Supplementary Information

Plasmon resonance dynamics and enhancement effects in tris(2,2'-bipyridine)ruthenium(II) gold nanosphere oligomers

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Methods

TEM Analysis

The samples for TEM were prepared by stabilizing the aggregates using 10% PVP aqueous solution. The stabilized aggregate sample was further diluted 1000 times with Milli-Q water to prevent extrinsic aggregation during solvent evaporation. Finally, a 10 µL aliquot of the diluted sample was dropped on a 400-mesh formvar/carbon-coated copper grid and allowed to settle for 4 min before removing the excess liquid with Kimwipe and drying at room temperature prior to loading into the TEM. Additional samples of more concentrated oligomers were also prepared in a similar manner to enable imaging of many particles on the TEM grid. Analysis and peak assignment can be confirmed through our structure-function correlation between UV-Vis spectra and TEM imaging. For additional corroborating results, the reader is encouraged to view previously published literature on computational simulations of the plasmon modes of different nanosphere oligomeric systems that are consistent with our findings and results.[1-4]

ICPOES Analysis

The samples for ICPOES analysis were prepared by drying at room temperature the settled aggregate particles obtained from a suspension from which unadsorbed Ru dye or free ions had been removed by repeated centrifugation at 6000 rpm. About 1.0 mg of the dried sample was accurately weighed into a glass vial, and then a mixture of 0.90 mL HCl: 0.15 mL HNO_3 was added. The solution obtained was evaporated almost to dryness at 95°C on OHAUS Guardian 7000 Hotplate for about 4 h. After cooling to room temperature, the digested sample was rehydrated and transferred into a graduated flask and diluted to volume with 2% HNO_3. The solution was filtered through a 0.22 µm membrane, and 5.0 mL of filtrate was transferred to a falcon tube for ICPOES measurements. The unbound dye in the supernatants and control samples were also treated in a similar way by matrix matching and appropriate dilution. Calibration standards (0-5 mg/L) were prepared prior to the analysis by appropriate dilution of the single-element stock solutions of Ru and Au with 2% HNO_3.

Estimation of $[Ru(BPY)_3]^{2+}$ Surface Coverage from ICPOES data

The maximum surface coverage was approximated by first calculating the surface area of a single nanosphere using the formula, $SA_{sphere} = 4\pi D^2$. This was then multiplied by the estimated number of particles in the measured Au concentration (mg/mL) for each of the samples to obtain the total surface area of the whole nanoparticles in nm^2. Similarly, the maximum amount of $[Ru(BPY)_3]^{2+}$ adsorbed in mg/mL is first converted to moles and then to the number of molecules using Avogadro's number. The ratio of the number of the adsorbed dye molecules to the total surface area of the nanospheres gives the estimate of the surface coverage in molecules/nm^2. It should be noted that these calculations assume that all the nanoparticles are perfect spheres with a diameter of 40 nm and 100 nm.

SERS Measurements

Initially, a 10 μL aliquot of the 40 nm oligomer aggregated with 2 μM $[Ru(BPY)_3]^{2+}$ was dropped onto a precleaned microscope slide and allowed to dry in air. Measurements at room temperature were performed on a Witech Alpha 300 confocal Raman microscope using a 50× objective. Samples were excited with a 457 nm (0.15 mW), 633 nm (1 mW) and 785 nm (20 mW) laser, and the scattered radiation was captured by the same objective and then sent in a spectrograph equipped with a CCD Camera. Similar procedure was used for the Raman measurements but with 1 mM and 2 μM $[Ru(BPY)_3]^{2+}$ concentrations. The spectra presented are the sum of 50 spectral accumulations, with 50 s total acquisition time.

