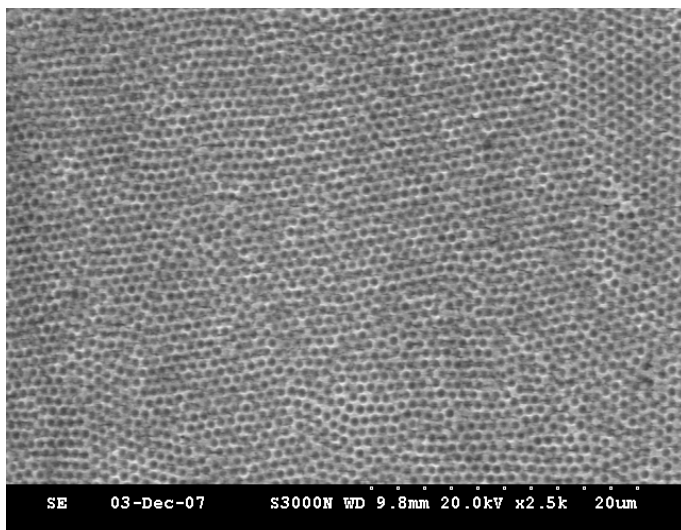
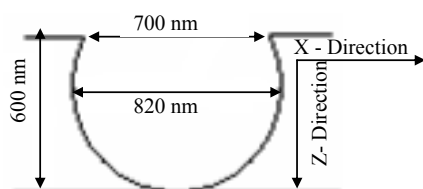


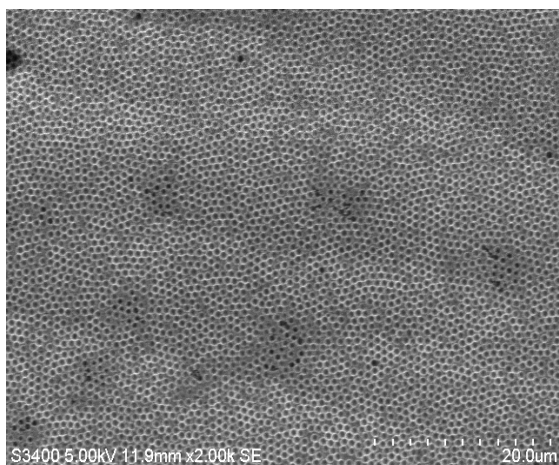
**S1.** (a) Extended SEM of gold nanocavity array on FDTO prepared by electrodeposition through templated 820nm polystyrene spheres.



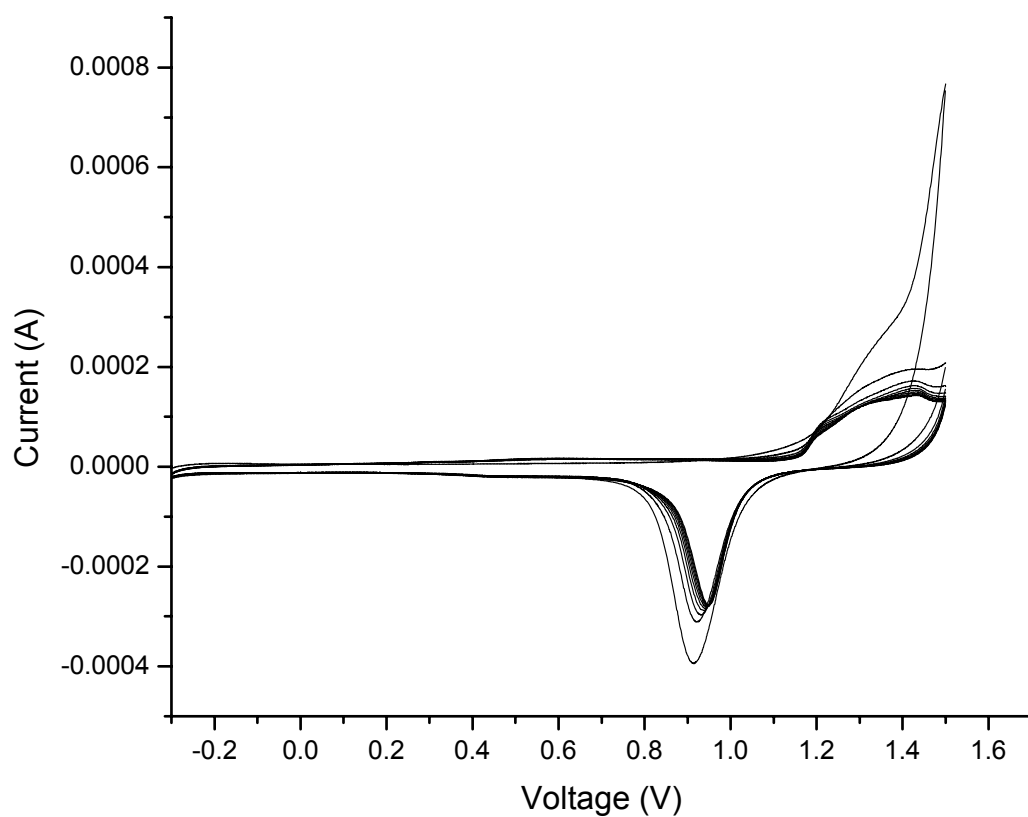
**(b)** Schematic demonstrating the dimensions of the cavity and scanning direction for imaging



