

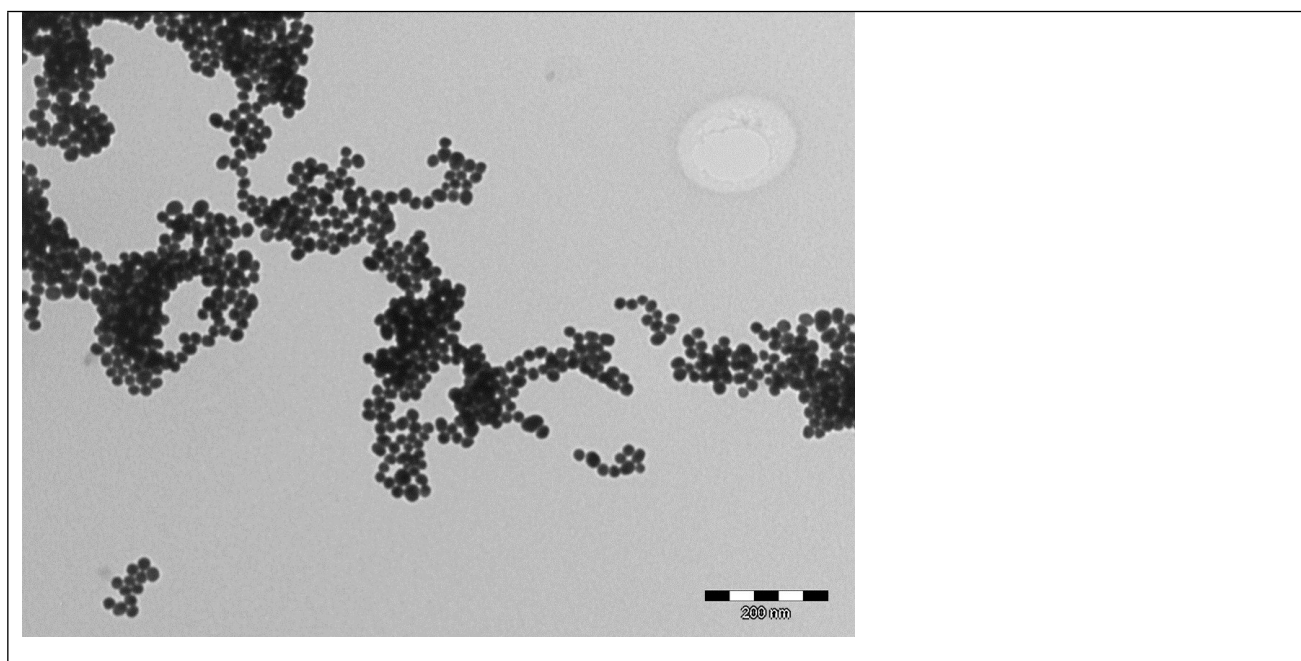
## A gold nanoparticles chemically modified gold electrode for the determination of surfactants