TA Measurements

The samples for transient absorption (TA) analysis were prepared by aggregating 40 nm nanospheres with 10 uM $[Ru(BPY)_3]^{2+}$. The polymer stabilized oligomers were then illuminated with a one box oscillator/regenerative amplifier setup (Solstice Ace, MKS Instruments Inc. Spectra-Physics). An 800 nm ultrafast pulse with 60 fs pulse duration and 5 kHz repetition rate is generated via a Ti-sapphire lasing medium. The beam is then split with a 95/5 beam splitter, sending 50 μJ for white light continuum generation in a sapphire crystal. The remaining power is sent through a two stage optical parametric amplifier with mixing module (TOPASprime and NIR UVis, MKS Instruments Inc. Spectra-Physics). This setup allows for a 235 - 1160 nm continuous tuning range for the pump pulse. Samples were pumped with a 454 nm pulse and probed with a broadband continuum where spatial and temporal overlap were confirmed with the cross-phase modulation of a reference standard. The power of the pulse beam was measured with a THORLABS PM100D Compact Digital Power and Every Meter Console and S120C Standard Photodiode Power Sensor. The sensor was fixed at the sample location and the power reading was averaged for thirty seconds. The mean power reading was recorded and converted to energy per pulse. Data was collected with an averaging time of 1 second and a total of 5 scans per sample (Surface Xplorer, Ultrafast Systems). After collection, data was processed for time zero correction, background subtraction, and chirp correction in Surface Xplorer.
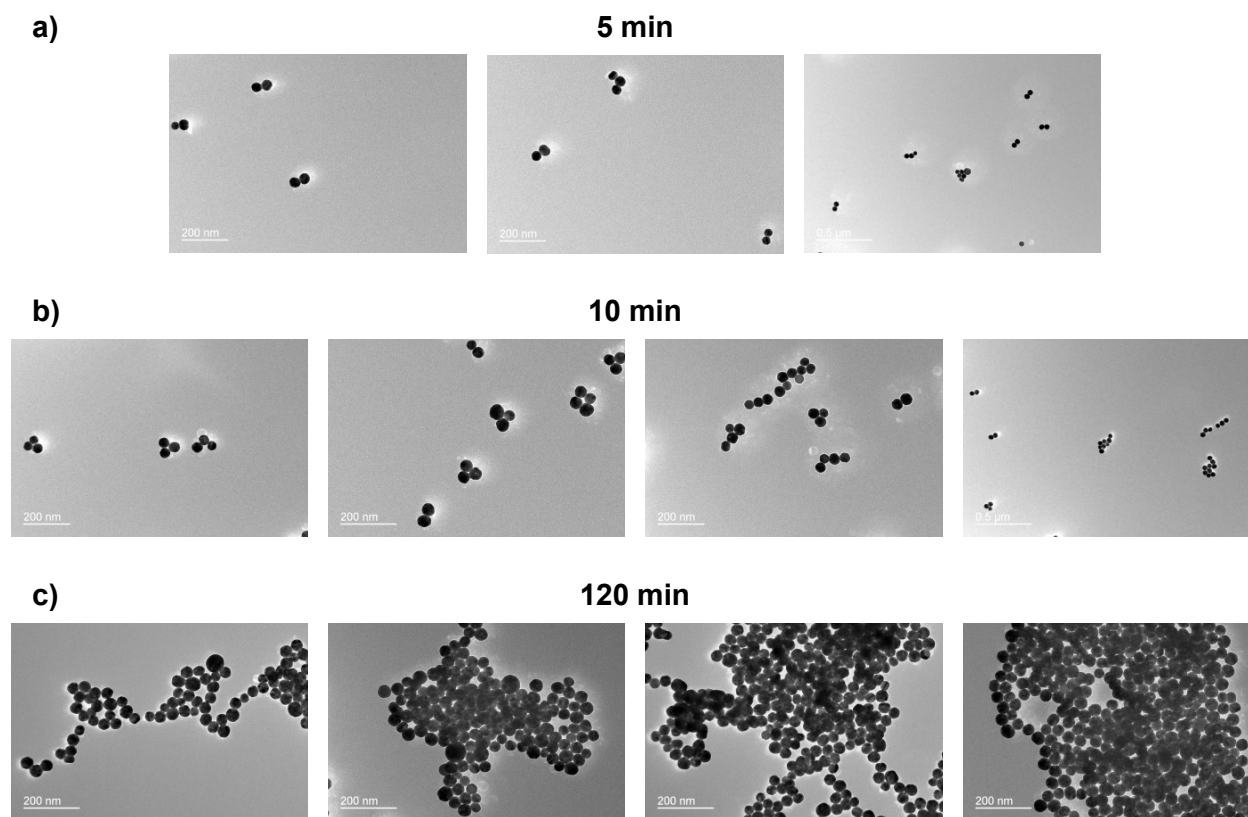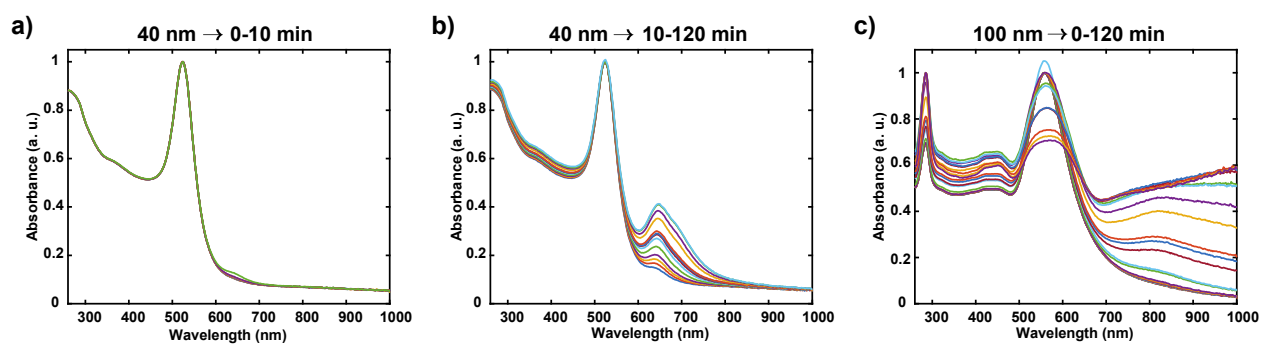
Results