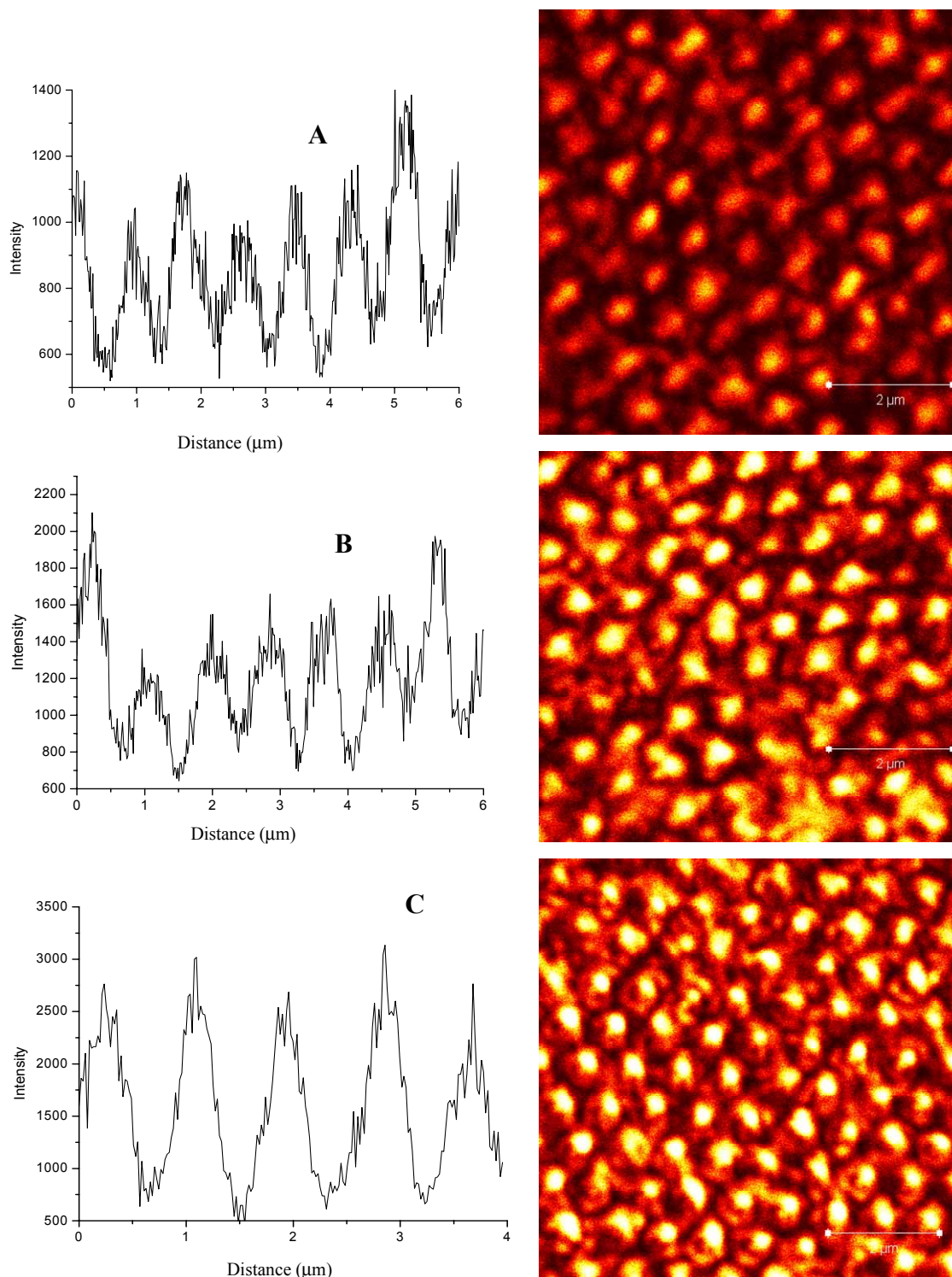
**S2** SEM image of cobalt nanocavities on FDTO prepared by electrodeposition through templated 820nm polystyrene spheres.