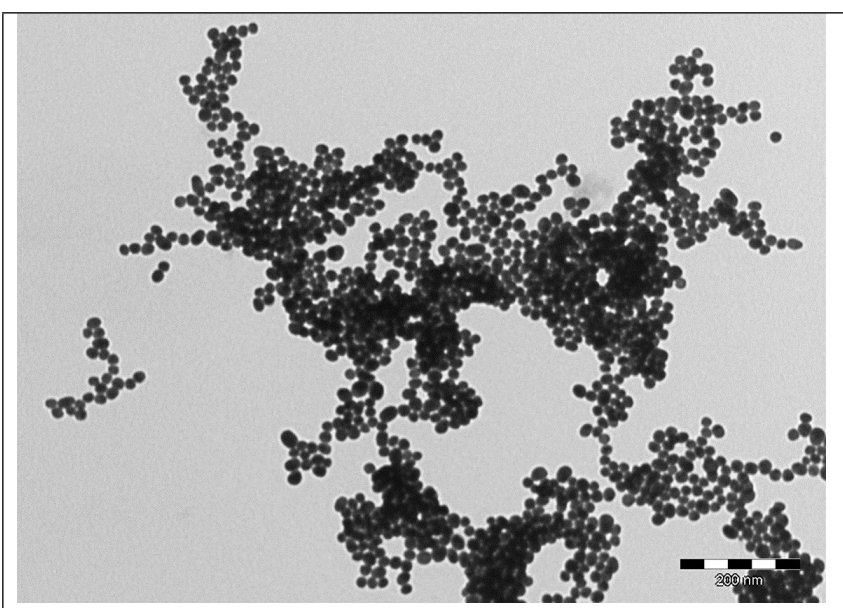
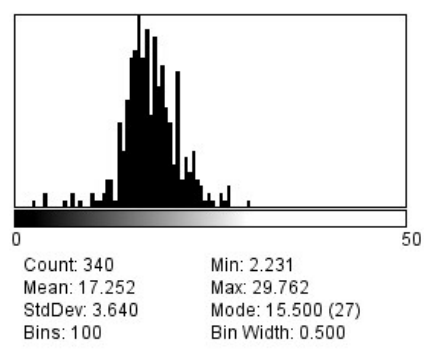
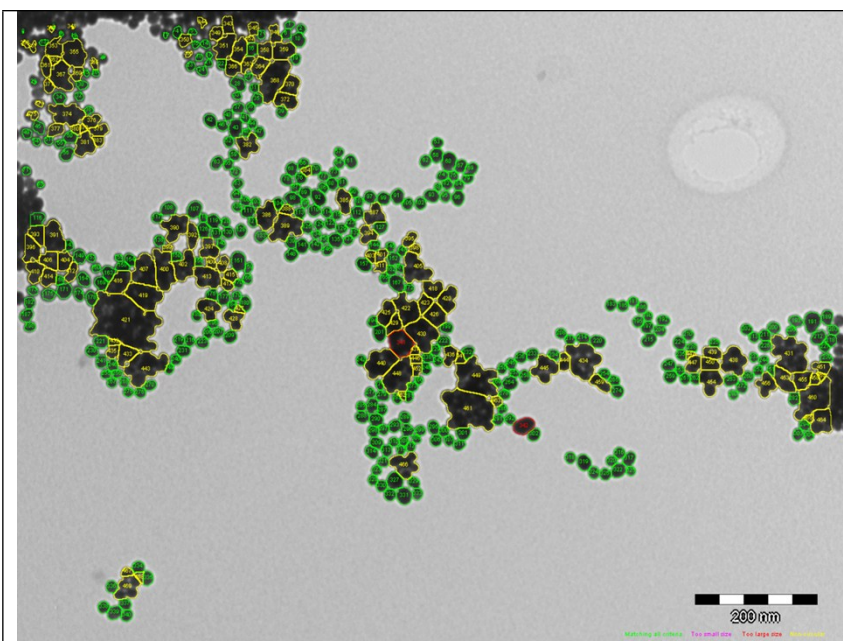
Daniele Merli, Chiara Ferrari, Elisa Cabrini, Giacomo Dacarro, Piersandro Pallavicini, Antonella Profumo

