Supporting Information

Highly Stable Silica-coated Gold Nanorods Dimers

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I- UV-visible spectroscopy:

I-1- pH controlled Assembly: Triggering the assembly by increasing the pH

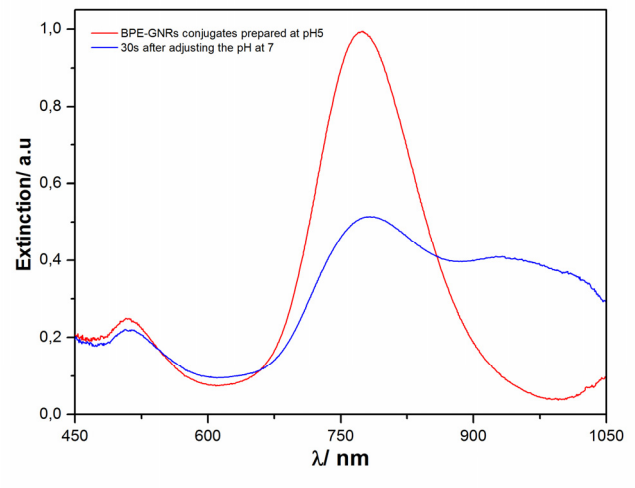


Figure S1: Extinction spectra for AuNRs pre-incubated in BPE solution at pH≈ 5.0 (red) and after increasing the pH to 7 with NaOH (blue).

I-2- Dimerization kinetics initiated by BPE at pH=7

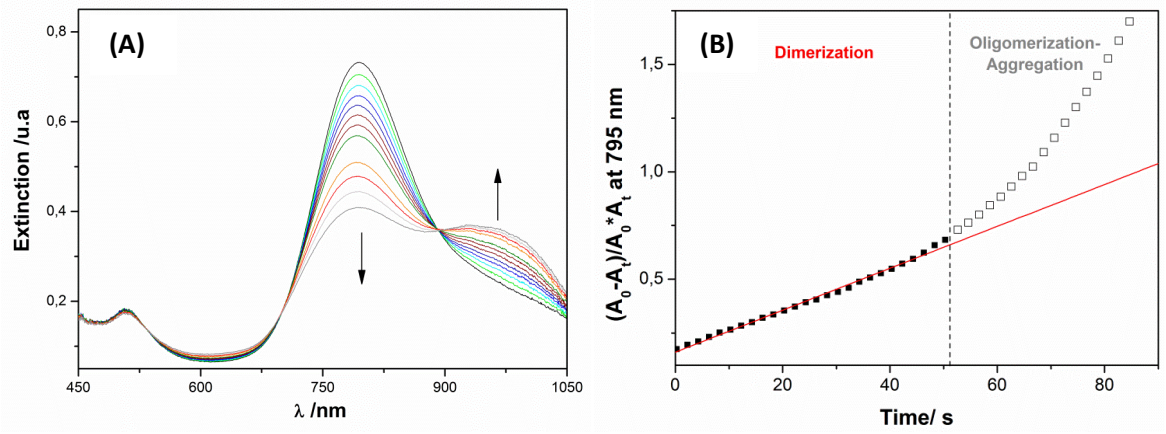


Figure S2: (A) Time-dependant Extinction spectra for AuNRs in water at pH≈ 7.0 (adjusted with NaOH) following the addition of BPE. **(B)** Kinetic analysis of AuNRs BPE-induced assembly at pH≈7 using the second order rate law detailed above.

Kinetic model for second order rate law governing the dimerization of gold nanorods:

We consider AuNRs particles in solution at a concentration [M]. In the framework of second order rate law characterized by the kinetic constant k, the disappearance of AuNRs monomers over time follows equation (1).

$$-\frac{d[M]}{dt} = k \cdot [M]^2 \qquad (1)$$

$$A_{LSPR} = A_t = \varepsilon \cdot l \cdot [M] \qquad (2)$$

$$A_0 = \varepsilon \cdot l \cdot [M]_0 \qquad (3)$$

The equation (1) is expressed using the corresponding absorbance A (Beer Lambert law (2)) and then integrated using the initial condition (3), providing:

$$\frac{A_0 - A_t}{A_0 \cdot A_t} = \frac{k}{\varepsilon \cdot l} \cdot t$$

where A_0 and A_t correspond to the absorbance of colloidal solution at t=0 (before addition of BPE) and t (after addition of BPE to induce the assembly). l is the optical path of the cell. ε the extinction coefficient of AuNRs monomers at the maximum of the longitudinal LSPR band.