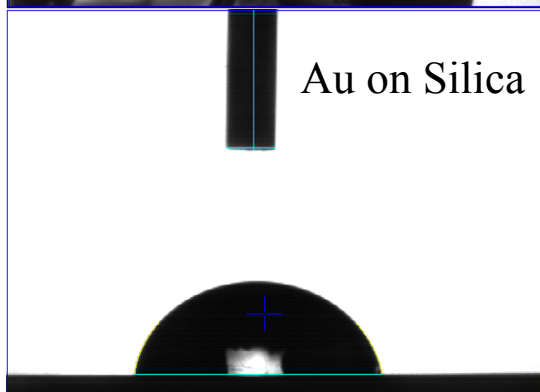
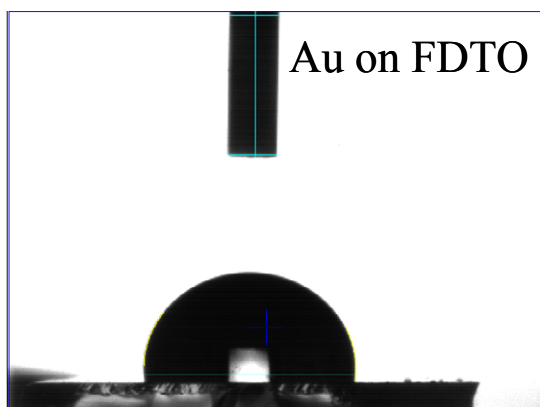
**S3.** Cyclic Voltammetry of the nanocavity array on FDTO in aqueous 0.5M H<sub>2</sub>SO<sub>4</sub>. Au cavity was used as working electrode Ag/AgCl (Sat. KCl) as reference electrode and platinum mesh as counter electrode.



**S4.** Confocal scanning emission images (left) and intensity vs distance in x-direction (right) of gold nanocavities filled with methanol/water solution of  $[\text{Ru}(\text{bpy})_2(\text{Qbpy})]^{2+}$ . Laser excitation intensity and detector gain are identical through each measurement. (A) After 5 min of sonication of gold nanocavities with the Ru dye some of the gold cavities are partially filled with dye. (B) After 15 min of sonication more cavities are filled to a higher extend as can be seen from an increased fluorescence intensity. (C) After 30min of sonication almost all of the cavities are completely filled with the dye. Sonication longer than 30 minutes did not increase the luminescence intensity further. All imaging conditions (e.g. Laser power etc.) were identical throughout.



