

Surface and Tip-Enhanced Raman Spectroscopy at the Plasmonic Hot Spot of a Coordination Complex-Conjugated Gold Nanoparticle Dimer

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Supporting Information

1. Discussions:

The UV-vis spectrum of the as-synthesized complex was characterized by intense ligand centered $\pi - \pi^*$ absorption bands (E - bands) at 230 and 264 nm with a broad band at 315 nm attributed to B-band corresponding to the aromatic ring of phenanthroline and 4-mercaptobenzoic acid ligands. (Figure 1A, manuscript). The bright red luminescent complex exhibited multiple emission bands in the range 550-750 nm ($\lambda_{\text{ex}} = 320$ nm) as shown in Figure 1A. This is attributed to the ligand sensitized emission associated with 4f-4f transition involving the 5D_0 excited state and the low-lying 7F_J ($J = 0 - 4$) levels of Eu(III) ions. The weak emission band centered at 580 and 650 nm appeared due to forbidden $^5D_0 \rightarrow ^7F_{0,3}$ transition; whereas the band at 593 nm was relatively strong, occurring due to magnetic $^5D_0 \rightarrow ^7F_1$ transition and is independent of co-ordination environment. On the other hand, the sharp peak centered at 614 nm due to $^5D_0 \rightarrow ^7F_2$ transition arising from induced electric dipole transition was indicative of slightly polarizable chemical environment around the Eu(III) site.¹ However, the considerably low intensity ratio of the electric dipole transition to the magnetic dipole transition was suggestive of symmetric environment around the co-ordination sphere.

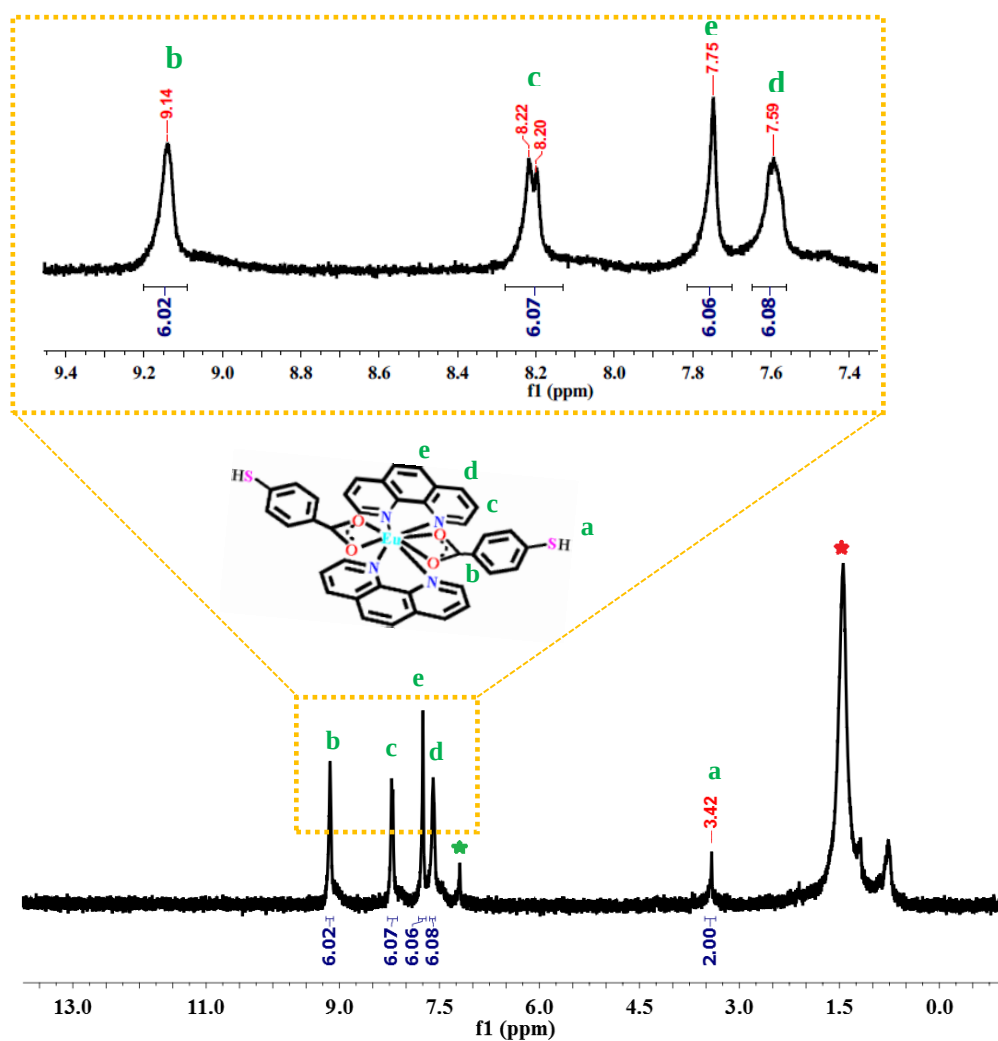


Figure S1. ^1H -NMR (400 MHz) spectra of $[\text{Eu}(\text{phen})_2(\text{MBA})_2]\text{Cl}$ in CDCl_3 . Top inset: shows the expanded view in the range 7-9.5 ppm comprising the aromatic protons. The peak at 3.42 ppm corresponds to sulphydryl group of p-mercaptobenzoic acid. The green asterisked peak corresponds to solvent peak (CDCl_3) and the red asterisked one corresponds to solvent water.

