Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Rh in the Gap: Maximizing E-Field Enhancement Within Nanorod Heterodimers

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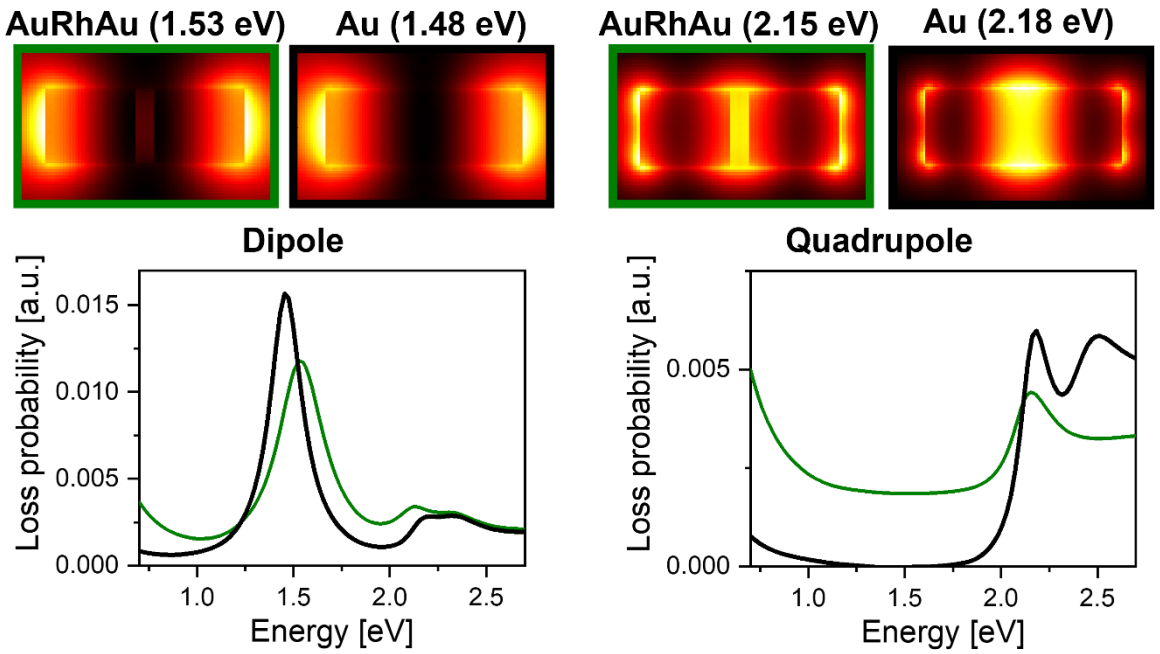

Figure S1. EELS simulations of a AuRhAu and a Au NR of identical total NR length and diameter, similar to the NRs shown in Figure 1. Left half: Simulated maps and spectra of the dipole mode. Spectra are obtained at the end of the NR. Right half: Simulated maps and spectra of the quadrupole mode. Spectra are obtained from the centre of the NR. Green lines: AuRhAu NR black lines: Au NR.

Table S1. Dimensions and LSPR energies of the simulated AuRhAu and Au NRs in Figure S1.

Structure	Diameter [nm]	L_{Au1} [nm]	L_{Rh} [nm]	L_{Au2} [nm]	Resonance energy dipole mode [eV]	Peak height dipole mode [a.u.]	FWHM dipole mode [eV]	Resonance energy quadrupole mode [eV]
AuRhAu	52	62	13	62	1.53	0.012	0.31	2.15
Au	52	137	n.a.	n.a.	1.48	0.016	0.21	2.18