**S5.** Contact angle measurements for water on (a) bare gold electrodeposited on FDTO and (b) gold nanovoid array on FDTO, (c) gold on silica.



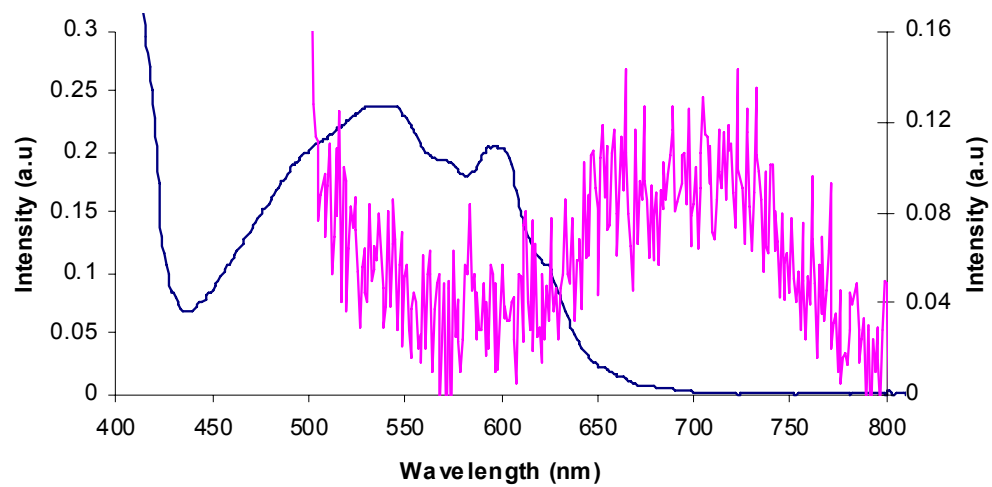
FDTO	75.58
Au cavity	93.98
Au on FDTO	94.09
Au on silica	81.81

**S6.** Contact angle measurements for methanol on (a) gold nanovoid array on FDTO, (b) bare gold electrodeposited on FDTO.