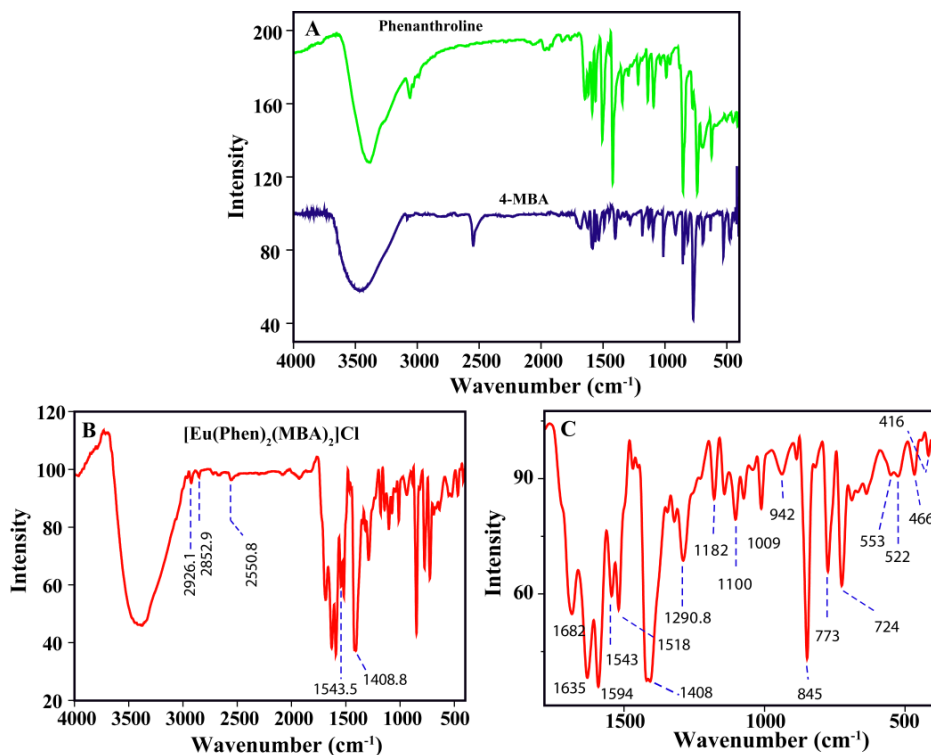


Figure S2. FTIR spectra of (A) phenanthroline (i) and 4-MBA (ii), (B) as synthesized $[\text{Eu}(\text{phen})_2(\text{MBA})_2]\text{Cl}$ complex and (C) expanded view of Figure S2B in the range 400-1800 cm^{-1} .

FTIR and Raman spectra analysis:

The bonding and co-ordination mode in so-synthesized Eu-complex based on FTIR and Raman spectral analysis are as follows: The disappearance of characteristic C=O stretching vibration at 1678 cm^{-1} upon complexation and appearance of peaks due asymmetric ($\nu_{\text{as}}(\text{COO}^-)$) and symmetric ($\nu_{\text{s}}(\text{COO}^-)$) stretching vibrations of carboxylate group at 1543 cm^{-1} and 1406 cm^{-1} , respectively, as shown in Figure S2B, indicated the participation of carboxyl group of 4-MBA ligand in metal co-ordination. In addition, the direction of their frequency shift and the corresponding shift difference ($\Delta\nu = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-) = 137 \text{ cm}^{-1}$) with respect to free ligand (4-MBA) indicated the bidentate co-ordination mode of the carboxyl group with the metal ion.² The peak at 2550 cm^{-1} corresponds to the stretching vibration of the -SH group in 4-MBA ligated to the metal centre through carboxyl group. The shift in the quadrupole vibrational bands appearing at 1682, 1635, 1518 and 1465 cm^{-1} due to ring vibration in phenanthroline along with weak band in the range 466-690 cm^{-1} indicated the metal ion

co-ordination to the phenanthroline ring³ (Figure S2C) A sharp peak appearing at 416 cm⁻¹ and 1594 cm⁻¹ was attributed to *Eu – O* stretching vibration and *C = C* aromatic stretch of the benzene ring. Further the peak appearing at 721 cm⁻¹ and 850 cm⁻¹ can be assigned to out of plane motion of hydrogen atoms on the heterocyclic ring of phenanthroline and hydrogen on the centre of the ring, respectively.⁴