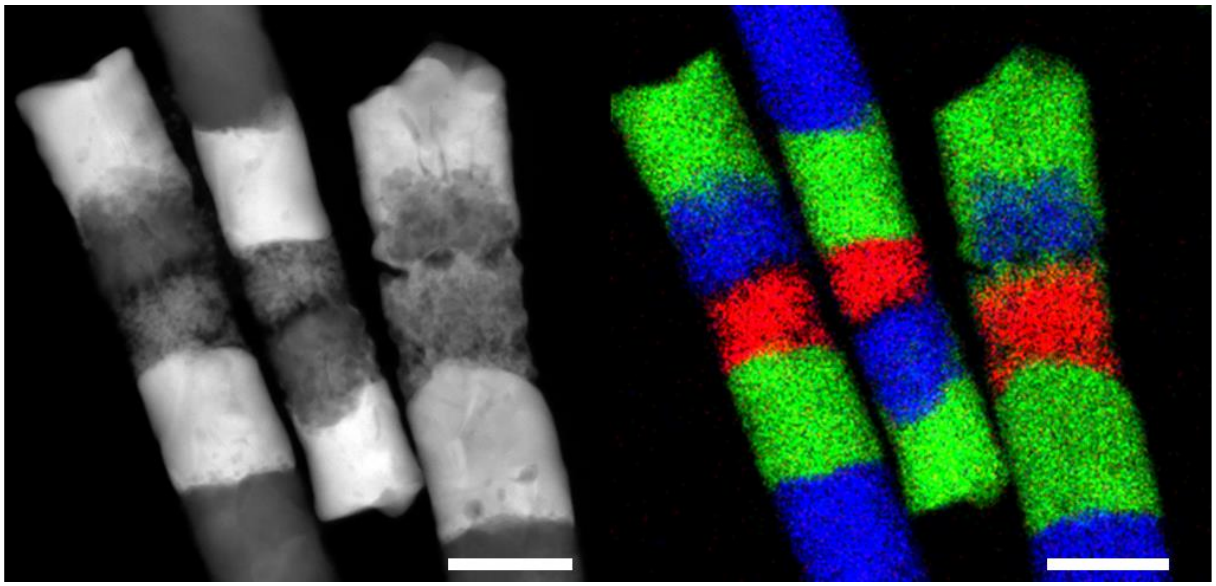

Figure S2. DF-STEM image and EDX map of NiAuRhNiAu NRs grown without using pulsed deposition of the Ni segment on top of the Rh segment. (green: Au, blue: Ni, red: Rh). Scale bar is 50 nm.

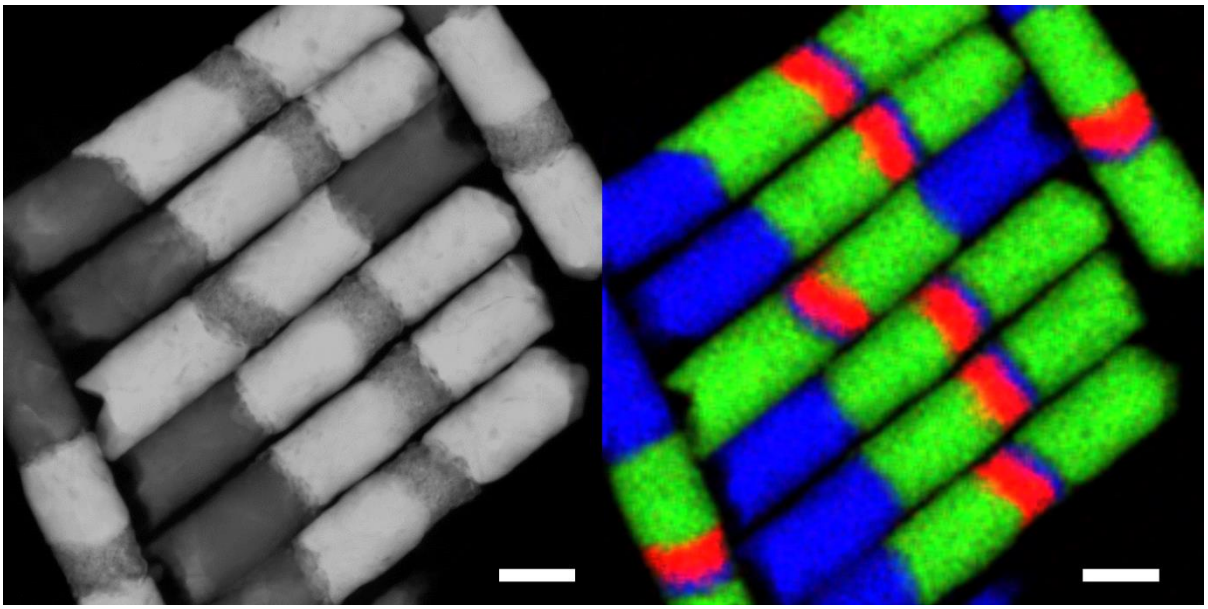

Figure S3. DF-STEM image and EDX map of NiAuRhNiAuNi NRs grown using pulsed deposition of the Ni segment on top of the Rh segment. (green: Au, blue: Ni, red: Rh). Scale bar is 50 nm.