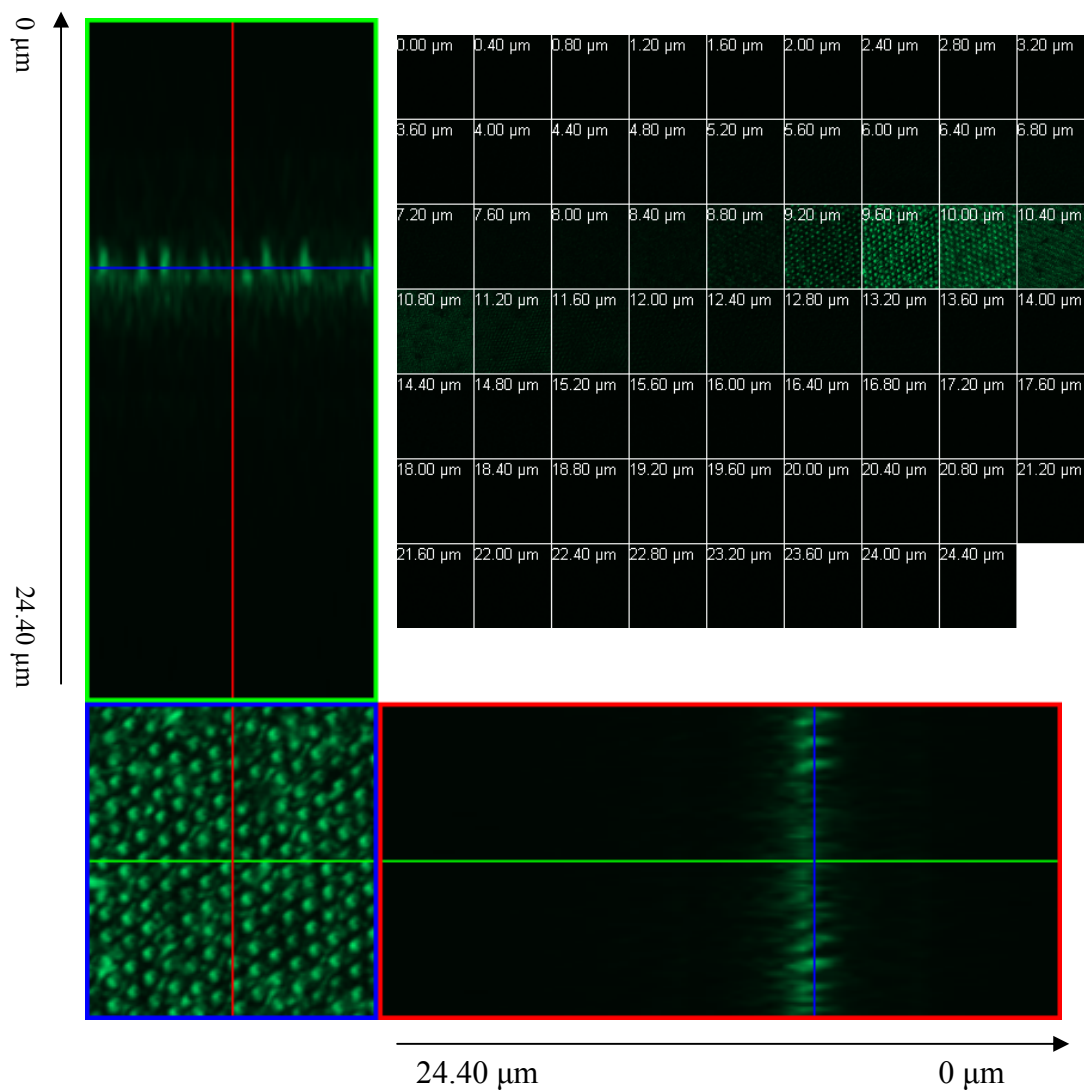


Au cavity on FDTO	7.47
Au FDTO	29.36

**S7.** Absorption (blue) and emission (pink) spectrum of fullerene in toluene.

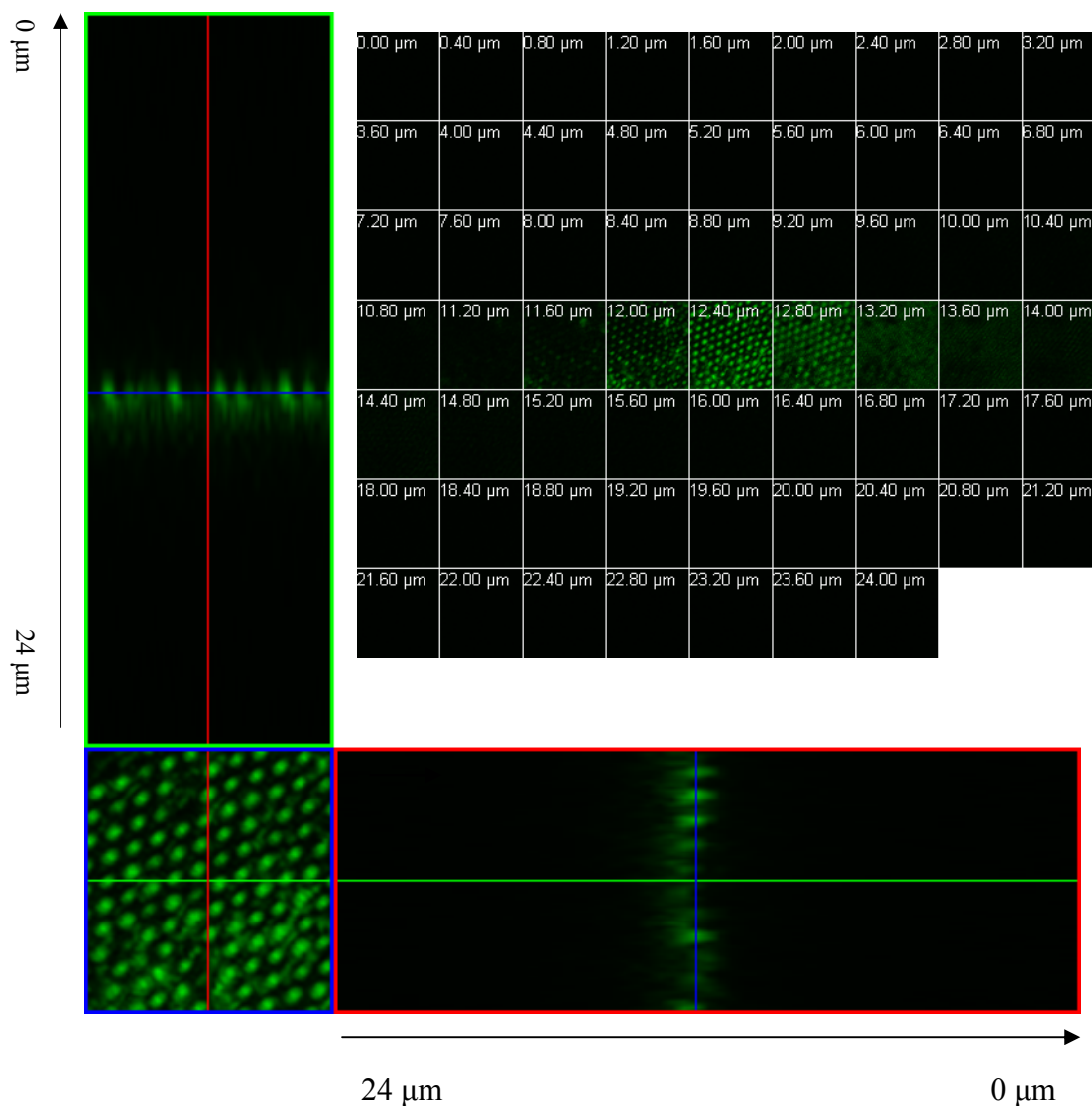


**S8.** Z-stack taken through y (red line) and x-directions (green line) direction across a gold nanocavity array filled with 1 mMol methanolic/water solution of  $[\text{Ru}(\text{bpy})_2(\text{Qbpy})]^{2+}$  dye at,  $\lambda_{\text{ex}}$ , 514 nm. Inset of figure shows the slices from Z-stack measurements. The measurements start from cover glass (0  $\mu\text{m}$ ) and pass through the dye solution (10-20  $\mu\text{m}$ ), then through the dye filled gold cavity. (See associated Video: S8)



