Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary material for The Application of Selective Surface Modification of Nanocavities Arrays to Compare Surface vs Cavity Plasmons in SERS enhancement

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Figure 1 shows Raman spectra of 1-nonanethiol selectively adsorbed at the edges of gold nanocavity arrays before and after the removal of polystyrene spheres. The spectrum is dominated by polystyrene peaks before removal of spheres, evident from aromatic ring breathing modes at 1001, 1200, 1602 cm^{-1}. SEM image of nanocavity arrays after the removal of spheres confirmed that an hours sonication in THF removed the polystyrene spheres completely from the substrate. Correspondingly, the Raman peaks associated with polystyrene spheres are absent after sonication of arrays in THF.

Figure 1(B) shows Raman modes associated with alkane thiol self assembled at the edges of nanocavity array after removal of spheres. The features around 1001 cm^{-1} and 1500 arise from skeletal vibrations of C-C stretching mode and CH_2 scissor vibrations respectively.

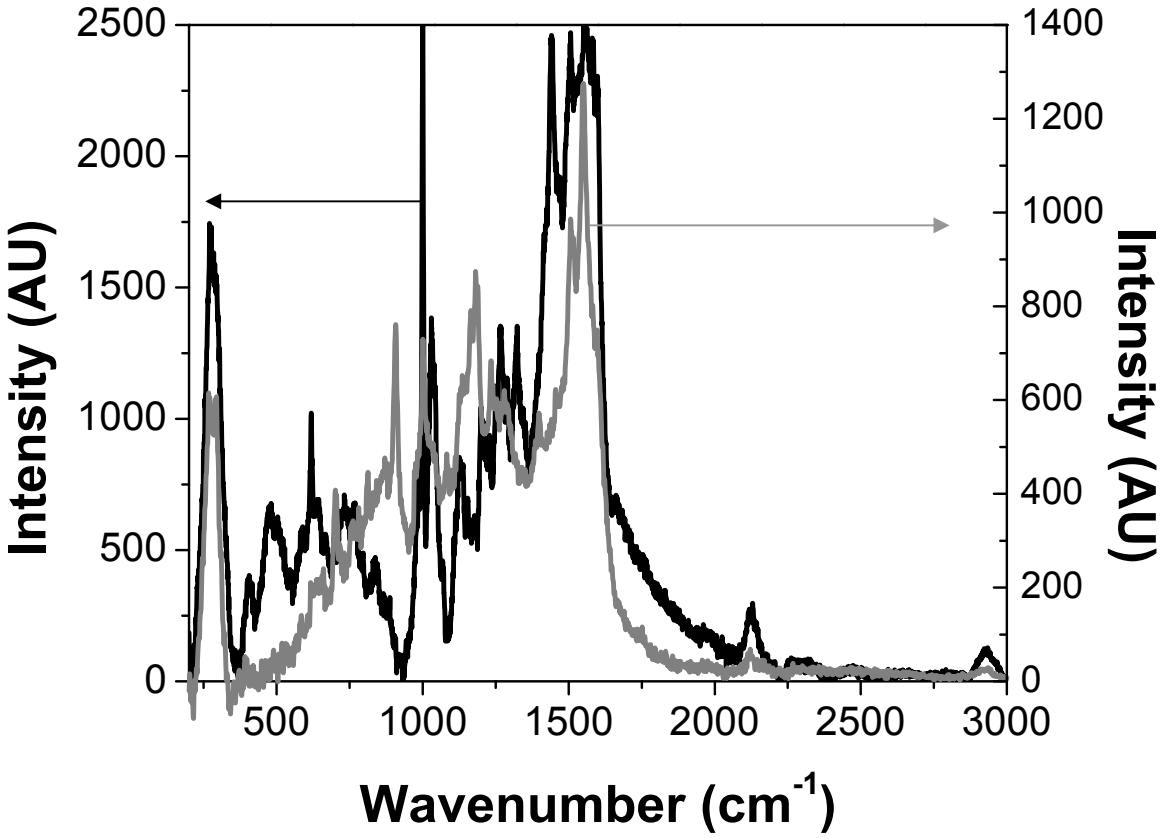

Figure S1: Raman spectra of edge modified gold nanocavity arrays with 1-nonanethiol (□) before dissolving polystyrene spheres (□) after dissolving polystyrene spheres in THF by sonication.