I-3- Incubation with the region-isomer (2,4')-BPE

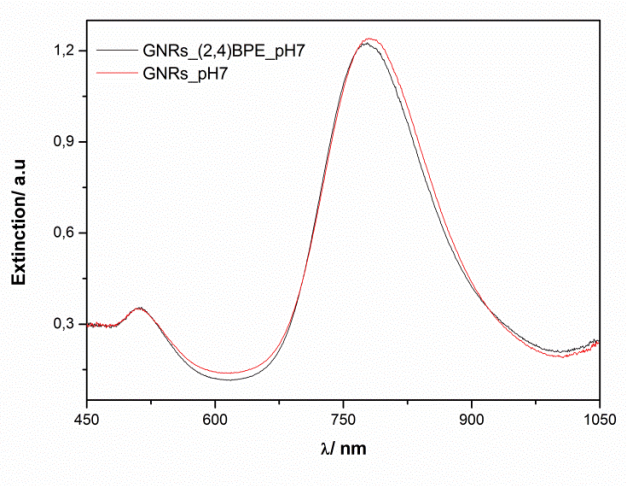


Figure S3: Extinction spectra recorded for Gold nanorods solution at pH 7 before (red line) and 24 h after incubation with (2.4')-BPE (black line)

I-4- Silica-coated gold nanorods

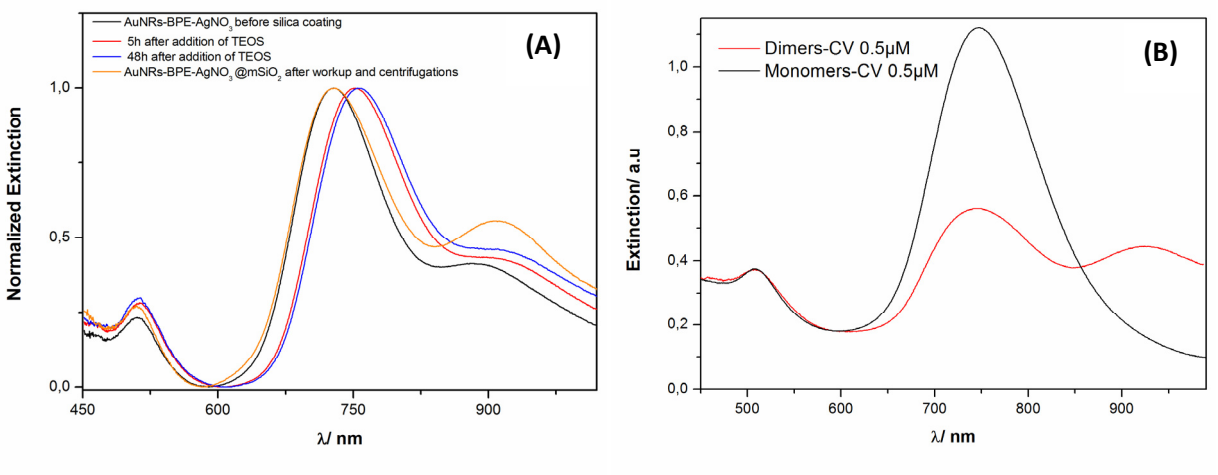


Figure S4: (A) Evolution of UV-visible spectra upon coating in mesoporous silica layer. **(B)** Extinction spectra recorded after centrifugation for AuNRs@$mSiO_2$ monomers and dimers incubated in 0.5µM solution of crystal violet (CV) in water.