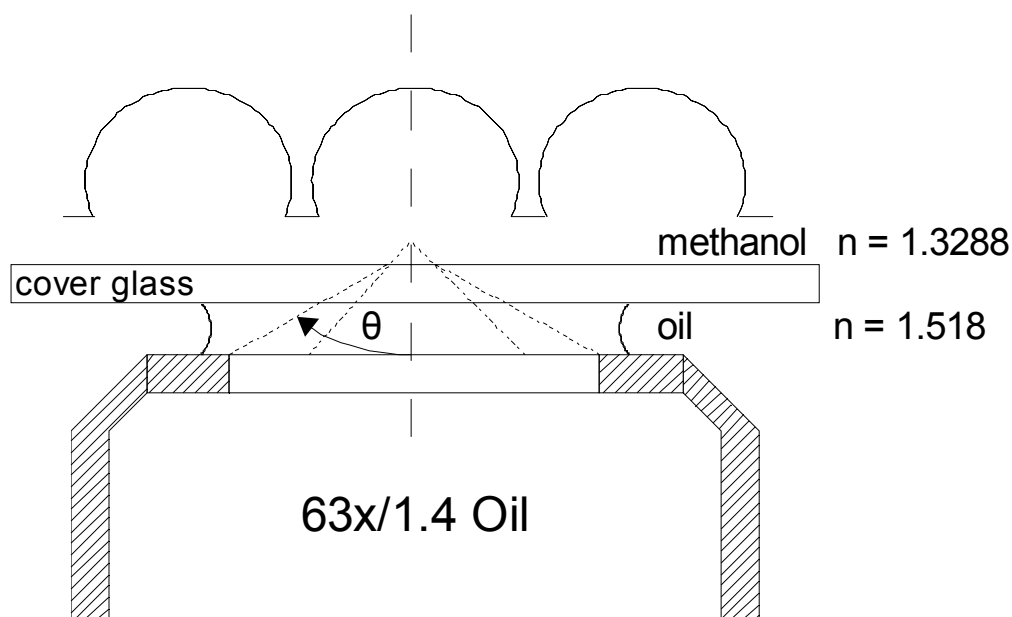


**S9.** Z-stack taken through y (red line) and x-directions (green line) direction across a gold nanocavity array filled with 1 mMol fullerene in toluene,  $\lambda_{ex}$  514 nm. Inset of figure shows the slices from Z-stack measurements. The measurements start from cover glass (0  $\mu\text{m}$ ) and pass through the dye solution (10 - 20  $\mu\text{m}$ ), then through the dye filled gold cavity (20-30  $\mu\text{m}$ ). . (See associated Video: S9)



### S10 Angle of illumination

Given the numerical aperture  $NA = 1.4$  of our 63x objective lens and the refractive index  $n = 1.518$  of the used immersion oil we calculate ( $NA = n \sin \theta$ ) the half-angle  $\theta$  of the light cone emerging from the objective lens as  $\theta = 67.26^\circ$ . However, due to the mismatch in refractive index at the cover slip/methanol interface this angle is only achieved in close proximity to the cover slip and decreases with increasing focusing-depth down to the limit given by the refractive index of methanol ( $n = 1.3288$ ). The minimal half-angle  $\theta$  of the light cone impinging onto the top of the cavity then is about  $61.09^\circ$ .



### **S11 Simulation of enhancement factors for [Ru(bpy)<sub>2</sub>(Qby)]<sup>2+</sup>**

The simulation is based on the reported plasmonic effect on  $k_f$  ( $k_{f,m} = G \cdot k_f$ ).