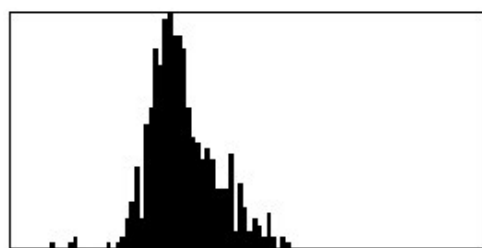
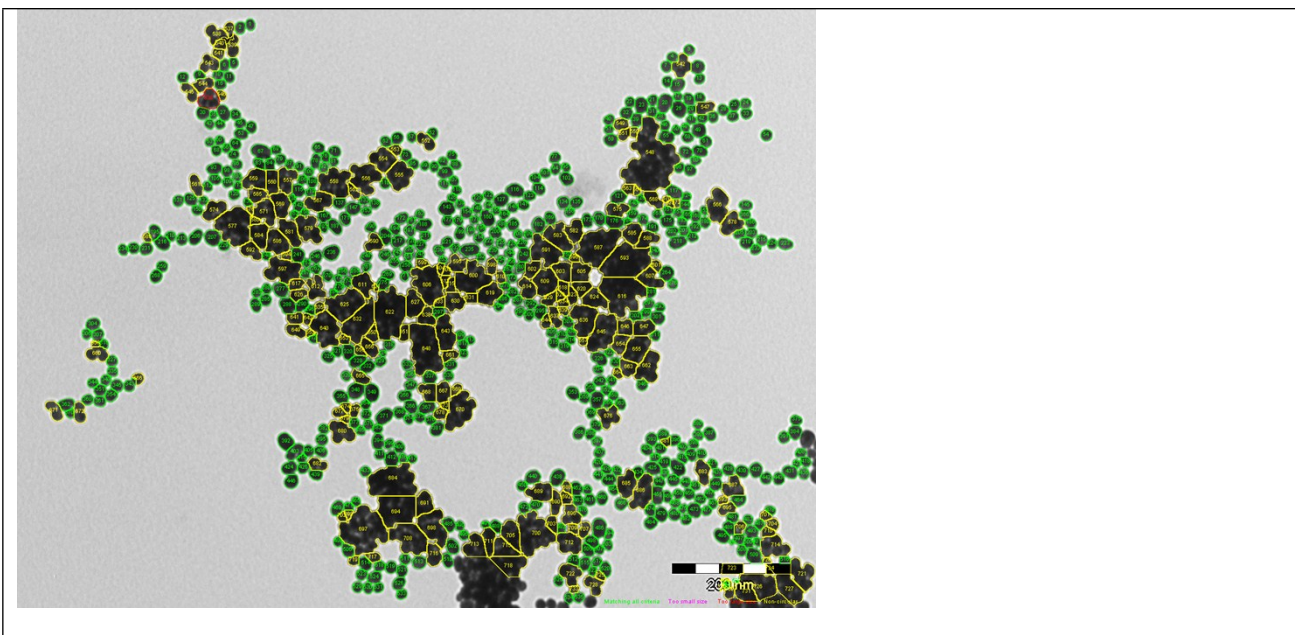
University of Pavia, Department of Chemistry, Via Taramelli 12, 27100 Pavia Italy.