Figure 2 shows Raman spectra of self assembled monolayer of $Ru(bpy)_2(Qbpy)]^{2+}$ dye selectively adsorbed at the edges of gold nanocavity arrays (A) before and (B) after dissolving polystyrene spheres. The spectrum is dominated by polystyrene peaks before the removal of spheres. Figure 2(B) shows the SERS signal coming from $Ru(bpy)_2(Qbpy)]^{2+}$ dye adsorbed at the edges of array after dissolving polystyrene spheres.

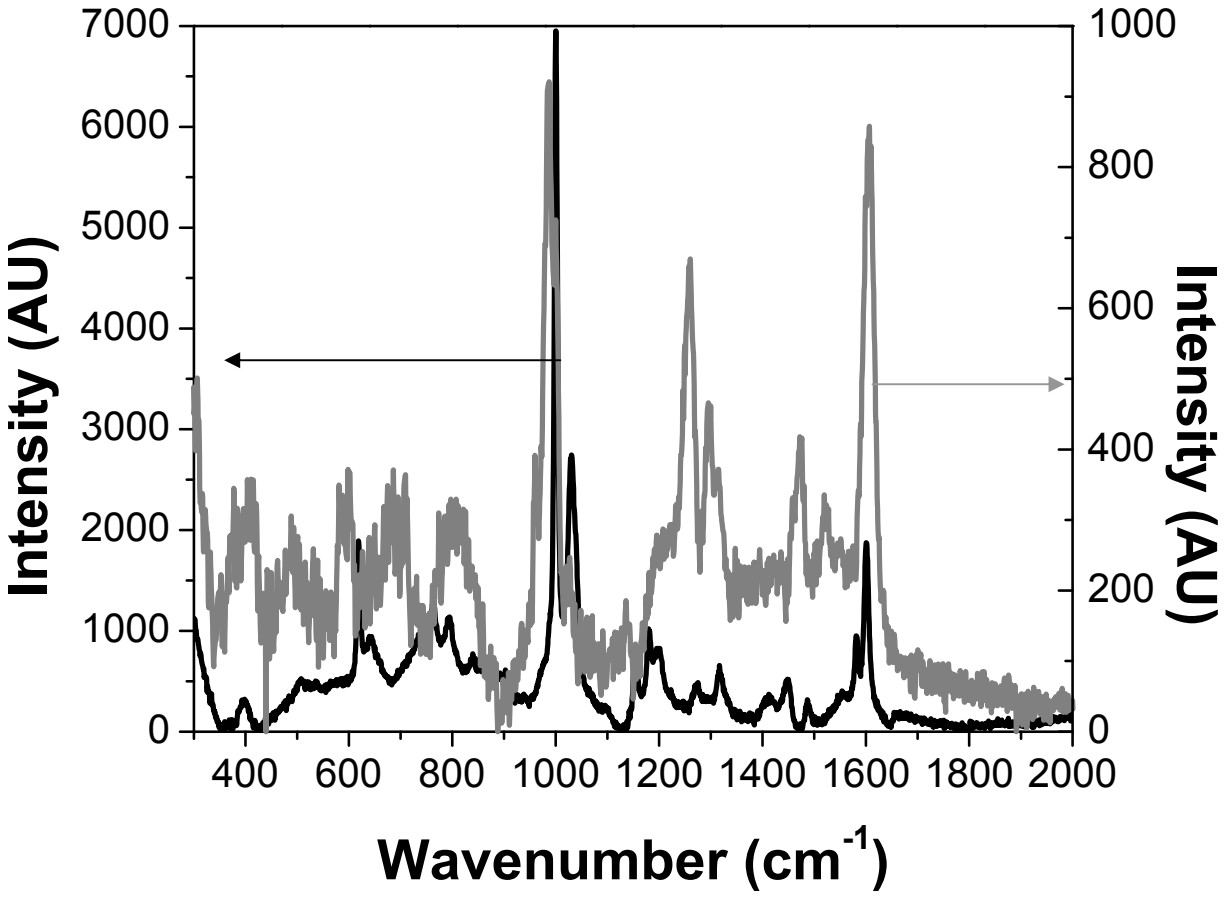

Figure S2: Raman spectra of edge modified 820gold nanocavity arrays with $Ru(bpy)_2(Qbpy)]^{2+}$ (□) before dissolving polystyrene spheres (□) after dissolving polystyrene spheres in THF by sonication