$k_f$  and  $k_{nr}$  are taken from Bierig, K.; Morgan, R. J.; Tysoe, S.; Gafney, H. D.; Streckas, T. C.; Baker, A. D. *Inorg. Chem.* **1991**, *30*, 3898.

```
%(Bierig 1991)
%in CH3CN
t0c = 1418; %lifetime [ns]
Q0c = 0.078; %quantum yield

% in water
t0w = 300; %lifetime [ns] (from our own measurements)
Q0w = 0.053; %quantum yield

kf = 5.5e4; %radiative rate [sec-1]
knr = 71e4; %non-radiative rate [sec-1] in CH3CN
knrw = 3.278e6; %non-radiative rate [sec-1] in aerated water (calculated from
t0w = 300 ns and kf)
knr = knrw; %use water

% G = kfm/kf, kfm = metal enhanced rate
% G is the "plasmonic enhancement factor" since it does
% not include any contributions from increased absorption or spatially
% directed emission
G = [0:1:1000]; %simulated range of G

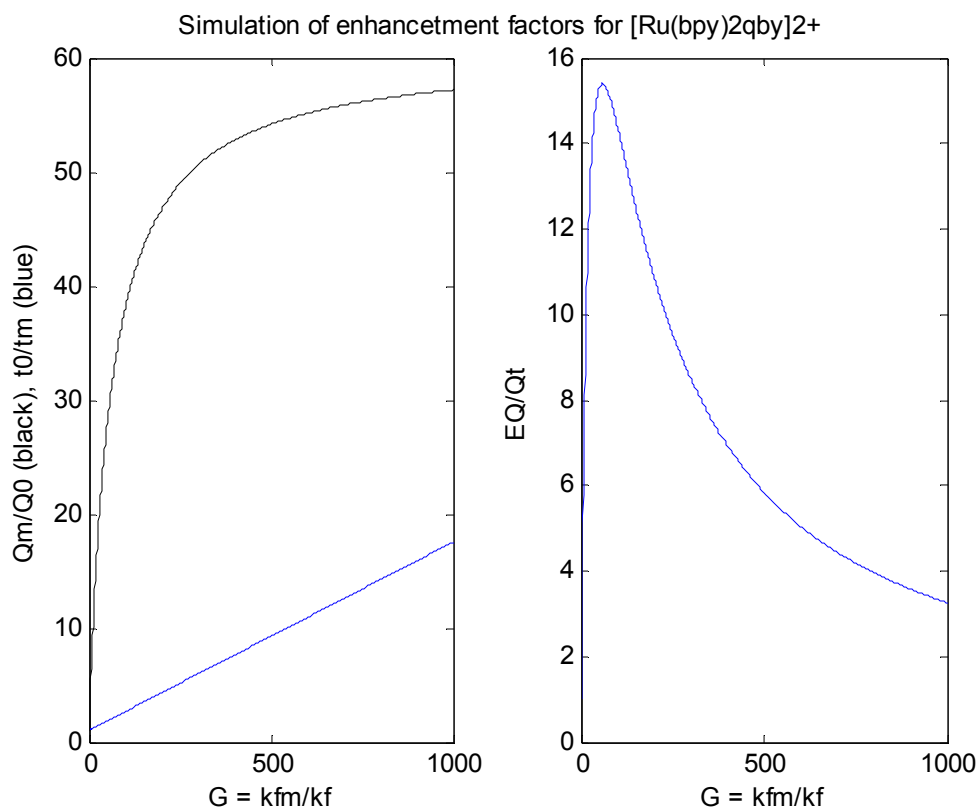
%quantum yields
Q0 = kf./(kf+knr);
Qm = (kf+G*kf)./(kf+G*kf+knr);

%lifetimes [ns]
t0 = 1./(kf+knr);
tm = 1./(kf+G*kf+knr);

%enhancement factor from Q
EQ = Qm./Q0; % note that equation describes a saturation curve

%enhancement factor from t
Et = t0./tm; % note that this equation is linear

%some plotting
subplot(1,2,1)
plot(G,EQ,'k',G,Et,'b')
subplot(1,2,2)
plot(G,EQ./Et)
```



Left: ratios  $\Phi_m/\Phi$  and  $\tau/\tau_m$  as a function of  $G$ . Right: ratio of  $E_Q = \Phi_m/\Phi$  and  $E_t = \tau/\tau_m$ .  
If we take and  $\Phi_m/\Phi = 15$  we get  $G = 19$  and  $\tau/\tau_m$  of 1.3, i.e. we would expect a decrease in lifetime  $\tau_m$  to about 230 ns if the ratio  $\Phi_m/\Phi = 15$  is due to plasmonic enhancement.

### **S12 Calculation of surface enhancement of Raman signal**

Number of molecules inside the cavity at the laser spot =  $1 \times 10^5$  (from footprint of molecule as monolayer on gold – reference: R.J, Forster, T.E. Keyes, J. Phys. Chem. B 1998, 102, 10004)

Number of molecule on FDTO (thin film) =  $5 \times 10^{11}$  (from cyclic voltammetry)

SERS intensity from gold cavity = 13750

SERS intensity from thin film of dye on FDTO = 1334

$$\text{SEF} = (I_{\text{Au}}/N_{\text{Au}})/(I_{\text{fdto}}/N_{\text{fdto}}) = (I_{\text{Au}}/I_{\text{fdto}})*(N_{\text{fdto}}/N_{\text{Au}}) = 10.3 \times 5 \times 10^6 = 5 \times 10^7$$