### SUPPLEMENTARY MATERIAL

#### SI1 – TEM images and dimension determination

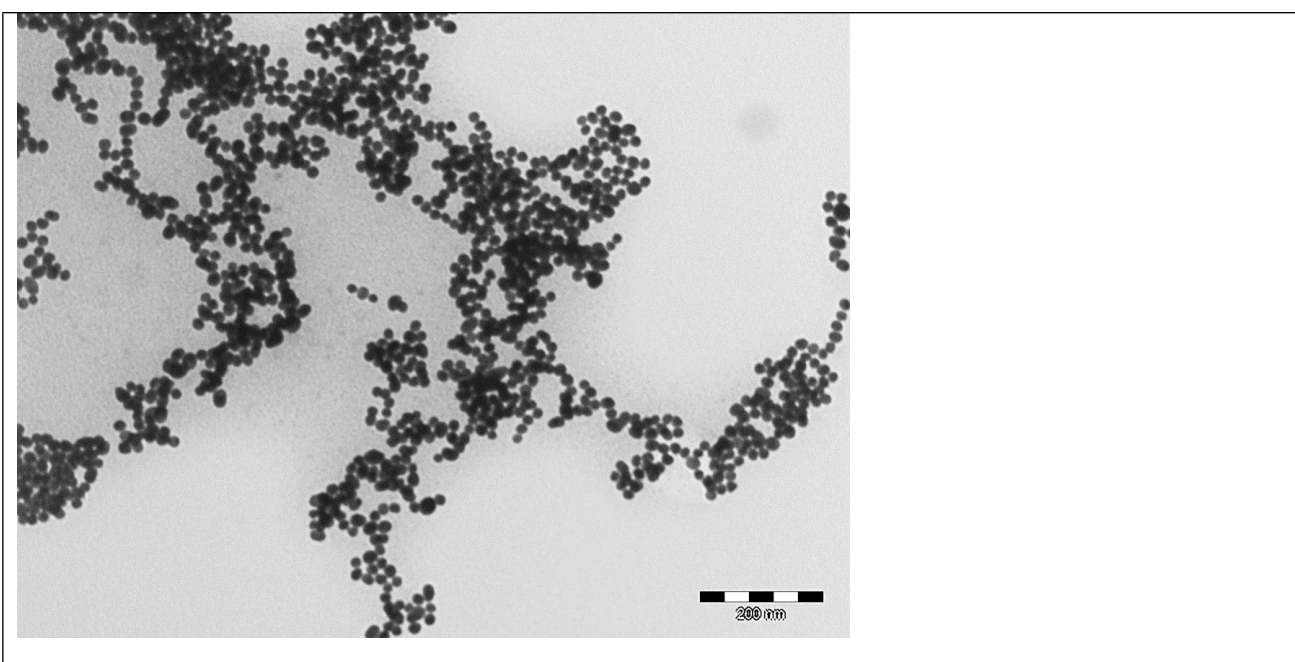


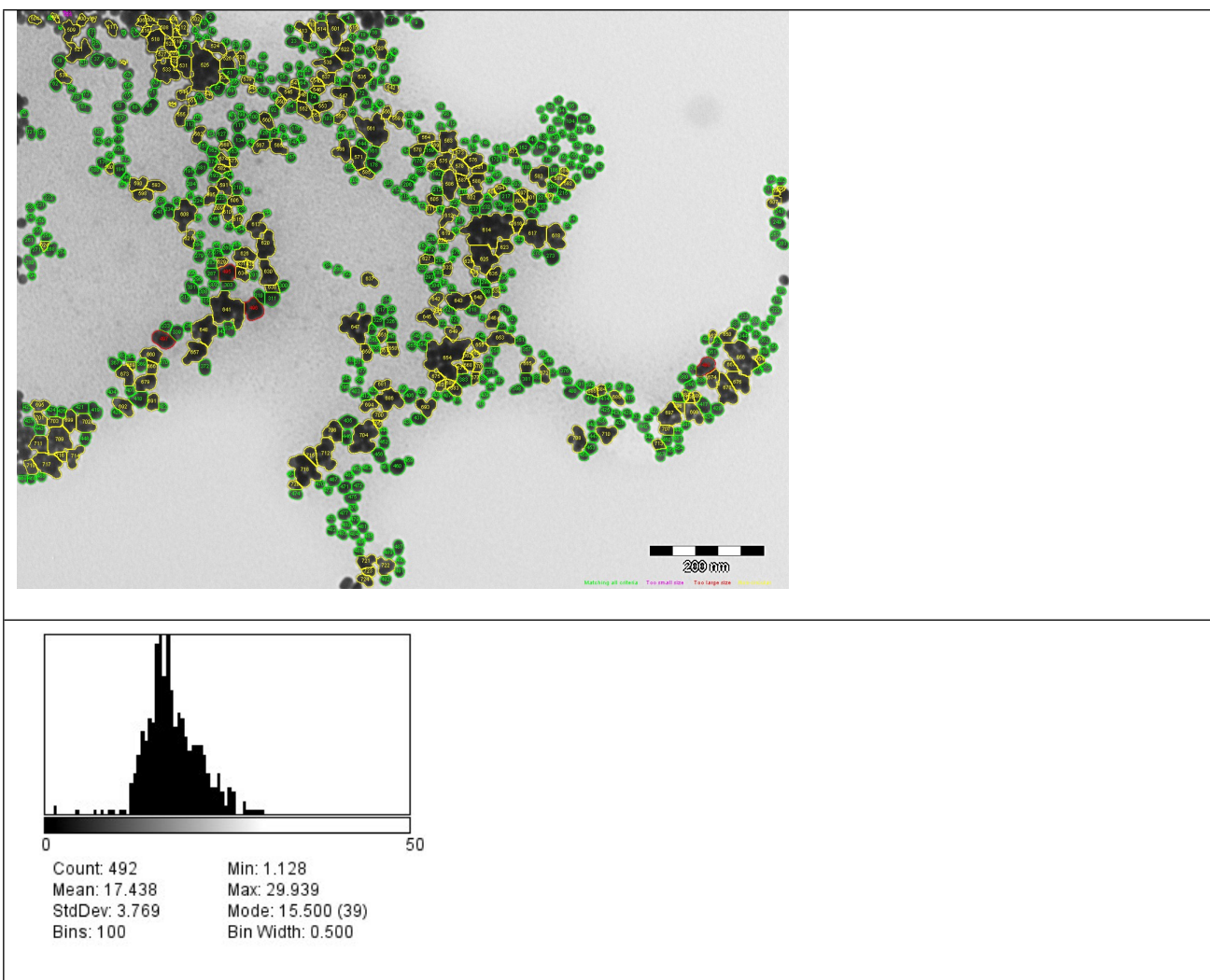




0 50

Count: 535      Min: 4.022  
Mean: 18.128      Max: 29.192  
StdDev: 3.617      Mode: 16.500 (40)  
Bins: 100      Bin Width: 0.500