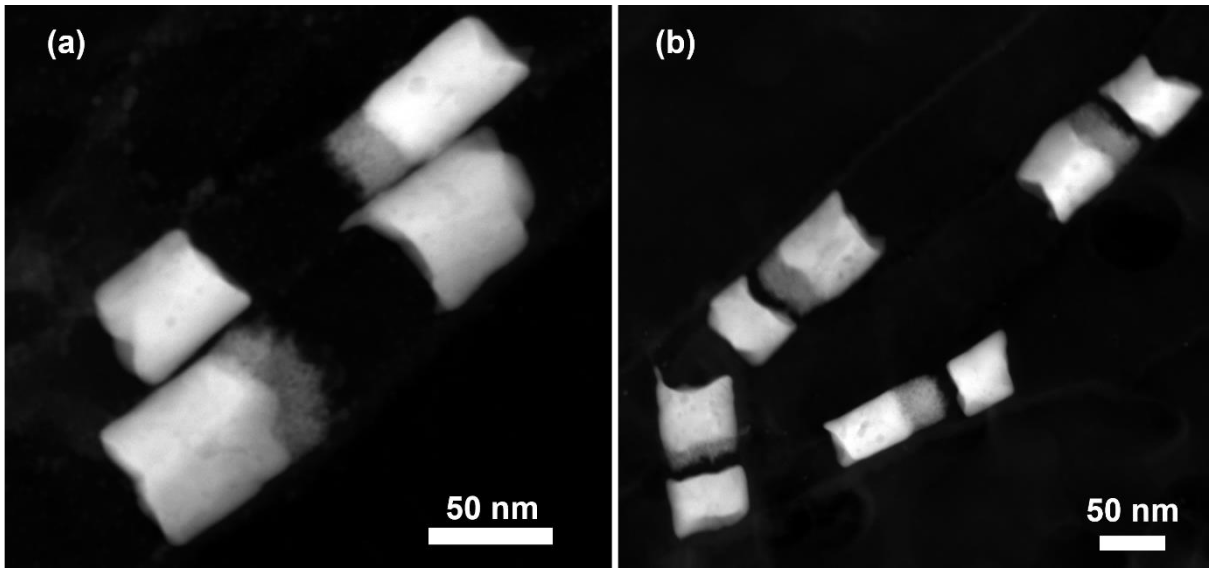

Figure S4. DF-STEM images of AuRh_Au NRs with different numbers of deposition pulses for the sacrificial Ni segment corresponding which can be used to adjust the gap size: (a) 10 pulses, (b) 5 pulses.