Further, Raman peaks appearing at 276 and 2566 cm⁻¹ (Figure 1D, Manuscript) correspond to *Eu – N* and *–SH* stretching vibration of free thiol group, respectively. In addition, a sharp peak appearing at 417 cm⁻¹ due to polarised Raman line of phenanthroline supported the co-ordination with metal and that at 553 cm⁻¹ corresponds to Eu-O-C-C vibration. The complex spectra exhibited a weak bands at 843 cm⁻¹ and 1183 cm⁻¹ due to $\gamma_{\text{bend}}(\text{COO}^-)$ and C-COOH stretching vibration of 4-MBA group; whereas strong peaks at 1591 cm⁻¹ and 1099 cm⁻¹ were assigned to C=C stretching and ring breathing vibration corresponding to the aromatic ring in 4-MBA. Strong peak appearing at 724 cm⁻¹ corresponds to out of plane $\gamma(\text{C-C})$ vibration comprising both phenanthroline and 4-MBA ligand.⁵ Additionally, peak appearing at 1420 cm⁻¹ is attributed to ($\nu_{\text{C=C}}, \nu_{\text{C=N}}$) vibration and that peak at 1298 cm⁻¹ and 1455 cm⁻¹ corresponds to ($\nu_{\text{C=C}} + \delta_{\text{CH}}$) vibration of aromatic ring in phenanthroline.^{6,7}

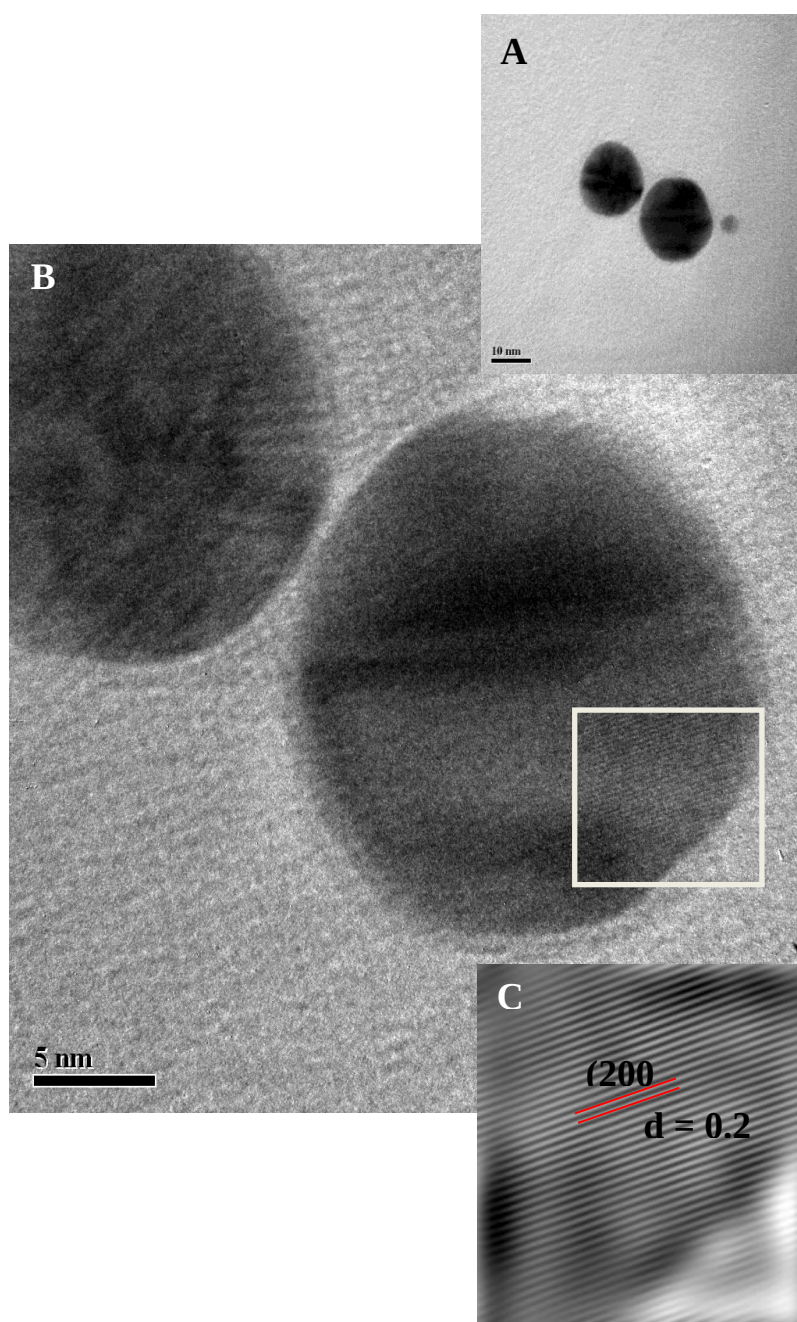


Figure S3. (A) A typical TEM image of gold nano dimer, (B) corresponding HR-TEM image of Au nano-dimer in Figure S3A. (C) IFFT image obtained from HRTEM image analysis of a select region (white box) from Figure S3B reveals gold lattice fringes with d-value = 0.2 nm corresponding to (200) plane.