Calculation of ratio of top surface area versus interior surface area

The top and the interior surface areas of the gold nanocavity arrays were estimated by analysis of SEM images using image J software. The surface area of a single cavity was calculated by using the equation for the area of a truncated sphere, $3\pi r^2$, where r is the radius of the sphere. The number of nano cavities in a defined area (the area of the SEM at constant magnification was used) was calculated from SEM image using Image J software. The total interior surface area of the nanocavity array was determined by multiplying the number of cavities determined from SEM image by the surface area of a single cavity. The area of top surface of cavity was determined by subtracting the area of all holes from the total area of the image. Table 1 shows the edge and internal cavity areas determined for each

cavity size and the associated intensity of the 1026 cm^{-1} Raman band. These areas were calculated from 7 μm^2 interrogation area under illumination and show that the interior and edge areas vary little as a function of cavity size. Table 2 shows similar data obtained using 633 nm as an excitation source.

Edge			Interior	
Cavity diameter (nm)	Area (μm^2)	Raman Intensity	Area (μm^2)	Raman Intensity
820	3	900	26	1200
600	2.34	14000	25	4000
430	2.1	9000	20	2000
240	3.14	25000	21	1000

Table 1: Active surface area and Raman intensity of the 1026 cm^{-1} peak for edge and interior modified cavity arrays of various cavity diameters. The wavelength of excitation was 785 nm.

Edge			Interior	
Cavity diameter (nm)	Area (μm^2)	Raman Intensity	Area (μm^2)	Raman Intensity
820	3	1800	26	4000
600	2.34	3500	25	3000
430	2.1	8300	20	2000
240	3.14	12000	21	3000

Table 2: Active surface area and Raman intensity of the 1026 cm^{-1} peak for edge and interior modified cavity arrays of various cavity diameters. The wavelength of excitation was 633 nm.