I-5- Stability of freezed AuNRs assembly

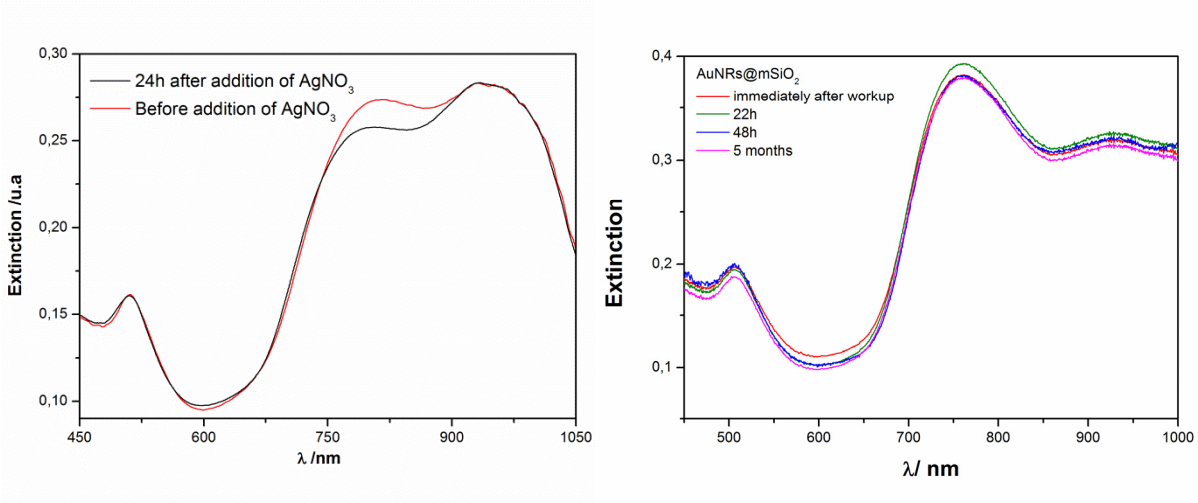


Figure S5: Monitoring the stability of assembly over time: Extinction spectra for AuNRs following the addition of silver nitrate to quench the assembly process (red line: immediately after silver nitrate addition; black line 24h after silver nitrate addition)

II- Raman scattering studies

II-1- Normal Raman spectra of BPE and isomers

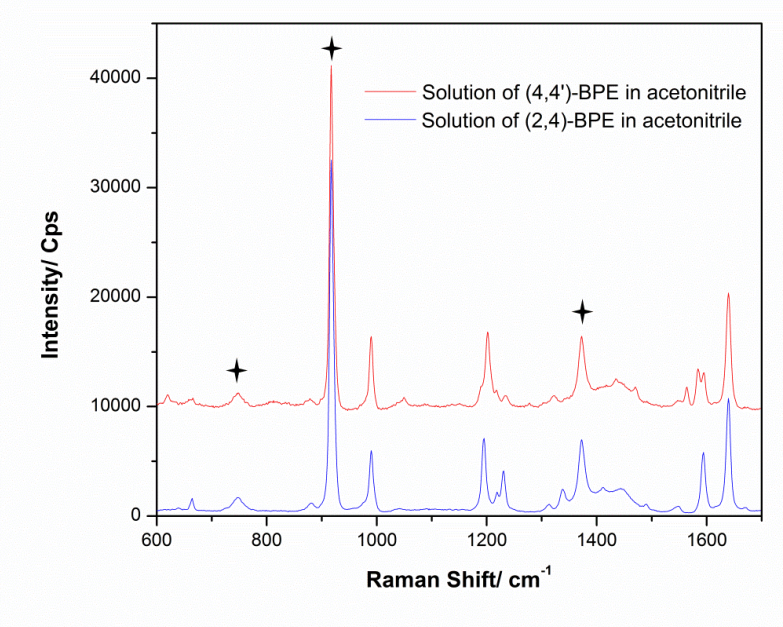


Figure S6: Comparison of Normal Raman spectra recorded for 0.1M (4,4')-BPE and (2,4')-BPE solution in acetonitrile. The Raman bands corresponding to the solvent are indicated by stars. (laser: λ_{exc}=785nm, exposure time of 10 seconds).