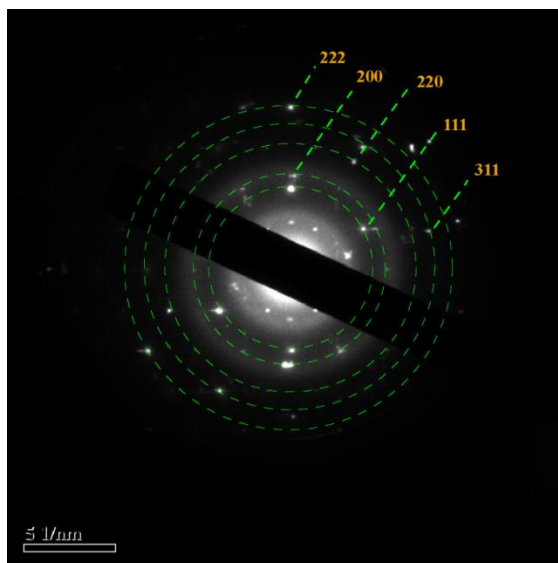


Figure S4. SAED pattern obtained from a representative Au nano-dimer showing diffraction corresponding to various planes of gold identified in the image by dotted circles.

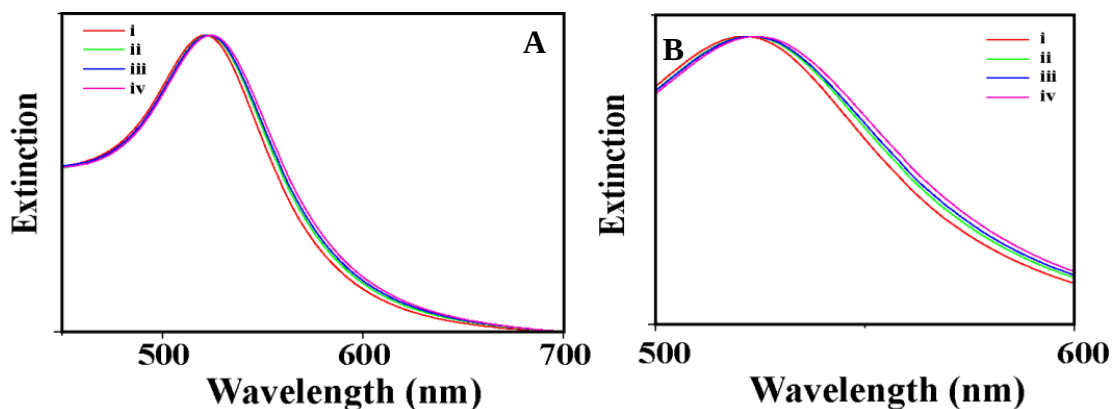


Figure S5. UV-vis spectra of (A) (i) as-synthesized cit-Au NP dispersion and cit-Au NP dispersions at different concentration of complex ($[\text{Eu}(\text{phen})_2(\text{MBA})_2]\text{Cl}$) (ii) 15 μM , (iii) 30 μM and (iv) 90 μM respectively, (B) expanded view of the UV-vis spectra in the range 500-600 nm showing red-shift and broadening with increasing concentration of metal complex (ii-iv) in cit-Au NP dispersion.

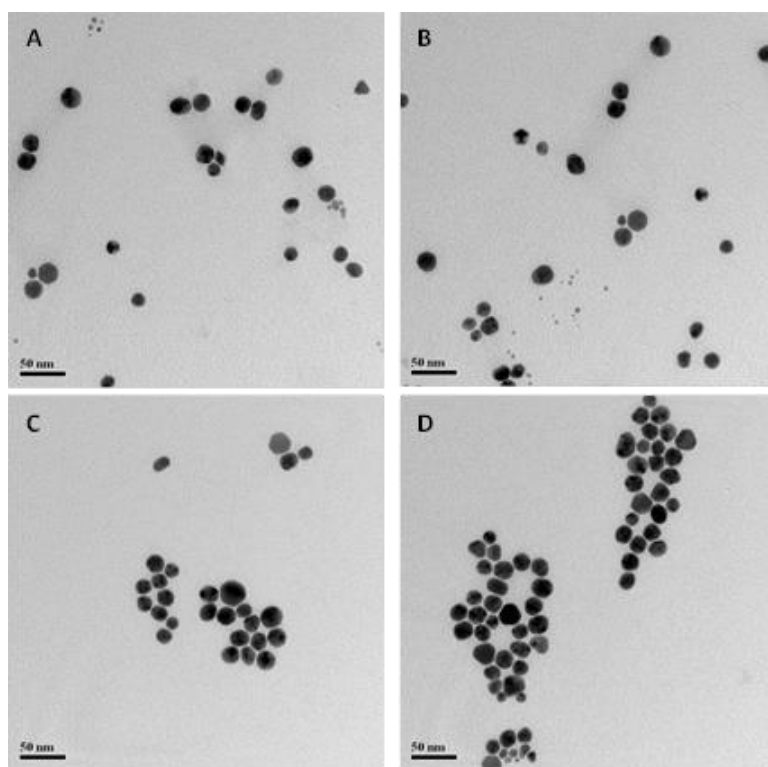


Figure S6. TEM images of as synthesised (A) and (B) Au nano-dimers; (C) and (D) Au NP discrete assemblies obtained at (A) and (B) 15 μM; (C) and (D) 90 μM of $[\text{Eu}(\text{phen})_2(\text{MBA})_2]\text{Cl}$ respectively.