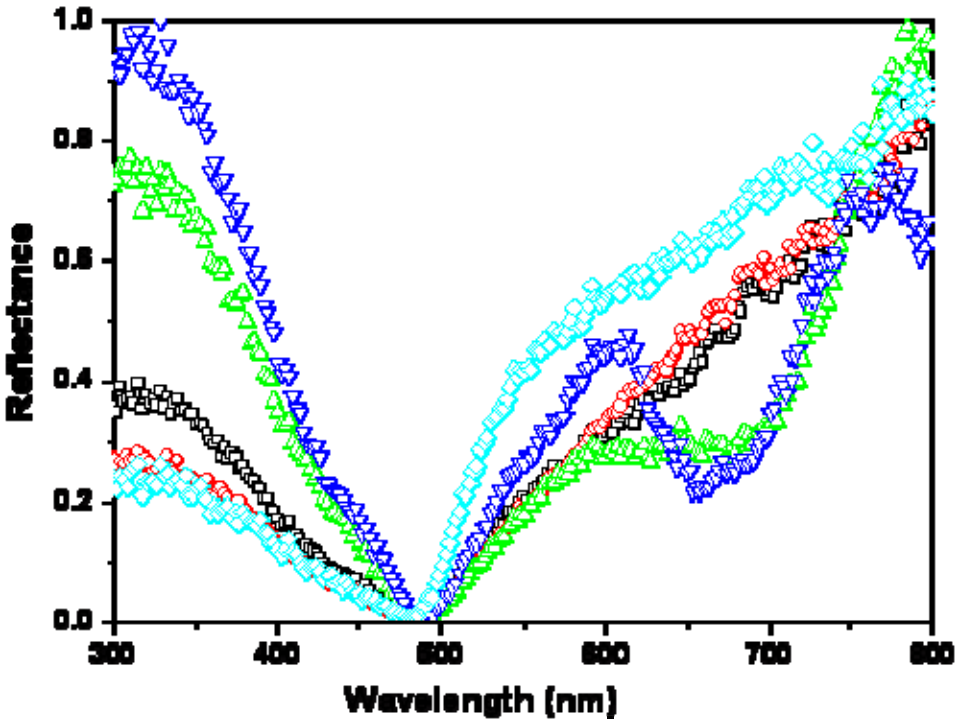

Figure S4. Reflectance spectra of (◊) smooth gold (□) 240 nm, (○) 430 nm, (Δ) 600 nm and (▽) 820 nm diameter arrays. The film thickness is approximately 0.8±0.04 (t_N= t/d = 0.8). Reflectance spectra were collected using a tungsten light source and an Ocean Optics Inc S2000 fibre optic detector. All spectra were normalised with reference to the reflection of a silver mirror.

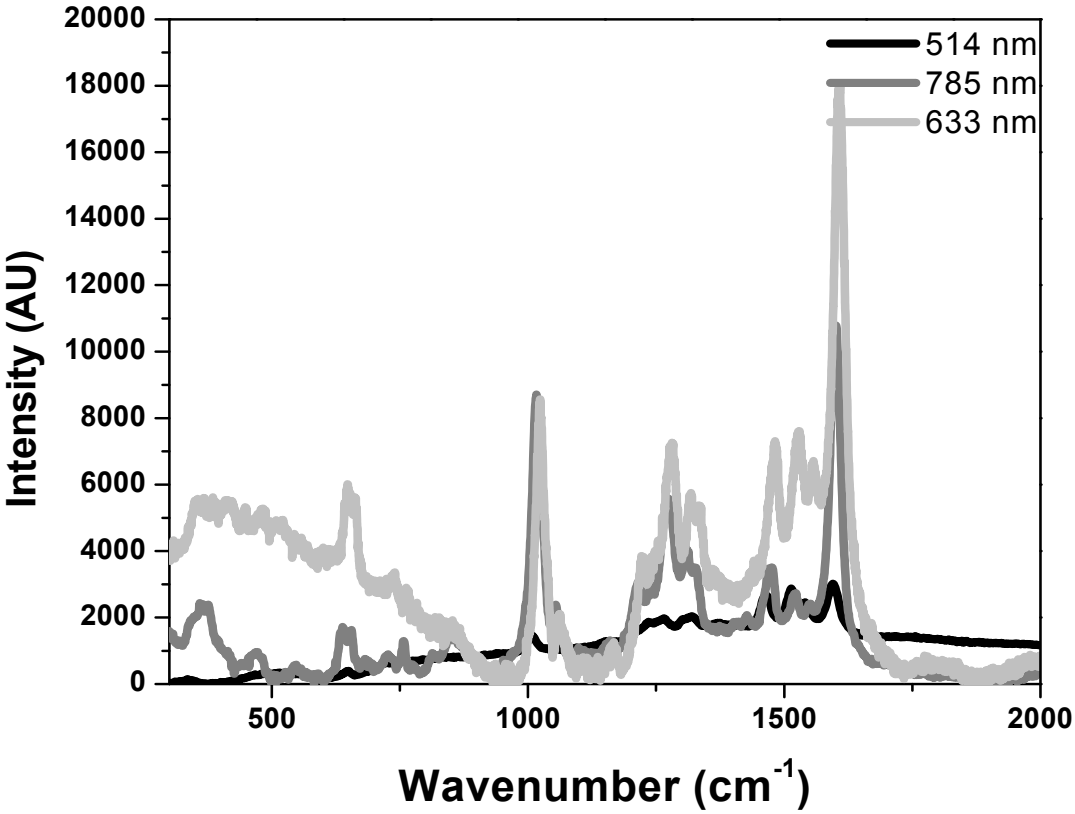

Figure S5: Raman spectra of monolayers of $[Ru(bpy)_2(Qbpy)]^{2+}$ dye adsorbed at the exterior edges of 430 nm diameter nanocavity array at the following excitation wavelengths: (a) 785 (b) 633 (c) 514 nm.