II-2- Additional SERS spectra

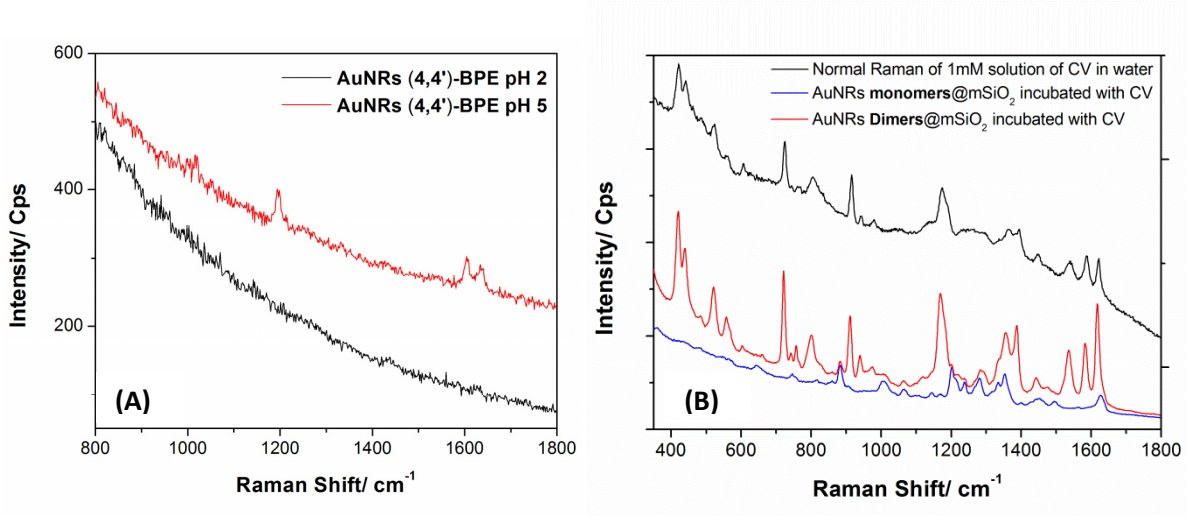


Figure S7: (A) Solution-based SERS spectra recorded for AuNRs incubated in 28 µM BPE solution at pH 2 and 5. **(B)** Normal Raman spectra for 1mM aqueous solution of CV (acquisition time 3x20s at λ_{exc}=785 nm), SERS spectra recorded for mesoporous silica coated-AuNRs monomers and dimers after incubation in CV solution (0.5µM), P=13.8mW, acquisition time 3x10s at λ_{exc}=785 nm.

III-3- Calculation of relative enhancement factors

The definition used here for the calculation of SERS enhancement factor is:

$$EF = \frac{\frac{I_{SERS}}{N_{SERS}}}{\frac{I_{ref}}{N_{ref}}}$$

I_{SERS} and I_{ref} correspond to the Raman intensity recorded in the presence of plasmonic particles and in normal Raman conditions, respectively. N_{ref} is the number of molecular probes (in the focal volume) in normal Raman conditions (easily calculated from the concentration of the Raman probe in solution). N_{SERS} is the number of Raman probes contributing to the SERS effect within the scattering volume probed by the exciting radiation. For EF calculations, we estimated that only molecules adsorbed in the areas of highly enhanced field intensity are relevant, namely, the molecules located at the edges (hemispherical tips) of isolated nanorods and in the gap junction of dimers.

Colloidal solution with AuNRs concentration of 1.34 nM whose pH was adjusted to 7, was split into two identical batches before addition of BPE derivatives. The first batch is the control experiment where no assembly is expected in the presence of (2,4'-BPE) while the second batch is subjected to (4,4')-BPE to initiate the assembly. SERS spectra of BPE were recorded for AuNRs monomers and dimers and the relative enhancement calculated as follows.

We consider N AuNRs particles in each colloidal batch before addition of BPE. $I_{isolated}$ and $I_{assembly}$ correspond to the SERS intensities of one specific vibration mode recorded for AuNRs@BPE in the presence of (2,4')-BPE and (4,4')-BPE, respectively. Those values are directly extracted from the experimental SERS spectra recorded in the same conditions (laser power, acquisition time...) for the two batches (see Figure 3-E in the article).

Calculation of Enhancement factor for monomers:

$$EF_M = \frac{\frac{I_{isolated}}{N^{SERS}_{(2,4)BPE}}}{\frac{I^{ref}_{(2,4)BPE}}{N^{ref}_{(2,4)BPE}}}$$

$I^{ref}_{(2,4')BPE}$ is the normal Raman scattering intensity of (2,4')-BPE at 0.1M in acetonitrile and $N^{ref}_{(2,4')BPE}$ is the number of (2,4')-BPE molecules in the confocal volume.