Figure S1:
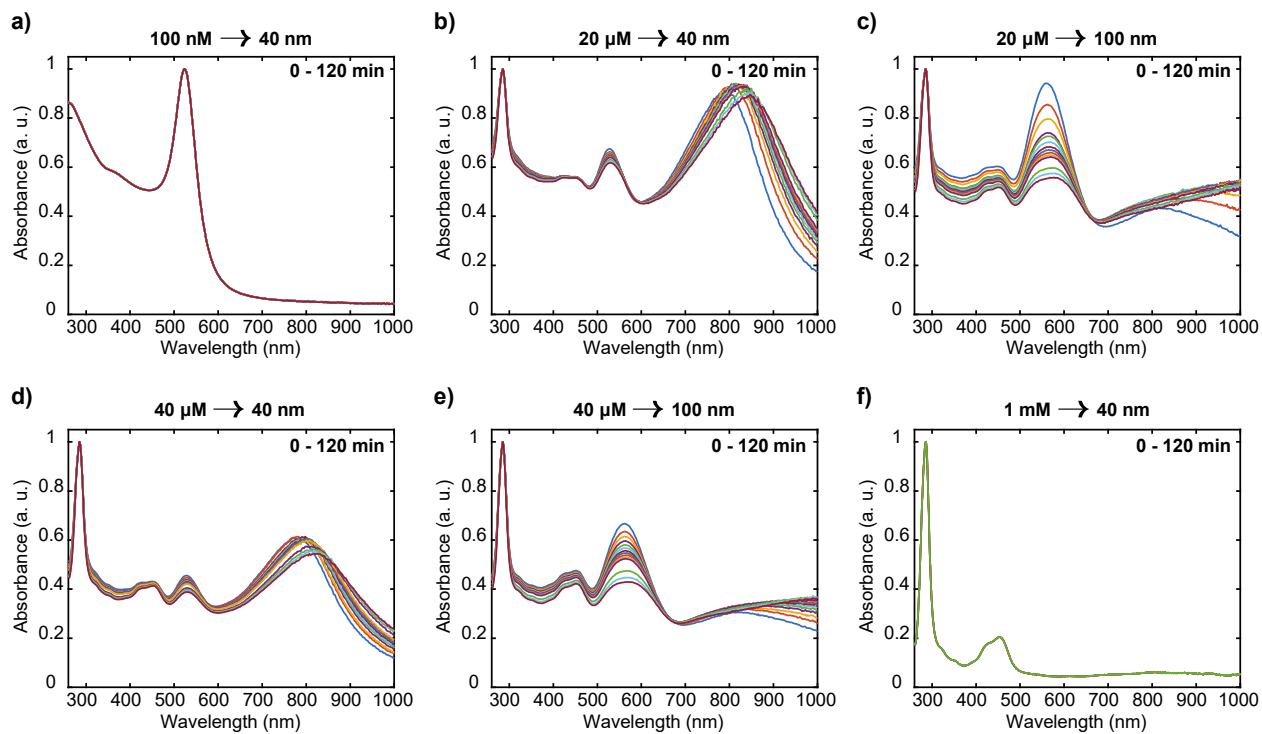
Fig. S1 Time evolution of the absorption spectra during the aggregation of 40 nm and 100 nm gold nanospheres with different $[Ru(BPY)_3]^{2+}$ concentrations. The systems are: (a) 100 nM, 40 nm AuNS. (b) 20 µM, 40 nm AuNS. (c) 20 µM, 100 nm AuNS. (d) 40 µM, 40 nm AuNS. (e) 40 µM, 100 nm AuNS. (f) 1 mM, 40 nm AuNS.