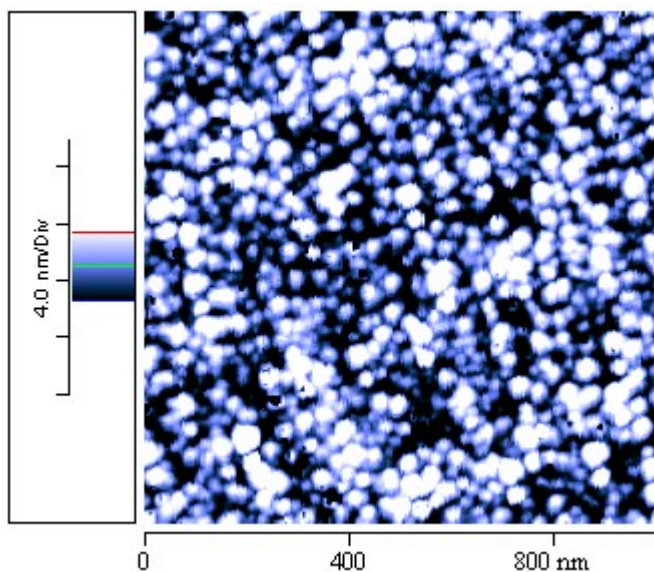




**Supplementary Figure S1 – TEM imaging and AuNP dimensional counting.** Each panel presents the original TEM image, an imaged with the AuNP selected for the count (green) and discarded (yellow), the histogram with the dimensional analysis