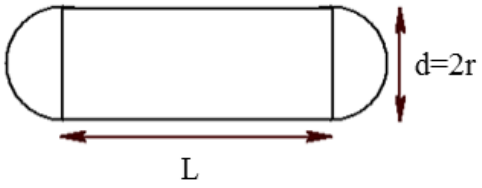
- In the presence of (2,4')-BPE in the medium, the AuNRs remain as isolated monomers and the recorded SERS intensity is:

$$I_{isolated} = N \cdot i_M$$

where i_M corresponds to the SERS intensity recorded for a single nanorod

$N^{SERS}_{(2,4')BPE}$ is the maximum number of (2,4')-BPE molecules in the focal volume which are adsorbed as a compact layer on the hemispherical caps of gold nanorods.

$$N^{SERS}_{(2,4')BPE} = N \cdot \frac{\pi d^2}{A_{BPE}}$$



where A_{BPE} is the molecular footprint of BPE on Au surface (0.18 nm^2), d the diameter of AuNRs and N is the number of gold nanorods in the probing volume.

$$N = C\,V \cdot N_A$$

C being the concentration of gold nanorod (1.34 nM), V the probed volume is estimated to be 2 pL and N_A the Avogadro's constant.

Table S1: calculated SERS EFs for AuNRs using (2,4')-BPE for three vibrational modes

	$I_{isolated}$	i_M	$I_{isolated}/(N_{SERS})_m$	$I^{ref}_{(4,4)BPE}$	EF_M
1637 cm^{-1}	$3.07x10^3$	1.90	$4.86x10^{-4}$	$1.48\ x10^4$	$3.93\ x10^3$
1198 cm^{-1}	$1.72\ x10^3$	1.06	$2.71x10^{-4}$	$8.24\ x10^3$	$3.95\ x10^3$
1020 cm^{-1}	$3.97\ x10^2$	0.24	$6.27x10^{-5}$	$6.11\ x10^3$	$1.23\ x10^3$

Calculation of Enhancement factor for dimers:

$$EF_D = \frac{\frac{I_{assembly}}{N^{SERS}_{(4,4)BPE}}}{\frac{I^{ref}_{(4,4)BPE}}{N^{ref}_{(4,4)BPE}}}$$

In the second batch incubated with (4,4')-BPE, the colloidal suspension contains N_M isolated AuNRs and N_D AuNRs dimers.

$$N = N_D + N_M$$

The degree of advancement of the dimerization process is defined as α. After assembly initiation with (4,4')-BPE, the relative proportions of monomers and dimers could be extracted from the extinction spectra. Assuming that the consumed AuNRs form mainly dimers, the LSPR extinction maximum of monomers may be exploited to estimate the amount of dimers in the final colloidal solution.

The recorded intensity $I_{assembly}$ contains the contributions of monomers and dimers to the global intensity.

$$I_{assembly} = I_M + I_D$$

where:

$$I_M = N_M \cdot i_M$$

Similarily, one defines i_D the SERS intensity recorded for a single dimer.

$$I_D = N_D \cdot i_D$$

The recorded SERS intensity for the resulting assembly is :

$$I_{assembly} = I_M + I_D = (1-\alpha) \cdot N \cdot i_M + \frac{\alpha}{2} \cdot N \cdot i_D$$

From the extinction spectra, it is possible to roughly estimate the proportion of AuNRs that remained as monomers (54%) and those that are involved in clusters such as dimers (46%). Thus, we estimate the degree of advancement of the dimerization α to be 0.46.

i_M is determined in the last paragraph. Thus I_M and I_D can be estimated.

$$N_{(4,4')BPE}^{SERS} = \left(\frac{\alpha}{2}\right) \cdot N \cdot \frac{S}{A_{BPE}}$$

where $N_{(4,4')BPE}^{SERS}$ is the maximum number of BPE in the focal volume which are adsorbed as a compact layer in the gap between two nanorods. The near-field mapping of Electric intensity for AuNR dimer, reveal that the hotspot spans a limited spatial region, roughly one third of the half sphere of the cylinder. The relevant surface of gold S to take into account is then :

$$S = \frac{1}{2} \cdot \frac{\pi d^2}{3}$$

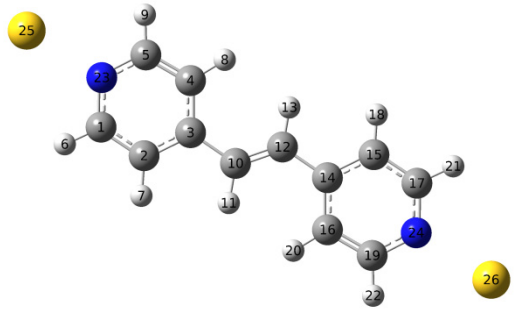
$I_{(4,4')BPE}^{ref}$ is the normal Raman scattering intensity of (4,4')-BPE at 0.18M in acetonitrile and $N_{(4,4')BPE}^{ref}$ is the number of (4,4')-BPE molecules in the confocal volume.