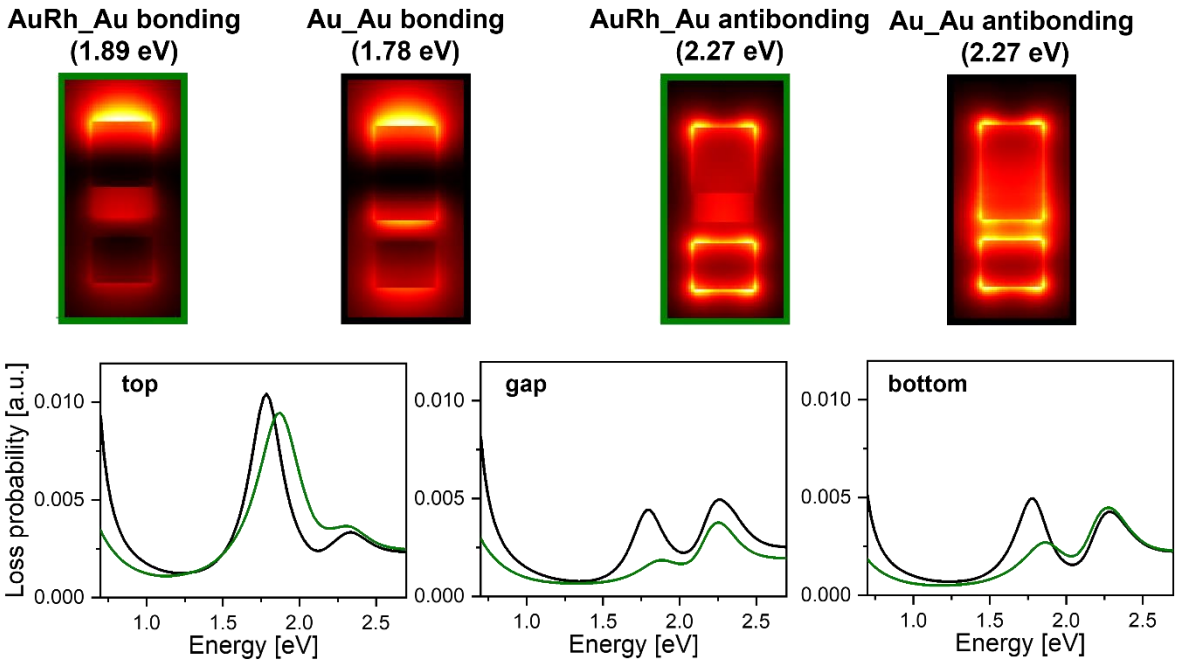

Figure S5. EELS simulations of a AuRh_Au and a Au_Au NR of identical total dimer length, gap size, diameter and individual NR lengths, similar to the NR dimers shown in Figure 2. Spectra are obtained at the top end, in the gap and at the lower end of the NRs (from left to right). Green lines: AuRh_Au NR black lines: Au_Au NR.

Table S2. Dimensions and LSPR energies of the simulated AuRh_Au and Au_Au NR dimers in Figure S4.

Structure	Diameter [nm]	L_{Au1} [nm]	L_{Rh} [nm]	L_{Gap} [nm]	L_{Au2} [nm]	Resonance energy bonding mode [eV]	Resonance energy antibonding mode [eV]
AuRh_Au	58	62	27	20	43	1.89	2.27
Au_Au	58	89	n.a.	20	43	1.78	2.27

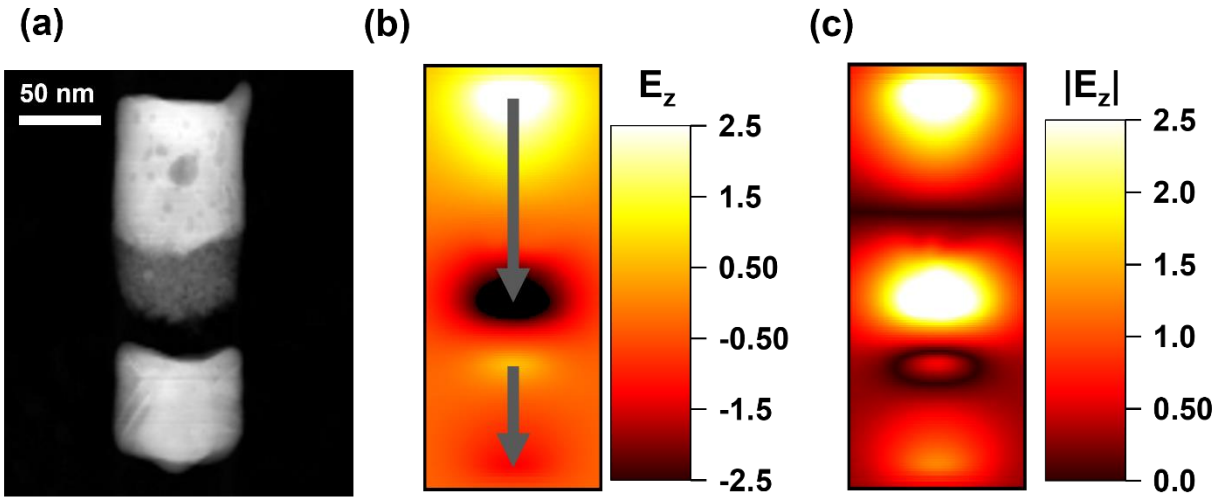

Figure S6. FDTD simulations of the AuRh_Au NR structure shown in Figure 2 at the bonding resonance. (a) DF-STEM image of the AuRh_Au NR. (b) FDTD simulation of the z-component of the E-field of a NR with comparable dimensions to the one shown in (a), 10 nm below the NR dimer, irradiated with a plane wave with longitudinal polarization of the incident light at the bonding resonance wavelength (i.e. 669 nm). Arrows indicate the expected direction of the E-field in the NR centre. (c) The norm of the z-component is shown.