Figure S2:

a) **5 min**

b) **10 min**

c) **120 min**

Fig. S2 Representative TEM images for more concentrated oligomer samples at different aggregation stages of 40 nm AuNS. (a) 0 - 5 min. (b) 5 - 10 min. (c) 10 - 120 min.

Figure S3:

Fig. S3 Time evolution of the absorption spectra during the inverse aggregation of 40 nm and 100 nm gold nanospheres with optimized $[Ru(BPY)_3]^{2+}$ concentrations of 2 μM and 10 μM, respectively. (a) 0 - 10 min, 40 nm AuNS. (b) 10 - 120 min, 40 nm AuNS. (c) 0 - 120 min, 100 nm AuNS.

**Table S1:** Optimization of ICPOES sample preparation procedure using $HCl:HNO_3$ (6:1)

Controls	Calculated (ppm)	Measured (ppm)
2.5 μM	1.8716	1.8599 ± 0.001
5 μM	3.7430	3.7321 ± 0.003
10 μM	7.4860	7.4649 ± 0.011
20 μM	14.9720	14.9599 ± 0.001
40 μM	29.9450	29.9247 ± 0.005
40 nm Au	1.00 (mg/mL)	1.03 (mg/mL) ± 0.001
100 nm Au	1.00 (mg/mL)	1.01 (mg/mL) ± 0.003

**Table S2:** Adsorption data as a function of $[Ru(BPY)_3]^{2+}$ concentration

C_0 (μM)	C_0 (mg/L)	C_{ads} (mg/L) 40 nm	C_{ads} (mg/L) 100 nm	Adsorption (%) 40 nm	Adsorption (%) 100 nm
2	1.50	1.32	1.29	88.30	86.00
5	3.74	3.09	2.91	82.60	77.79
10	7.49	5.13	4.68	68.60	62.59
20	14.97	8.46	7.69	56.53	51.40
30	22.46	9.44	7.65	42.03	34.08
40	29.94	9.96	7.22	32.69	24.11