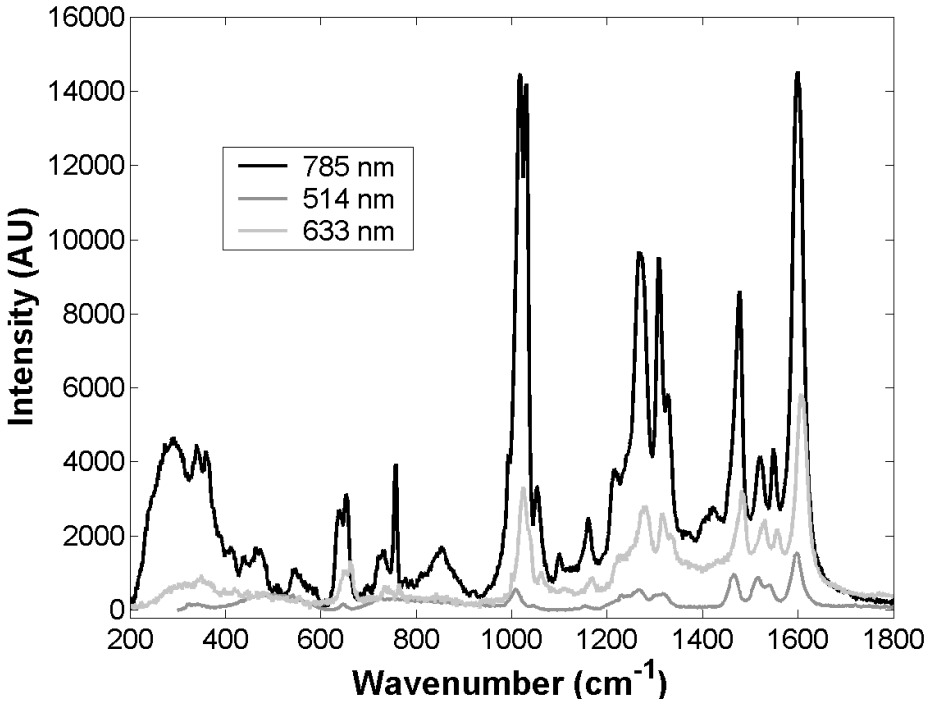

Figure S6: Raman spectra of monolayers of $[Ru(bpy)_2(Qbpy)]^{2+}$ dye adsorbed at the exterior edges of 600 nm diameter nanocavity array at the following excitation wavelengths: (a) 785 (b) 633 (c) 514 nm.