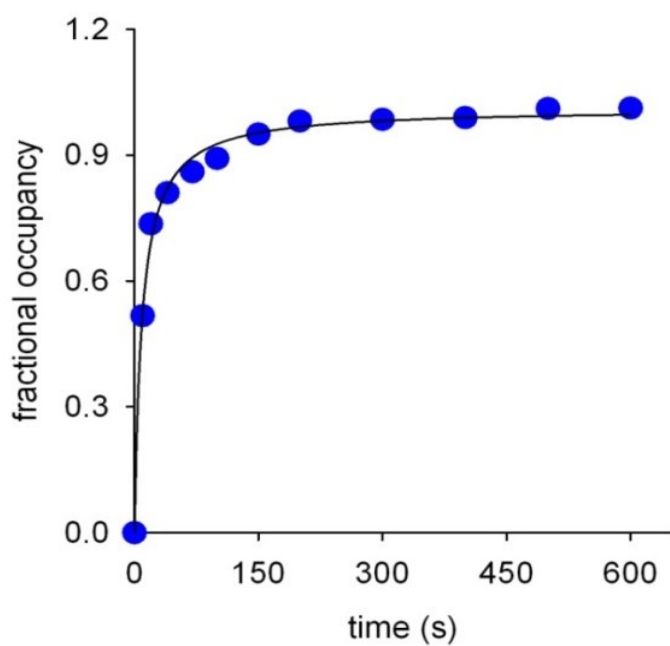


## SI2 – AFM imaging



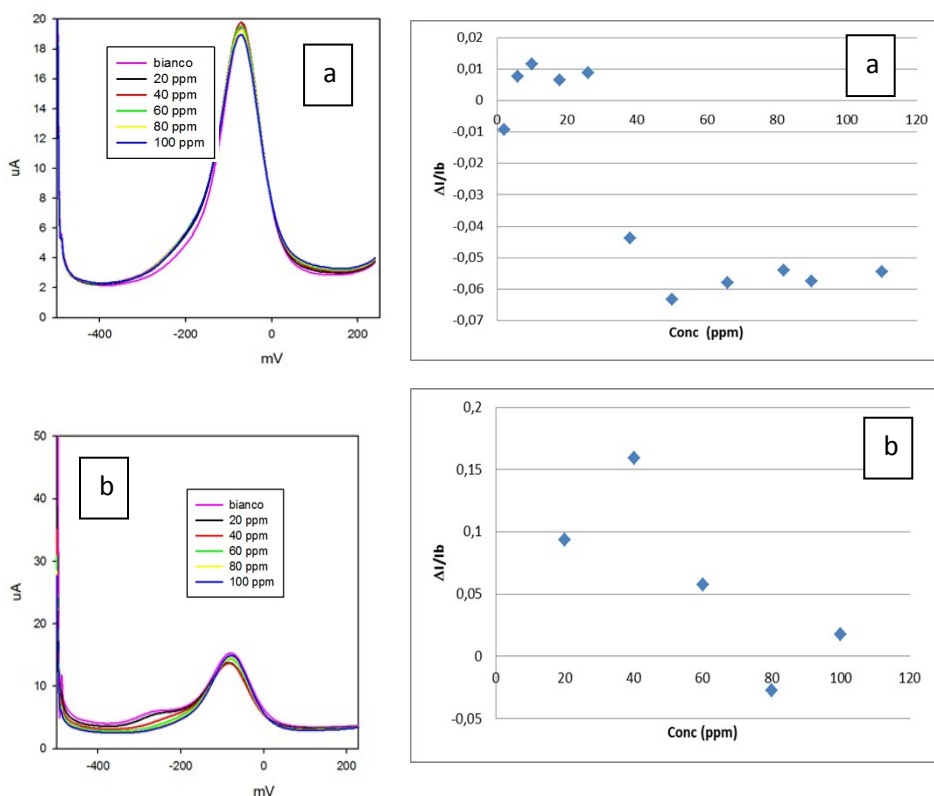
**Figure SI2 – AFM imaging.** AFM topography image (tapping mode) on a  $1\mu\text{m} \times 1\mu\text{m}$  area. On this image, 607 nanoparticles were counted in the whole  $1\mu\text{m} \times 1\mu\text{m}$  area. The image was taken on a surface simulating the NpCME, as the latter cannot be directly imaged by AFM due to geometric instrumental constraints. A glass slide was coated with a 300 nm gold layer (details in the experimental), and the surface underwent the same treatment with 1,4-benzenedimethanethiol and AuNP as the electrode. The AFM image confirms the coating with AuNP. For objects with size smaller than the curvature radius of the tip, convolution must be taken into account. Measured size of the particles in AFM imaging, though, is compatible with the actual size of the objects ( $d = 17.6\text{ nm}$ , measured with TEM imaging) and nominal curvature radius of the tip (i.e. 10 nm). Using a relation reported in literature [C. Bustamante, J. Vesenska, C.L. Tang, W. Rees, M. Guthold, R. Keller, *Biochemistry*, 1992, **31**, 22-26] an expected size of 24 nm is obtained, in good agreement with a measured apparent size of 22(3) nm. Counting of objects in the  $1000 \times 1000\text{ nm}$  area also allowed to calculate a number of  $6.07 \times 10^{10}\text{ AuNP}/\text{cm}^2$ , reassuringly similar to what we calculated for NpCME.