Figure S4:
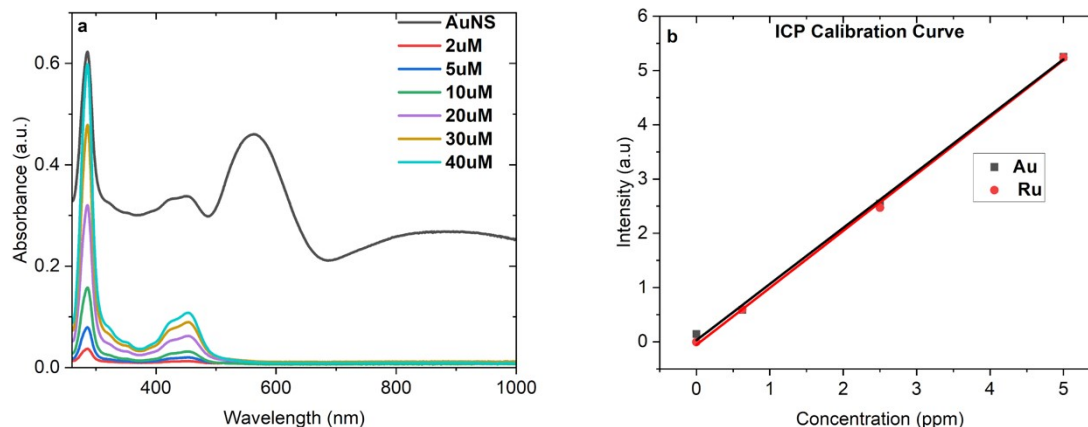
Fig. S4 (a) Optimization of centrifugation to recover aggregates. The disappearance of the plasmon peak in the supernatant signifies good recovery of the nanoparticles. (b) Double element calibration of standards for matrix matching (R^2 = 1 for Ru, and 0.9995 for Au).

Figure S5:
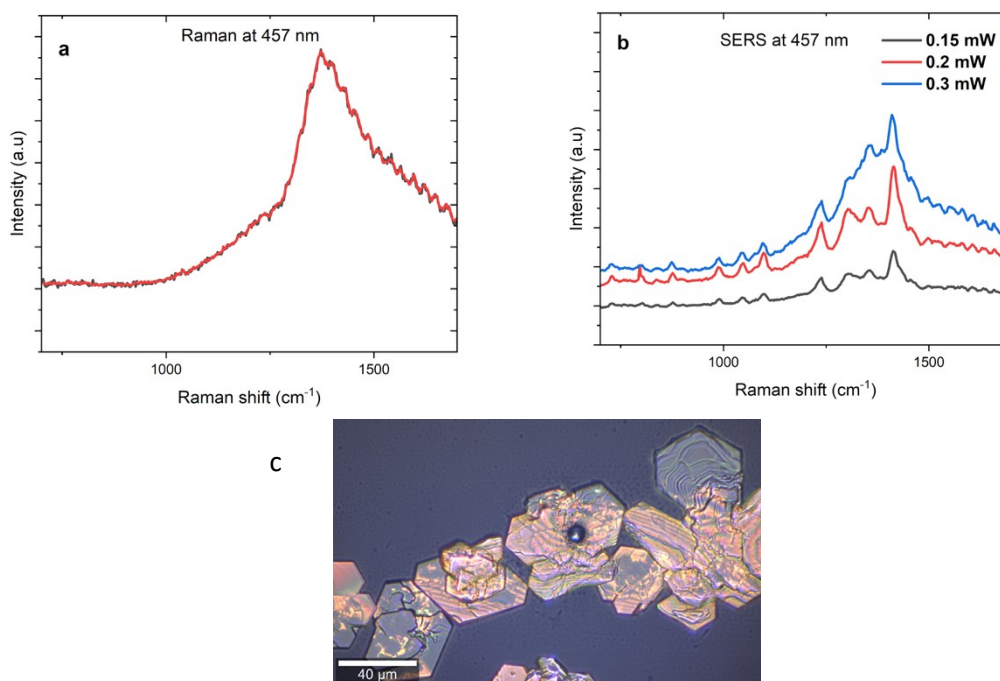
Fig. S5 (a) Raman spectrum of $[Ru(BPY)_3]^{2+}$ showing a strong fluorescence background at 457 nm (0.15 mW). (b) SERS spectra at 457 nm showing improved signal to noise ratio. The deformation of the ring breathing peak at 1039 cm-1 can be seen which shows structural transformation. (c) Image of the sample showing the photodamage even at 0.15 mW.

References:

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