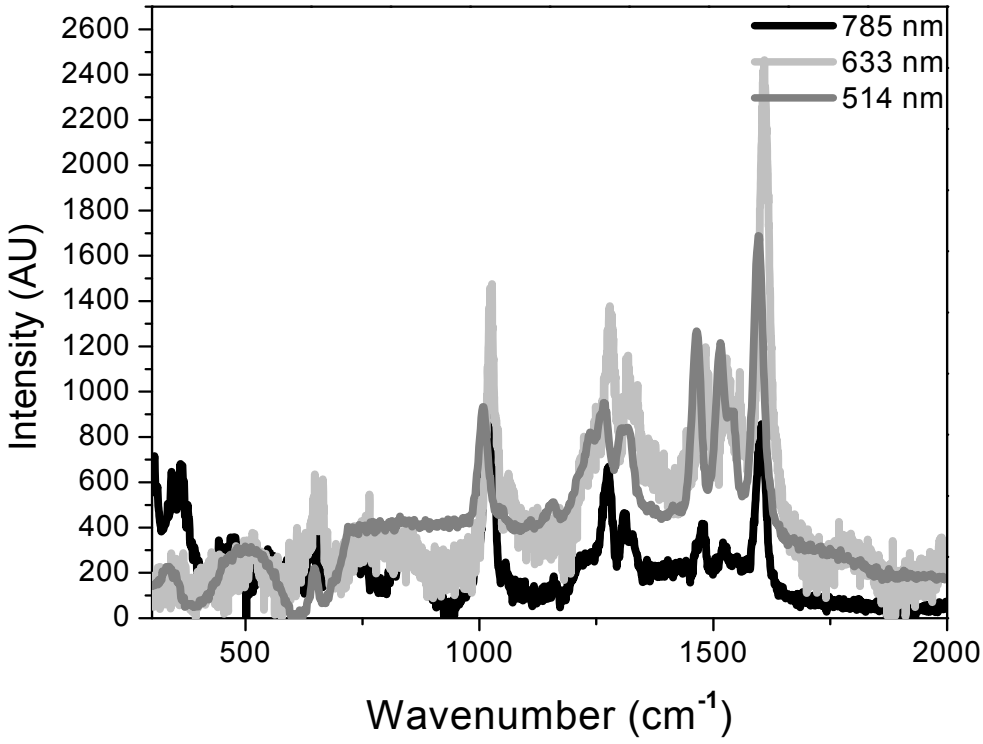

Figure S7: Raman spectra of monolayers of $[Ru(bpy)_2(Qbpy)]^{2+}$ dye adsorbed at the exterior edges of 820 nm diameter nanocavity array at the following excitation wavelengths: black, 785 light grey, 633 dark grey 514 nm.

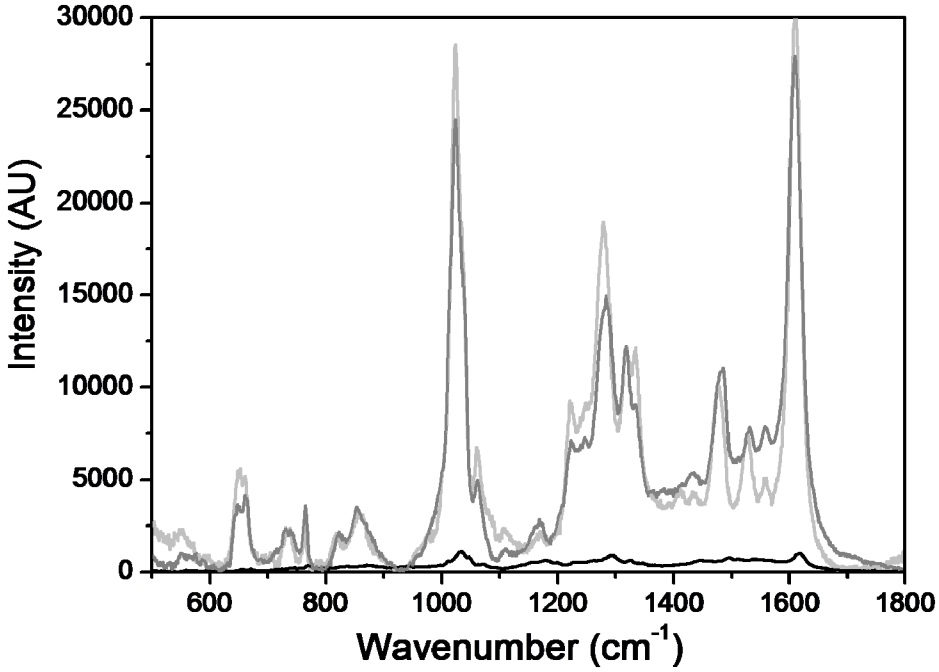

Figure S8: Raman spectra of monolayers of $[Ru(bpy)_2(Qbpy)]^{2+}$ dye adsorbed at the exterior edges of 240 nm diameter nanocavity array (dark grey), the interior walls of 240 nm diameter nanocavity array (black) and the 240 nm diameter nanocavity array which has been fully coated in $[Ru(bpy)_2(Qbpy)]^{2+}$(light grey). Excitation wavelength was 785 nm. These spectra have not been normalised for molecular coverage in order to allow permit comparison of signal intensity.