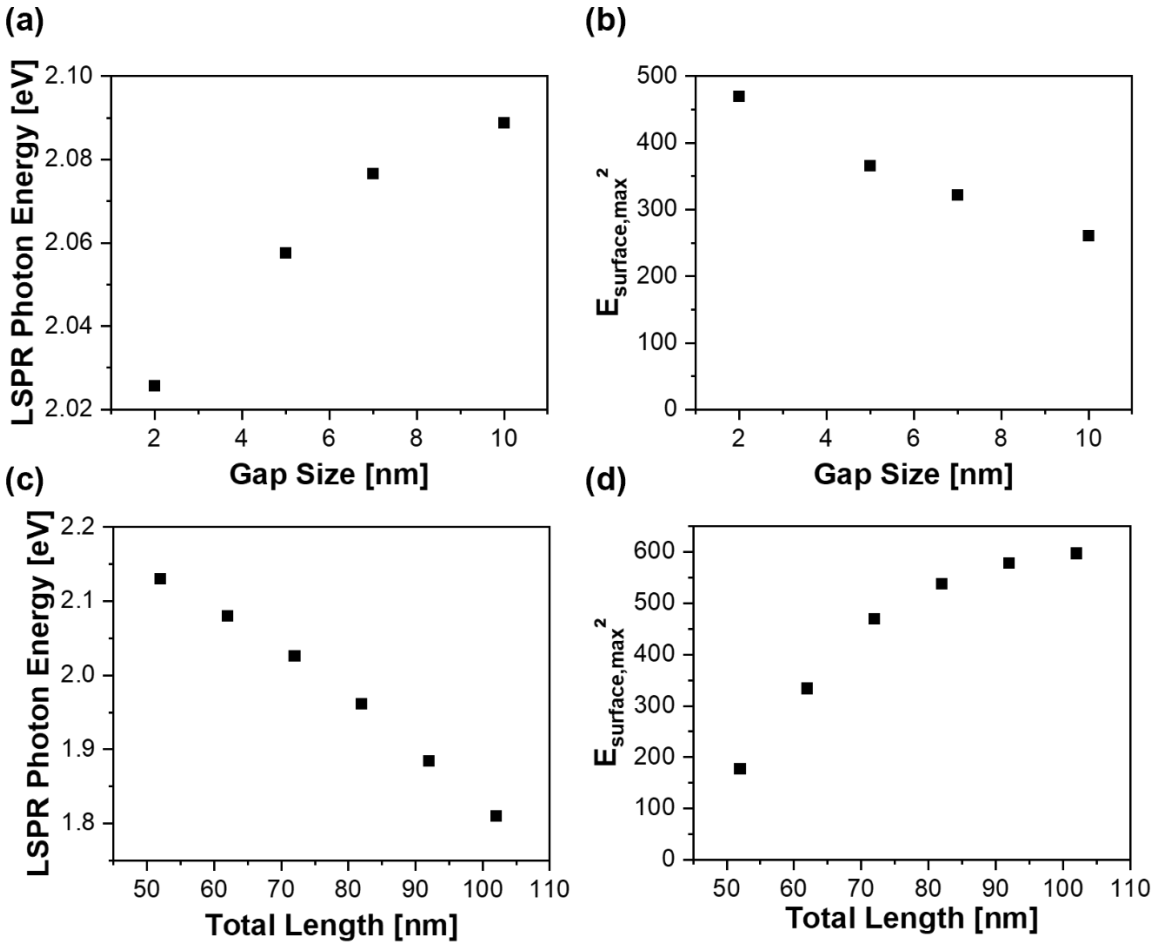

Figure S7. (a, b) Effect of gap size: (a) LSPR photon energy and (b) maximum of the square of the surface E-field enhancement on the Rh segment in AuRh_Au NRs with different gap sizes. L_{Au1} = 30 nm; L_{Rh} = 5 nm; L_{gap}= varied; L_{Au2} = 35 nm (c, d) Effect of total NR length: (c) LSPR photon energy and (d) maximum of the square of the surface E-field enhancement on the Rh segment in AuRh_Au NRs with different total lengths at a constant gap size of 2 nm. L_{Au1}+ 5 nm = L_{Au2}; L_{Rh} = 5 nm; L_{gap}= 2 nm

