulk} is the number of molecules probed for a bulk sample, and N_{sers} is the number of molecules probed in the SERS. The areas of the 1582 cm^{-1} band were used for the intensities I_{sers} and I_{bulk}. We chose this band because it was the strongest band in the spectra. N_{bulk} was determined based on the Raman spectrum of a 0.1 M 4-MBT or 0.1M 1,4-BDT solution in 12 M NaOH$_{(aq)}$ and the focal volume of our Raman system (1.48 pL). When determining N_{sers}, we assumed that the 4-MBT molecules were adsorbed as a complete monolayer with a molecular footprint of 0.19 nm^2.[17] For 1,4-BDT, the molecular footprint was 0.54 nm^2.[15] These assumptions represent the theoretically maximum number of molecules and is therefore an overestimate. Thus, the calculated EF will likely be an underestimate rather than an overestimate of the enhancement. As 4-MBT and 1,4-BDT do not present any absorption bands matching the laser wavelength used in this study, any possibility of resonance Raman effects can be ruled out from the calculated EFs.
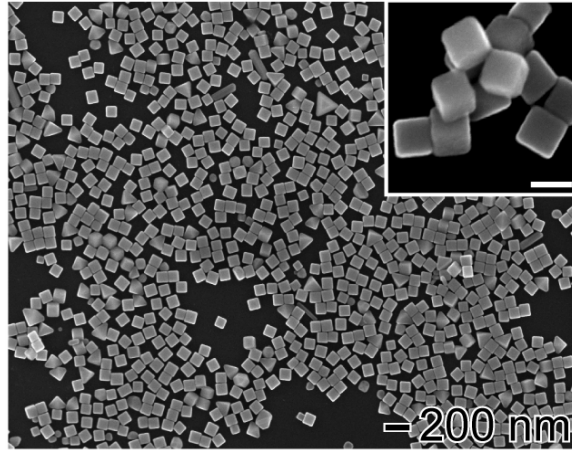
Figure S1. SEM image of the sharp Ag nanocubes employed in our SERS measurements. Their average edge length was 100 ± 5.7 nm. The scale bar in the inset corresponds to 100 nm.
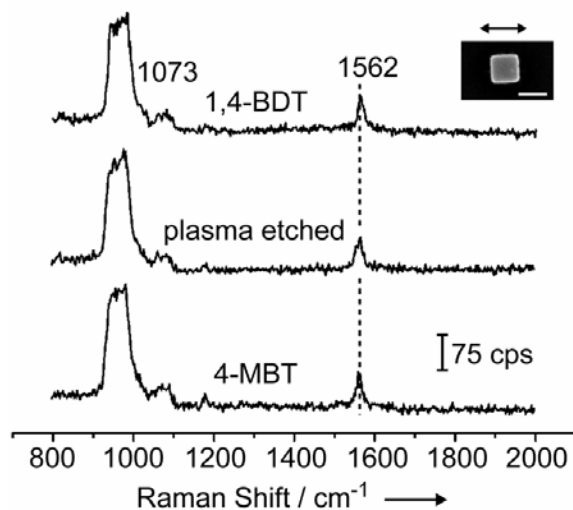
Figure S2. SERS spectra from a single Ag nanocube functionalized with 1,4-BDT (top), followed by plasma etching for 2 min (middle) and immersion in a 4-MBT solution (bottom). No major change in the SERS spectrum (middle trace) was observed after plasma etching. Also, the SERS spectrum did not change after immersing the sample in a 4-MBT solution, indicating that the 1,4-BDT molecules could not be displaced by 4-MBT. While 4-MBT interacts with Ag through one sulfur atom assuming a vertically tilted orientation with respect to the Ag surface, 1,4-BDT interacts with Ag as a dithiolate in which the aromatic ring assumes a flat orientation.[13-15,17] Consequently, it is reasonable that the 4-MBT molecules, due to their vertical orientation, are more susceptible to the oxygen plasma and, therefore, can be more easily etched away from the Ag surface. In addition, the interaction between Ag and 1,4-BDT (via 2 sulfur atoms) is expected to be much stronger than the interaction between Ag and 4-MBT (via 1 sulfur atom). Combined together, it is not hard to understand why the adsorbed 1,4-BDT molecules could not be displaced by 4-MBT. The scale bar in the inset corresponds to 100 nm.
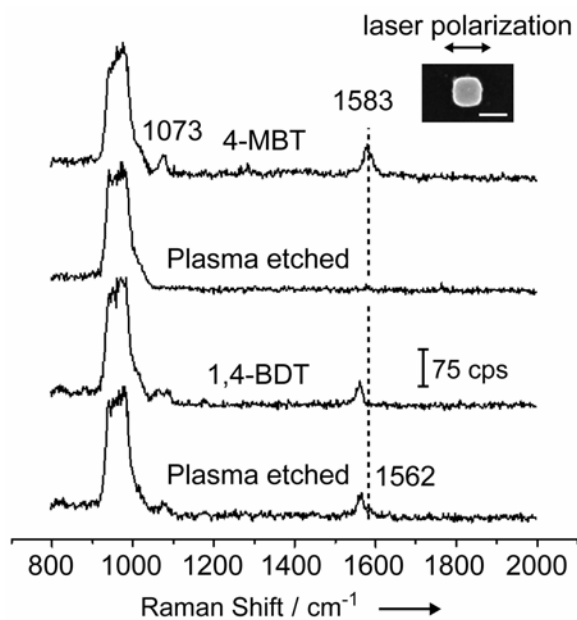
Figure S3. SERS spectra from a single Ag nanocube functionalized with 4-MBT (top), plasma etching for 2 min (second trace), followed by immersion in a 1,4-BDT (third trace) and plasma etching for another 2 min (bottom). When 1,4-BDT molecules were adsorbed on the surface of the nanocube, they could not be easily removed via plasma etching. The scale bar in the inset corresponds to 100 nm.
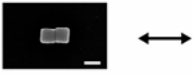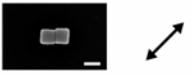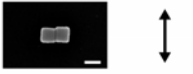
	4-MBT	Plasma etched (hot-spot isolation)	Re-immersrion in 1,4-BDT
⟷	2.2e+7	1.0e+8	1.9e+7
⟋	2.0e+6	4.1e+6	1.6e+6
↕	6.8e+5	4.4e+5	5.4e+4
⟷	5.9e+5	——	3.7e+5
⟷	2.3e+6	——	1.9e+6

Figure S4. Summary of the Enhancement Factors (EFs) calculated using Eq. (1) for the dimers and individual Ag nanocubes functionalized with 4-MBT, followed by plasma etching for 2 min and immersion in a 1,4-BDT solution. The arrow denotes the laser polarization direction in each case. The scale bars in the insets correspond to 100 nm.

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