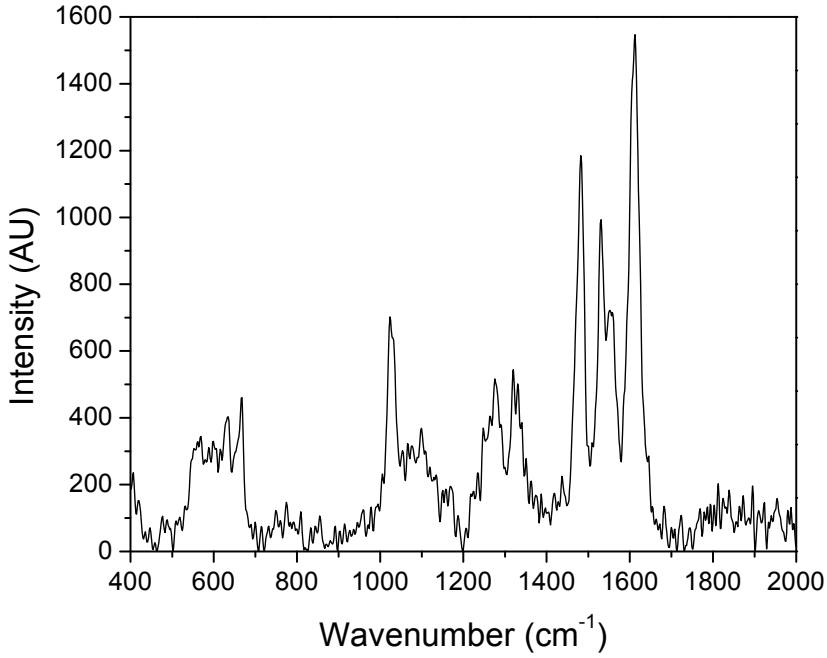

Figure S9 shows the resonance Raman spectra of $[Ru(bpy)_2(Qbpy)]^{2+}$ at 514 nm excitation from a thin film of $[Ru(bpy)_2(Qbpy)]^{2+}$ dye on a glass slide.

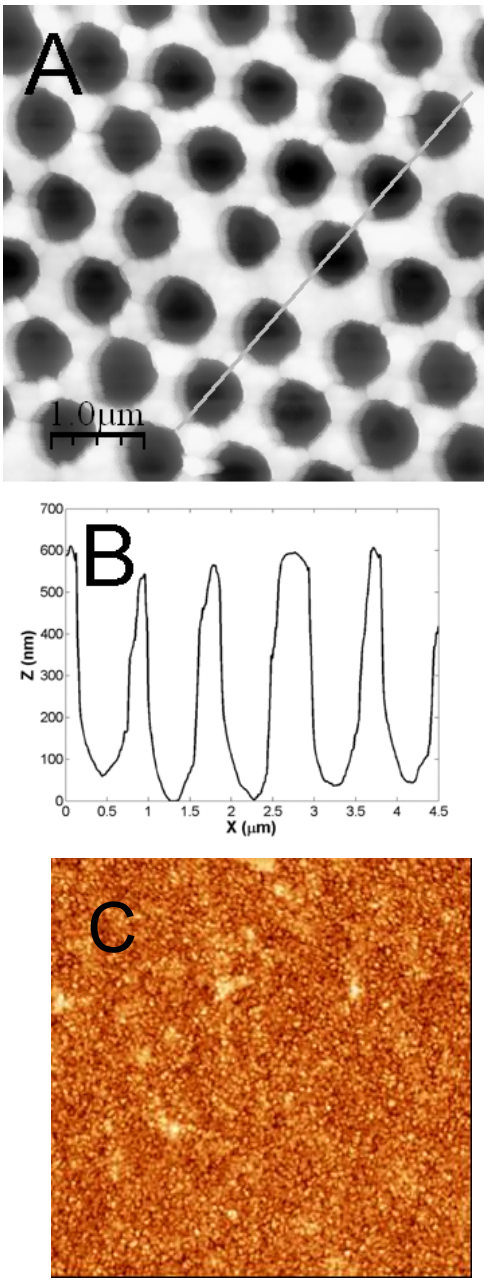

Figure S10: AFM image of nanocavity arrays formed by electrodeposition through a polystyrene sphere template (A) and height profile corresponding to the grey line across the array (B), AFM image of smooth gold surface. The image dimensions are 5 μm by 5 μm.