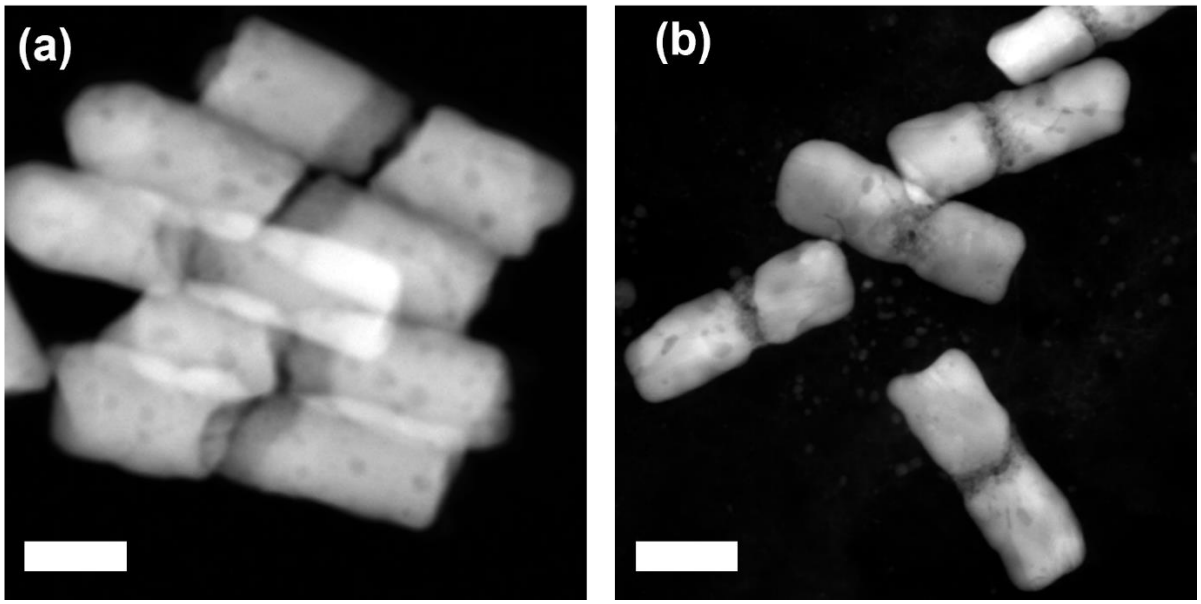

Figure S8. (a, b) DF-STEM images of AuRh_Au NR dimers (a) and AuRhAu NRs (b). Scale bars are 50nm.

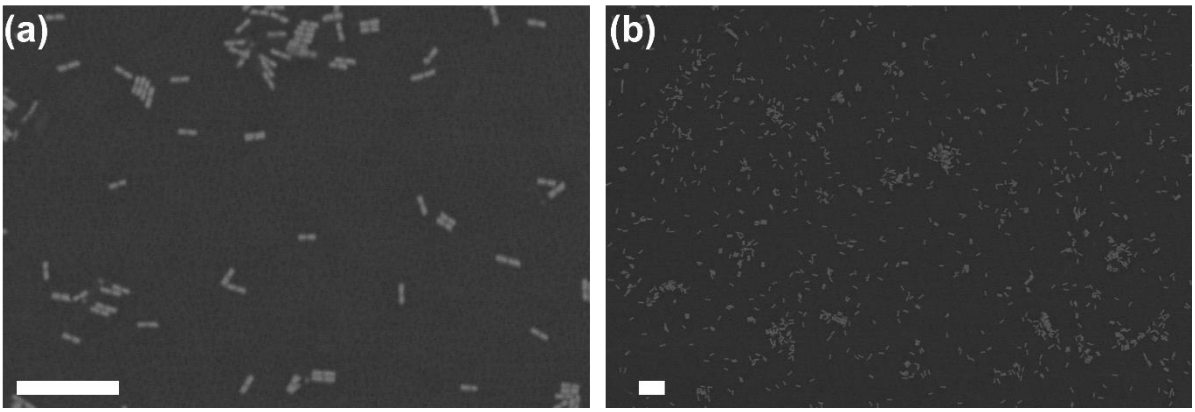

Figure S9. (a, b) SEM images showing the distribution of AuRh_Au NR dimers on an AAO membrane used for Raman measurements. Scale bars are 1 μm.