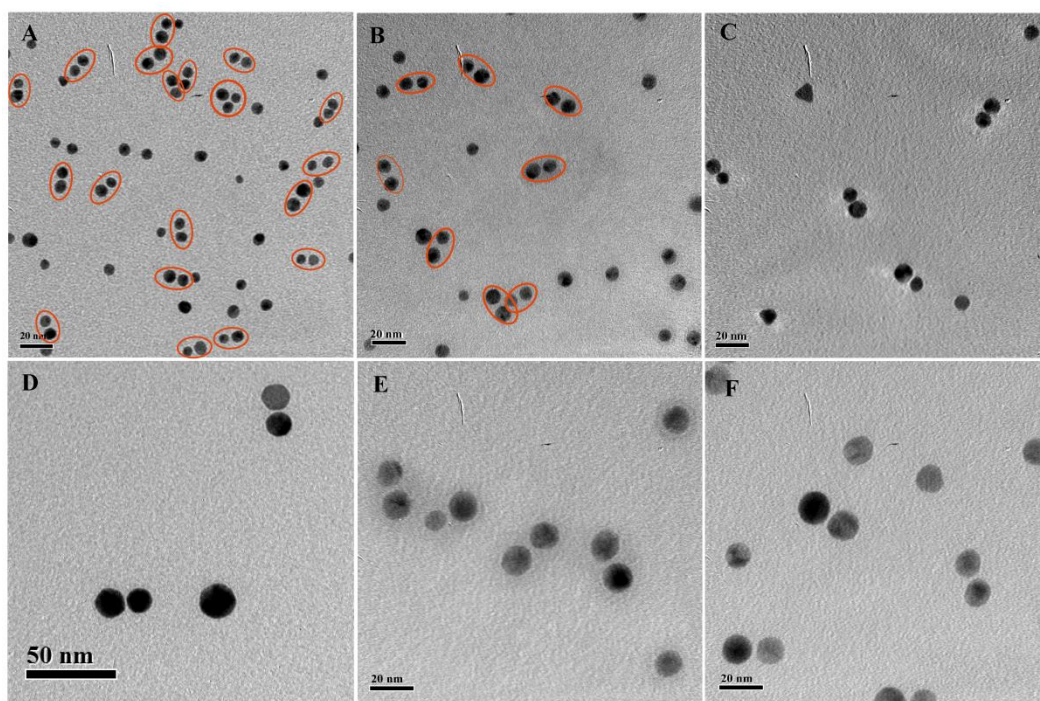


Figure S7. Representative TEM images of Au nano-dimer (**A-F**) obtained at complex concentration of 30 μM in cit-Au NP dispersion.

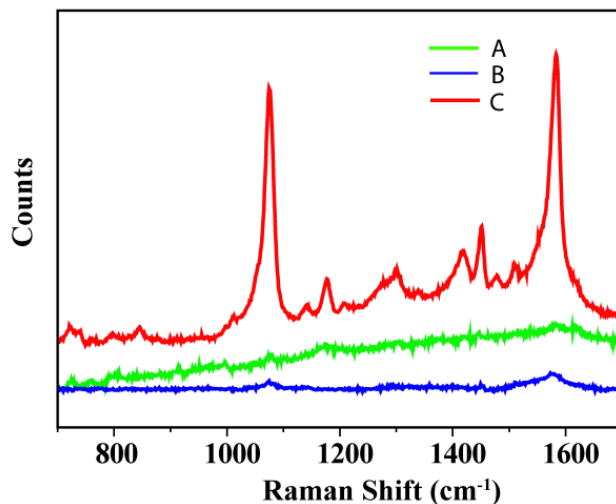


Figure S8. (A) Raman spectrum of cit-Au NPs obtained after centrifugation at 20627 rcf for 15 min at 15 °C. SERS spectra of metal complex bridged Au nano-dimer at laser excitation wavelength (B) 532 and (C) 632.8 nm. (Objective -100 $\times$, time - 20 s)

2. Calculation of SERS Enhancement Factor (EF):

The average enhancement factor ⁸ is given by,

$$EF = \frac{I_{SERS} N_{bulk}}{I_{normal} N_{SERS}} \quad (1)$$

where N_{bulk} and N_{SERS} are the number of molecules of the metal complex in bulk and the number of metal complex in the Au nano-dimers under the laser excitation beam; whereas I_{norm} and I_{SERS} are the measured intensities for normal Raman scattering from the bulk complex and SERS intensity of the metal complex in Au nano-dimers, measured with 632.8 nm laser source. The measurement was carried out with 100 $\times$ objective (numerical aperture = 0.9) with an acquisition time of 20 s for each measurement. We considered the average Raman scattering intensities - I_{norm} and I_{SERS} - obtained from the average of at least 10 different Raman measurements, for acquisition carried over different probed

area under 632.8 nm laser illumination. We assumed in our calculation that one hot-site contained only one complex molecule.