**S13 – Adsorption kinetics of 1,4-benzenedimethanethiolbenzendimethanthiol on the bare gold electrode**



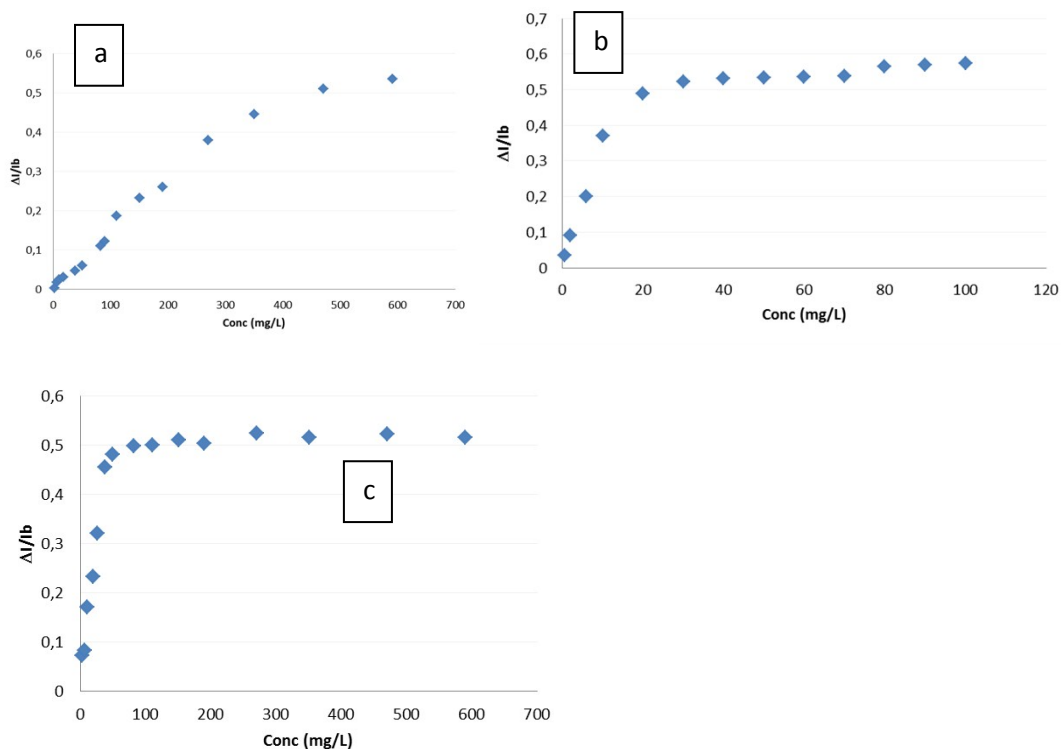
**Supplementary Figure S13.** Adsorption kinetic of 1,4-benzenedimethanethiolbenzendimethanthiol on bare gold electrode (fractional occupancy vs time)

**Supplementary Figure S14 – response of the  $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$  probe at the plain Au electrode on addition of surfactants**



**Figure S4.** Response (DPV and relative current plot) of 5 mM  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  towards increasing concentration of (a) BC and (b) SDS at the plain Au electrode. Plots of  $\Delta I/I_b$  ( $\Delta I$  = redox marker current at any surfactant addition,  $i_c$ , with respect to the signal obtained in absence of the surfactant,  $i_b$ , divided for  $i_b$ ) vs concentration of the added surfactant are reported. Electrochemical conditions are described in the text. It can be seen that a scattered response is observed, with  $\Delta I/I_b$  oscillations from zero that are 1 order of magnitude lower than in the case of the Np-modified electrode. Reference electrode: Ag/AgCl/3 M NaCl. Other electrochemical conditions are reported in the text.

## SI 5 - Response of 5 mM $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ towards different surfactants at NpCME



**Figure S5.** Response of 5 mM  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  towards (a) sodium sulphosuccinate, (b) CTAB and (c) Tween 20 at the NpCME. Plots of  $\Delta I/I_b$  ( $\Delta I$  = redox marker current at any surfactant addition,  $i_c$ , with respect to the signal obtained in absence of the surfactant,  $i_b$ , divided for  $i_b$ ) vs concentration of the added surfactant are reported. Electrochemical conditions are described in the text.