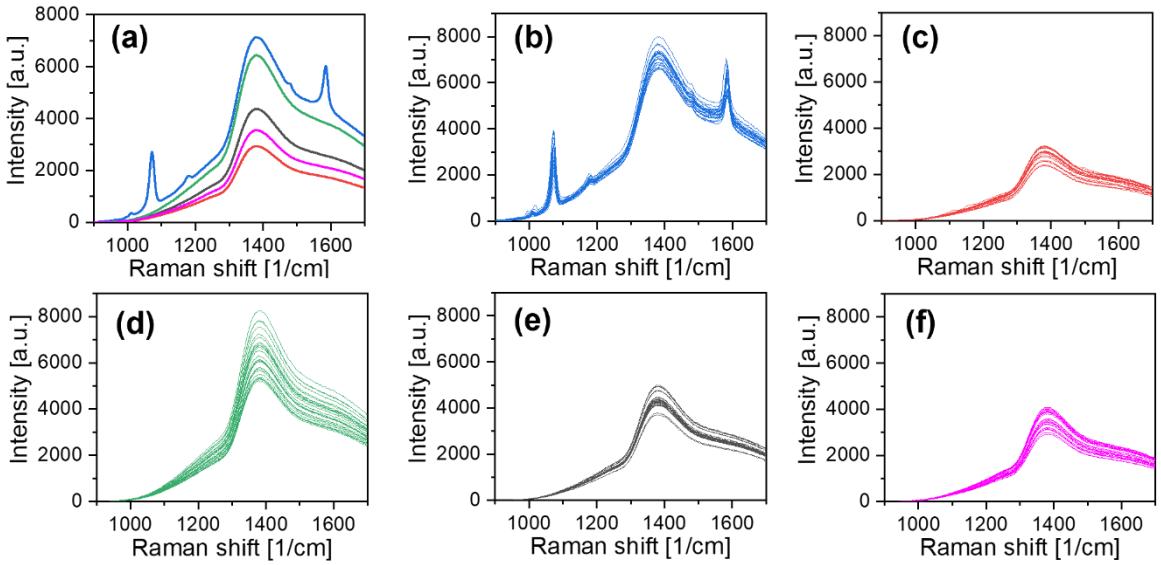

Figure S10. (a) Mean of the 25 Raman measurements of AuRh_Au NR dimers (blue line), AuRhAu NRs (red line), Rh NRs (green line), a SiO_2 coated AAO membrane (grey line) and a bare AAO membrane (pink line). (b-f) Raw data of the 25 Raman spectra acquired from the different samples: (b) AuRh_Au NR dimers, (c) AuRhAu NRs, (d) Rh NRs, (e) SiO_2 coated AAO, (f) Bare AAO membrane. The envelope background signal originates from the glass slide placed underneath the samples.

Table S3. Dimensions and simulated LSPR energies of the AuRh_Au NR dimers, AuRhAu and Rh NRs used for the Raman measurements.

Structure	Diameter [nm]	L_{Au1} [nm]	L_{Rh} [nm]	L_{Gap} [nm]	L_{Au2} [nm]	Density of NRs/ NR dimers [1/µm]	Resonance wavelength bonding/ dipole mode [nm]
AuRh_Au	57 ± 5	83 ± 8	19 ± 2	6 ± 3	77 ± 22	2.9 ± 0.7	865
AuRhAu	41 ± 8	65 ± 12	12 ± 2	n.a.	65 ± 12	3.3 ± 1.7	940
Rh	55 ± 7	n.a.	126 ± 19	n.a.	n.a.	3.9 ± 0.7	n.a.