Concentration of as synthesized Cit-Au NPs = 0.95 nM^9

Therefore number of moles of Cit-Au NPs in the 5 mL reaction volume = 0.95×10^{-12}

Therefore, total number of NPs in 5 mL reaction volume = $0.95 \times 10^{-12} \times N_A$

$$= 5.721 \times 10^{11}$$

The percentage yield of dimer, trimer and tetramer as obtained after reaction of Cit-Au NP dispersion with Eu-complex in the reaction mixture was found to be 51.8 %, 7.2 % and 0.28 % respectively.

Therefore,

Number (population) of dimers in 5 mL reaction volume = 1.4817×10^{11}

Number (population) of trimers in 5 mL reaction volume = 0.2059×10^{11}

Number (population) of tetramers in 5 mL reaction volume = 0.0085×10^{11}

Now,

Total number of ligating complex molecules in the 5 mL Au NP dispersion undergoing reaction to yield 51.8 % dimers, 7.2 % trimer and 0.28 % tetramer - neglecting the contribution from multimers - can be calculated as follows:

Number of complex molecule in 5 mL reaction volume forming dimer = Number of dimer in 5 mL reaction volume = 1.4817×10^{11}

Number of complex molecule in 5 mL reaction volume forming trimer = $2 \times$ Number of trimer in 5 mL reaction volume = $2 \times 0.2059 \times 10^{11} = 0.4118 \times 10^{11}$

Number of complex molecule in 5 mL reaction volume forming tetramer = $4 \times$ Number of tetramer in 5 mL reaction volume = $4 \times 0.0085 \times 10^{11} = 0.0340 \times 10^{11}$

Total number of complex molecules ligating Au NPs in 5 mL dispersion

$$= (1.4817 + 0.4118 + 0.0340) \times 10^{11} = 2 \times 10^{11}$$

Volume of the Au NP dimer dispersion dropcast (probed under laser illumination) = 0.1 mL

Therefore, total number of complex molecule ligating Au NPs in probed volume, N_{SERS}

$$= \frac{2 \times 10^{11} \times 0.1}{5}$$

$$= 4 \times 10^9$$

Average SERS intensity = $I_{SERS} = 9459.7$

Now,

Concentration of the Eu-complex molecule considered for normal Raman measurement = 3 mM

Volume of Eu-complex molecule dropcasted = 0.1 mL

Total number of Eu-complex molecule in the probed volume, N_{bulk} can be calculated as follows:

$$\text{Moles of Eu-complex in 0.1 mL solution} = 3 \times 10^{-7}$$

$$\text{Therefore total number of complex molecule probed} = 3 \times 10^{-7} \times N_A = 18.069 \times 10^{16}$$

Normal Raman scattering intensity, $I_{norm} = 267$

Considering equation (1), average enhancement factor was estimated to be,

$$EF = \frac{9459.7 \times 18.069 \times 10^{16}}{267 \times 4 \times 10^9} = 1.6 \times 10^9$$

3. Calculation of TERS Enhancement Factor (EF):

The TERS enhancement factor is calculated taking into account the contrast factor obtained from the ratio of near-field and far-field Raman scattering intensity and their corresponding scattering area.^{10,11}

The enhancement factor is calculated using equation 1 and 2 as below:

$$Contrast = \frac{I_{near\ field}}{I_{far\ field}} = \frac{I_{tip\ down} - I_{tip\ up}}{I_{tip\ up}} \quad (1)$$

$$Enhancement\ Factor = Contrast \times \frac{A_{focus}}{A_{tip}} = Contrast \times \frac{d_{focus}^2}{d_{tip}^2} \quad (2)$$

where $I_{near\ field}$ and $I_{far\ field}$ refers to the tip-enhanced near-field and tip-retracted far-field Raman signal intensity, A_{focus} and A_{tip} refers to far-field laser scattering area and near-field laser scattering area at the tip-apex, d_{focus} refers to diameter of laser focus and d_{tip} refers to two times the radius of curvature of the tip. It is to be noted that during TER spectra collection, far field signal may be present as background. Therefore, the near-field Raman scattering intensity $I_{near\ field}$ is defined as difference between the Raman scattering intensity in tip-down and tip-up mode whereas far-field Raman scattering intensity $I_{far\ field}$ refers to Raman intensity at tip-up mode. The EF is calculated with respect to peak at 1078 cm^{-1} and 1588 cm^{-1} obtained using SFM(TF)-TERS. The calculated diameter

of laser focal spot is 1838 nm and tip radius of TF-TERS probe (Bruker) = 20 nm. The Raman peak intensity values obtained using TF-TERS set-up are tabulated below (Table S1):

Table S1: Raman peak intensity values corresponding to wavenumbers 1078 cm⁻¹ and 1588 cm⁻¹ at tip-down and tip-up modes as obtained from SFM (TF)-TER spectra.

