

Supplementary Information

Encoding Molecular Information in Plasmonic Nanostructures for Anti-counterfeiting Application

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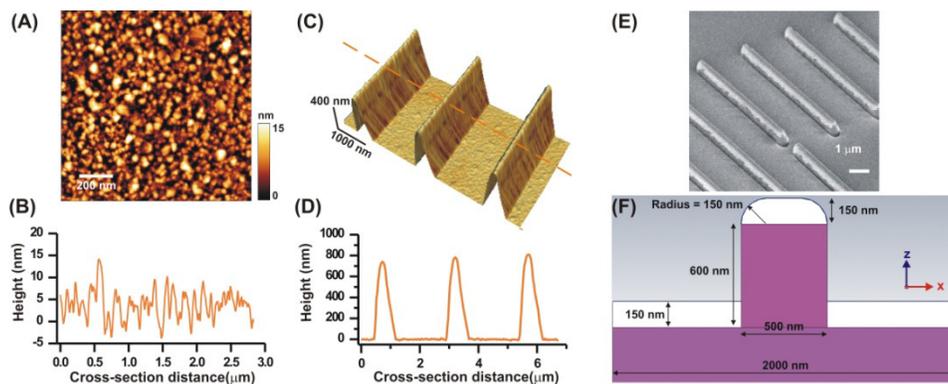


Fig. S1 Tapping mode AFM topographic image of (A) silver film, (C) silver nanowires and the corresponding cross-section profiles of (B) silver film and (D) nanowires. (E) Tilted SEM image of the as-prepared Ag nanowires – 100-nm Ag deposited on polymer nanowires. (F) Schematic of the nanowire used in simulation.

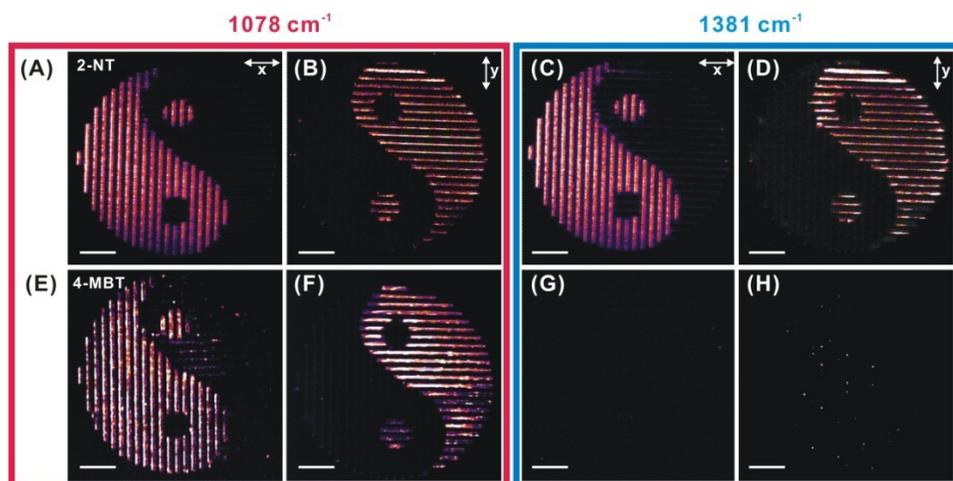


Fig. S2 2D Raman imaging “Taiji” patterns functionalized with (A – D) 2-NT molecules and (E – H) 4-MBT molecules. (A, B, E, F) SERS mapping images collected at 1078 cm^{-1} , a Raman window where both molecules have overlapping molecular vibrations. (C, D, G, H) SERS mapping images collected at 1381 cm^{-1} , a unique fingerprint spectral window that is specific to 2-NT, and not observed in 4-MBT. (A, C, E, G) Raman mappings performed using x -polarization. (B, D, F, H) Raman mappings performed using y -polarization. Each Raman map area is $60 \times 60\ \mu\text{m}^2$. All scale bars are $10\ \mu\text{m}$.

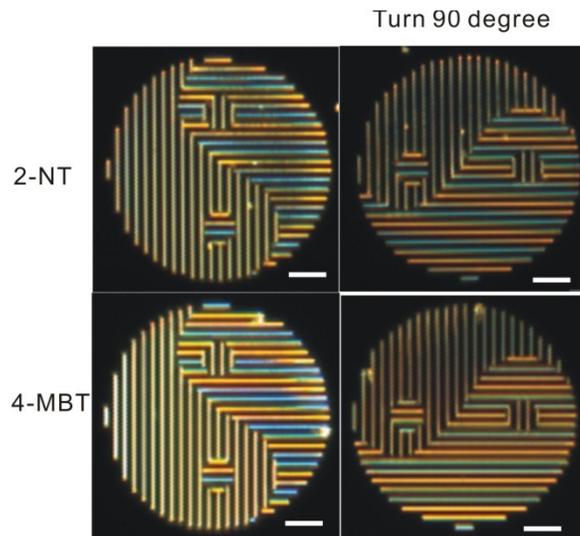


Figure S3. The darkfield optical images of silver “Taiji” structures functionalized with 2-NT and 4-MBT. All scale bars are 10 μm .

Calculation of SERS enhancement factor

The experimental Raman enhancement factor (EF) for the Ag coated polymer substrate is estimated using the equation: $EF = \left(\frac{I_{SERS}}{N_{SERS}} \right) / \left(\frac{I_{ref}}{N_{ref}} \right)$, where I_{SERS} is the intensity of the specific Raman band from the analyte adsorbed on a SERS active substrate, and N_{SERS} is the number of molecules contributing to I_{SERS} . Similarly, I_{ref} is the intensity of the same Raman band from the bulk analyte, normalized with the laser power and acquisition time, and N_{ref} is the number of molecules that yield I_{ref} . Here, 1079 cm^{-1} Raman band is selected for EF calculation. For a more comprehensive estimate of EF, we utilize the average intensity from 10 sample points of the substrate. The average I_{SERS} is around 337.8 counts per second (cps). The radius of the diffraction-limited laser beam is obtained by measuring the intensity profile of 100-nm fluorescence beads. The diameter of the laser beam is measured at $\sim 520 \text{ nm}$, and the area is $A = \pi r^2 = 2.12 \times 10^5 \text{ nm}^2$. Taking $4.5 \times 10^{14} \text{ molecules/cm}^2$ for a monolayer of 4-MBT on silver (assume the binding of 4-MBT on silver is similar to that of gold),¹ the number of molecules excited under the laser spot is approximated at 9.56×10^5 molecules.

The average I_{ref} is measured at 0.57 cps using an 1 M 4-MBT ethanolic solution as a reference solution. For the determination of N_{ref} , the confocal volume is obtained by measuring the intensity profile of fluorescence beads immersed in ethanol solution, which simulates the condition of normal Raman signal (I_{ref}) measurement. The measured laser diameter and the focal depth (h) are 910 nm and 4320 nm, respectively. The effective excitation volume (V) is $V = A \times h = 2.81 \times 10^9 \text{ nm}^3$. The larger confocal volume in ethanol solution than that in ideal dry condition is caused by the distortion of laser spot in solution.²⁻⁶ The number of 4-MBT molecules in ethanol ($1 \text{ mol}\cdot\text{L}^{-1}$) excited by the laser beam is therefore $N_{ref} = 1.69 \times 10^9$ molecules. The average enhancement factor, based on mean intensity from 10 sample points, is estimated to be $\sim 1.05 \times 10^6$.

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