Table S2: calculated SERS EFs for AuNRs using (4,4')-BPE for three vibrational modes

	$I_{assembly}$	I_M	I_D	$\frac{I_D}{N_{(4,4)BPE}^{SERS}}$	$\frac{I_{(4,4)BPE}^{ref}}{N_{(4,4)BPE}^{ref}}$	EF_D
1637 cm^{-1}	1.53 $x10^4$	1.66 $x10^3$	1.36 $x10^4$	5.64 $x10^{-2}$	1.23$x10^{-7}$	4.57 $x10^5$
1198 cm^{-1}	1.62 $x10^4$	9.28 $x10^2$	1.53 $x10^4$	6.33 $x10^{-2}$	6.86$x10^{-8}$	9.21 $x10^5$
1020 cm^{-1}	3.94 $x10^3$	2.14 $x10^2$	3.73 $x10^3$	1.53 $x10^{-2}$	5.09$x10^{-8}$	3.01 $x10^5$

III- DFT calculations : Optimized geometries and three lower frequencies for 2,4 and 4,4 BPE coordinated to gold

III-1- (4,4')BPE-Au2



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19	C	1.1731730	0.0000000	7.9883560
20	H	0.0998610	0.0000000	6.1491490
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26	Au	2.4131960	0.0000000	11.0209570

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Frc consts --	0.0003			0.0008			0.0026		
IR Inten --	1.5984			0.7684			0.0000		
Raman Activ --	0.0000			0.0000			3.4453		
Depolar (P) --	0.7284			0.5947			0.7500		
Depolar (U) --	0.8428			0.7458			0.8571		
Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
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3 6	0.00	0.15	0.00	0.00	0.08	0.00	0.00	-0.14	0.00
4 6	0.00	0.27	0.00	0.00	-0.09	0.00	0.00	-0.24	0.00
5 6	0.00	0.23	0.00	0.00	-0.09	0.00	0.00	-0.28	0.00
6 1	0.00	-0.13	0.00	0.00	0.34	0.00	0.00	-0.14	0.00
7 1	0.00	-0.09	0.00	0.00	0.37	0.00	0.00	-0.06	0.00
8 1	0.00	0.40	0.00	0.00	-0.23	0.00	0.00	-0.29	0.00

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14	6	0.00	0.15	0.00	0.00	0.08	0.00	0.00	0.14	0.00
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16	6	0.00	0.27	0.00	0.00	-0.09	0.00	0.00	0.24	0.00
17	6	0.00	-0.02	0.00	0.00	0.22	0.00	0.00	0.16	0.00
18	1	0.00	-0.09	0.00	0.00	0.37	0.00	0.00	0.06	0.00
19	6	0.00	0.24	0.00	0.00	-0.09	0.00	0.00	0.28	0.00
20	1	0.00	0.40	0.00	0.00	-0.23	0.00	0.00	0.29	0.00
21	1	0.00	-0.13	0.00	0.00	0.34	0.00	0.00	0.14	0.00
22	1	0.00	0.33	0.00	0.00	-0.22	0.00	0.00	0.35	0.00
23	7	0.00	0.09	0.00	0.00	0.06	0.00	0.00	-0.24	0.00
24	7	0.00	0.09	0.00	0.00	0.06	0.00	0.00	0.24	0.00
25	79	0.00	-0.06	0.00	0.00	-0.03	0.00	0.00	0.04	0.00
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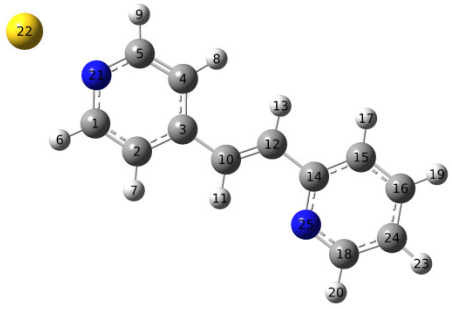
III-2- (2,4')-BPE-Au