<u>Wavenumber (cm⁻¹)</u>	<u>Intensity</u> (Tip-down)	<u>Intensity</u> (Tip-up)	<u>Contrast Factor</u>
1078	196	12	15.3
1588	258	14	17.4

Therefore,

TERS-EF with respect to peak at 1078 cm⁻¹:

$$Enhancement\ Factor = Contrast \times \frac{d_{focus}^2}{d_{tip}^2} = 3.2 \times 10^4$$

and TERS-EF with respect to peak at 1588 cm⁻¹:

$$Enhancement\ Factor = Contrast \times \frac{d_{focus}^2}{d_{tip}^2} = 3.67 \times 10^4$$

Dicussions:

In TERS, when a laser is focussed into the tip-apex, a large area encompassing the molecule of interest (positioned in the hot-site of the dimeric structure) is likely to be illuminated due to laser focus spot resulting in the generation of far-field in addition to near-field at the tip-apex. Therefore,

far-field Raman signal (SERS) originating from all molecules within the laser spot will always contribute to the total TERS signal. Therefore, overall TERS signal (tip-in) is a cumulative effect of Raman scattering in the near vicinity of the tip (near-field) and from the rest of the laser illuminated area (far-field).

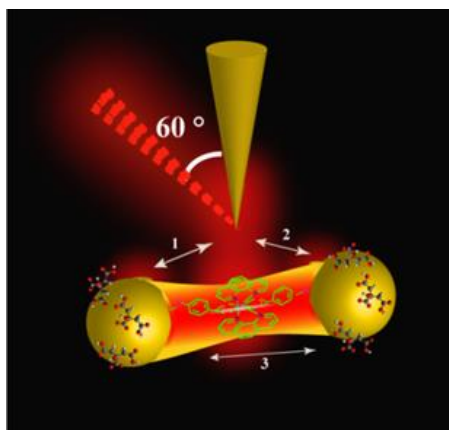
$$\text{TERS signal} = I_{\text{near-field}} + I_{\text{far-field}}$$

However, in case of monolayer or single molecule coverage, the far-field signal is barely noticeable. In that case, the noise level can be considered as an upper bound for the far-field intensity, which would lead to the underestimation of the EF. This clearly suggested that TERS signal enhancement would be more than SERS enhancement.

Now, let us consider various possible geometries for TERS measurements,

- (i) An ideal TERS (-only) signal could be obtained when an appropriate laser, is focussed at the metal (preferably Au) tip aligned with the axis of the molecular bond. The enhanced electric field generated at the tip apex would then lead to the high enhancement of Raman scattering of the molecule placed underneath it, provided the field polarisation is aligned with the tip-molecular bond axis.
- (ii) Now when the molecule of interest is placed in the junction between tip-metal substrate (molecule adsorbed on metal surface), within close proximity ($\sim 1-2$ nm), the gap-mode effect between the tip and metal substrate would lead to the largest field enhancement,¹² the Raman scattering intensity of which would be significant.
- (iii) Now, let us consider a molecule positioned in the hot-spot between two plasmon active metal nanoparticles (Au) as is the case in our study, then tip-induced Raman enhancement would depend on the polarisation of vibrational bonds of the molecule with respect to the coupled particle surface and that of tip. If it is aligned such that the vibrational mode is polarized along the direction perpendicular to the axis joining the two nanoparticles and thus parallel to the tip then the enhancement can be expected (in an ideal scenario) to be maximum with little reduction in enhancement would be found for the tilted geometry of the same. Additionally, there can be redistribution of hot spots in the presence of the tip as interaction between fields generated by the

tip and each nanoparticle may also become part of the system (Schematic S1). Thus the enhancement at the hot-spot in the presence of the tip would be more complex than simple interaction between the field generated by the tip and the molecular bond. In a side illumination geometry, the direction of field polarization is found to be nearly parallel to the tip axis. Therefore, in addition to above mentioned factor, the enhancement due to the tip will depend upon the alignment of the metal complex positioned in the hot-spot of dimeric nanostructure with respect to the tip-axis. Thus, despite redistribution of the plasmon enhanced electric field generated at the tip sample junction one can still consider the overall enhancement as to have occurred in the presence of the tip.



Schematic S1. Plausible schematic showing the side illumination geometry in TERS set-up and the redistribution of hot-spot upon tip approach to the sample (metal complex ligated Au nano-dimer).

However, the actual field enhancement depends upon many other factors, which include tip-size, tip material, tip radius, tip-sample distance, tip-sample alignment and dielectric properties of the probe molecule. In addition, laser focus aberration may also lead to a decrease in near field signal while leaving the spectral background maximum. Thus considering all the above factors, TERS enhancement factor of 10^4 can be considered as lower bound value.

This is in contrast to SERS enhancement factor of 10^9 which is calculated from signals derived from an ensemble average of large number of molecules (metal complex positioned in a hot spot) for diffraction limited laser focus. SERS signal arises from enhanced electric field at the hot-spot due to

the coupled plasmon arising out of dimeric Au nanostructures for incident light polarised along the dimer axis considering top illumination geometry. Additionally, polarization of the vibrational modes normal to the metal surface plane would also lead to the preferential enhancement.