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15	C	3.5427700	0.0362980	6.5716540
16	C	3.4869150	0.0554260	7.9609390
17	H	4.4955540	0.0560740	6.0549230
18	C	1.1049520	-0.0146430	7.7702890
19	H	4.3981890	0.0902610	8.5471920
20	H	0.1150230	-0.0357240	8.2182700
21	N	1.0700470	-0.0051660	-0.6774260
22	Au	0.8680300	0.2620400	-2.9860690
23	H	2.1459000	0.0444270	9.6594180
24	C	2.2423710	0.0300710	8.5806450
25	N	1.1444270	-0.0334000	6.4416380

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Red. masses --	4.0121			6.7042			6.3164		
Frc consts --	0.0015			0.0039			0.0085		
IR Inten --	0.3354			0.4946			0.3426		
Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
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2 6	0.02	-0.11	0.00	-0.02	0.26	0.02	0.19	0.09	0.00
3 6	0.03	0.08	0.00	-0.02	0.20	0.02	0.20	0.02	-0.03
4 6	0.03	0.25	0.00	-0.03	0.16	0.02	0.18	-0.05	-0.05
5 6	0.03	0.21	0.00	-0.03	0.14	0.02	0.15	-0.05	-0.05
6 1	0.01	-0.28	0.00	-0.02	0.27	0.02	0.15	0.13	0.03
7 1	0.02	-0.24	0.00	-0.02	0.30	0.02	0.21	0.14	0.02
8 1	0.04	0.42	0.00	-0.03	0.11	0.02	0.19	-0.11	-0.06
9 1	0.04	0.35	0.00	-0.03	0.09	0.02	0.14	-0.11	-0.07
10 6	0.02	0.08	0.00	-0.02	0.16	0.02	0.20	0.02	-0.03
11 1	0.02	0.14	-0.01	-0.02	0.10	0.03	0.18	0.03	-0.05
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13 1	0.02	-0.11	0.02	-0.02	0.23	0.01	0.19	0.00	0.08
14 6	0.00	-0.01	0.01	0.00	0.04	0.02	0.05	0.00	0.02
15 6	0.00	-0.18	0.02	0.00	0.06	0.01	-0.02	0.01	0.13
16 6	-0.01	-0.19	0.02	0.02	-0.08	0.01	-0.16	0.01	0.13
17 1	0.01	-0.30	0.03	0.00	0.19	0.00	0.02	0.03	0.22
18 6	-0.02	0.13	0.00	0.02	-0.24	0.03	-0.14	-0.03	-0.09
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22 79	-0.01	-0.02	0.00	0.01	-0.06	-0.02	-0.06	0.00	0.00
23 1	-0.03	-0.04	0.01	0.04	-0.36	0.03	-0.31	-0.02	0.00
24 6	-0.02	-0.04	0.01	0.03	-0.24	0.02	-0.21	-0.02	0.01
25 7	-0.01	0.14	0.00	0.01	-0.11	0.03	-0.01	-0.02	-0.09