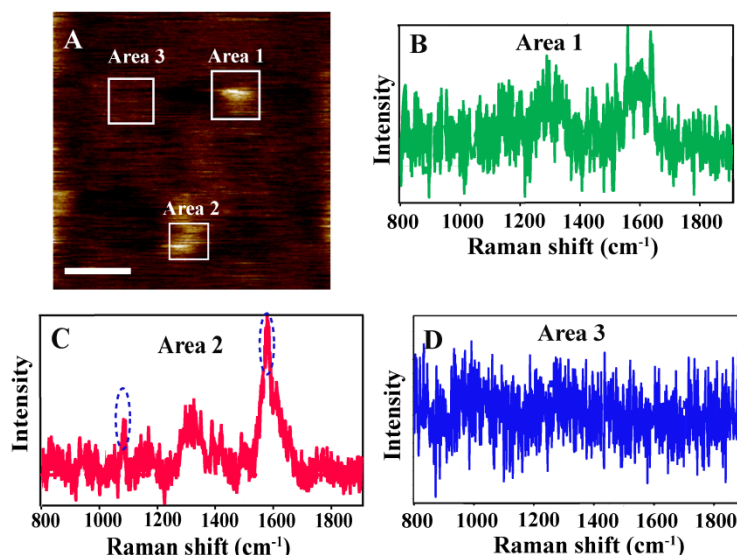


Figure S9. (A) TF amplitude feedback topograph (scale = 0.15 μm) showing representative individual Au NP (area 1), dimeric Au NP (area 2) and corresponding TER spectra as in (B) and (C), respectively, (D) featureless Raman spectrum corresponding to area 3 in Figure S9A.

References

1. Divya. V.; Biju, S.; Varma, R. L.; Reddy, M. L. P. Highly efficient visible light sensitized red emission from europium tris[1-(4-biphenoyl)-3-(2-fluoroyl)propanedione](1,10-phenanthroline) complex grafted on silica nanoparticles. *J. Mater. Chem.* **2010**, 20, 5220–5227.
2. Nakamoto, K.; McCarthy, P. J. Spectroscopy and Structure of Metal Chelate Compounds, JohnWiley & Sons, New York, NY, USA, 1968.
3. Schilt, A. A.; Taylor, R. C. Infra-Red spectra of 1: 10- Phenanthroline metal complexes in the rock salt region below 2000 cm^{-1} . *J. Inorg. Nucl. Chem.* **1959**, 9, 211-221.

4. Qin, W.; Zhang, Y.; Liu, W.; Tan, M. Synthesis and infrared and fluorescence spectral properties of luminescent terbium and europium complexes with open-chain carboxylate crown ethers. *Spectrochimica Acta Part A* **2003**, *59*, 3085-3092.
5. Michota, A.; Bukowska, J. Surface-enhanced Raman scattering (SERS) of 4-mercaptobenzoic acid on silver and gold substrates. *J. Raman Spectrosc.* **2003**, *34*, 21–25.
6. Tsaryuk, V.; Zolin, V.; Legendziewicz, J.; Szostak, R.; Sokolnicki, J. Effect of ligand radicals on vibrational IR, Raman and vibronic spectra of europium β -diketonates. *Spectrochimica Acta Part A* **2005**, *61*, 185–191.
7. Tsaryuk, V.; Zolin, V.; Puntus, L.; Savchenko, V.; Legendziewicz, J.; Sokolnicki, J.; Szostak, R. Vibronic spectra and details of the structure of europium nitrates with derivatives of 1,10-phenanthroline. *Journal of Alloys and Compounds* **2000**, *300–301*, 184–192.
8. Wang, T.; Zhang, Z.; Liao, F.; Cai, Q.; Li, Y.; Lee, S. T.; Shao, M. The Effect of Dielectric Constants on Noble Metal/Semiconductor SERS Enhancement: FDTD Simulation and Experiment Validation of Ag/Ge and Ag/Si Substrates. *Sci. Rep.* **2014**, *4*, 4052.
9. Dutta, A.; Paul, A.; Chattopadhyay, A. Effect of Temperature on the Aggregation Kinetics of Partially Bare Gold Nanoparticles. *RSC Adv.* **2016**, *6*, 82138-82149.
10. Sabanes, N. M.; Driessen, L. M. A.; Domke, K. F. Versatile Side-Illumination Geometry for Tip-Enhanced Raman Spectroscopy at Solid/Liquid Interfaces. *Anal. Chem.* **2016**, *88*, 7108–7114.
11. Mehtani, D.; Lee, N.; Hartschuh, R. D.; Kisliuk, A.; Foster, M. D.; Sokolov, A. P.; Maguire, J. F. Nano-Raman spectroscopy with side-illumination optics. *J. Raman Spectrosc.* **2005**, *36*, 1068–1075.

12. Yang, Z.; Aizpurua, J.; Xu, H. Electromagnetic field enhancement in TERS Configurations. *J. Raman Spectrosc.*, **2009**, *40*, 1343–1348.