IV- DDA calculations : near-field mapping of the electric field intensity

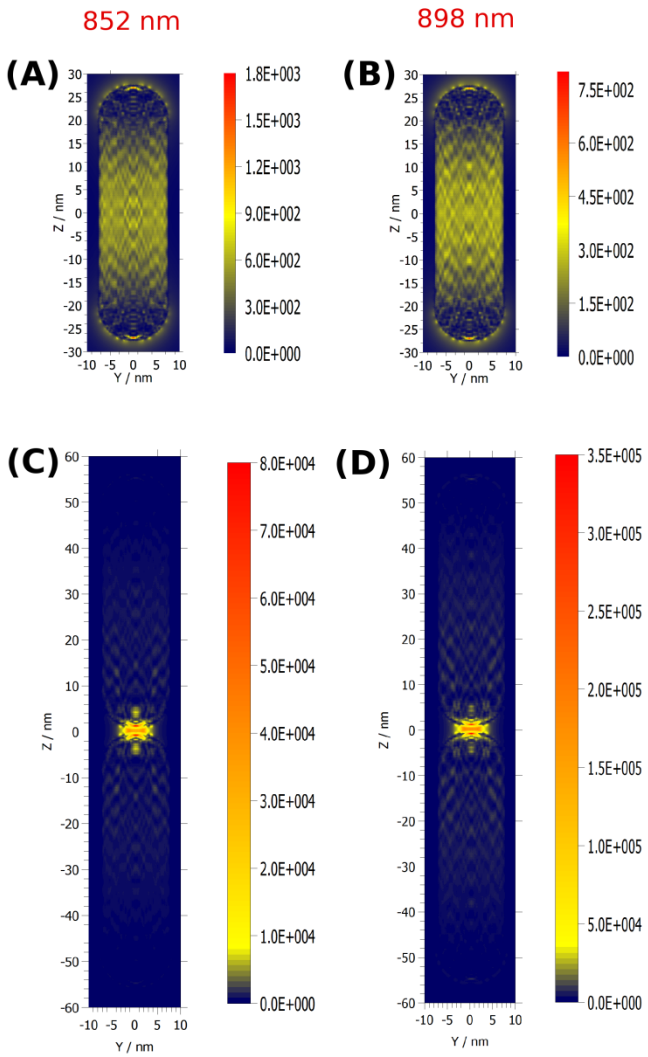

Figure S8: Electric field intensity profiles for AuNRs monomer and dimer at the Raman Stokes wavelength 852 nm (A, C) and 898 nm (B, D)

V- Additional TEM and SEM images and histogram analysis

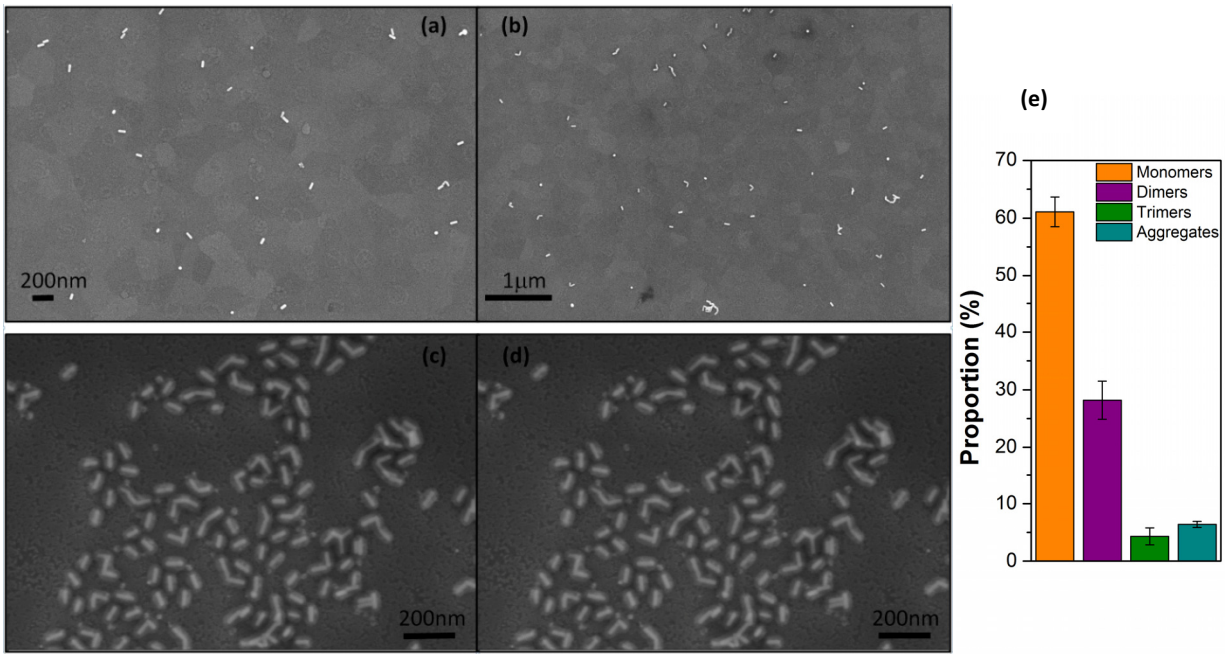

Figure S9: (a,b) Low magnification SEM images of AuNRs assemblies after silver-induced termination. **(c,d)** Low magnification SEM images of AuNRs assemblies after silica coating. **(e)** Histogram analysis of AuNRs@mSiO_2 assembly composition after silica encapsulation (376 individual nanorods were examined and categorized by species (monomer, dimer, trimer, etc.).