Supporting information

Experimental section

Silver nitrate (99.9999% purity), hydroxylamine hydrochloride (99.9999% purity), adenine, adenosine and 5'-AMP were purchased from Sigma-Aldrich. Magnesium sulphate was from BDH chemicals and sodium hydroxide was from Riedel-de-Haën. Aqueous solutions were prepared using doubly distilled, deionised (DDI) water from a Barnstead NANOpure Diamond™ system. All glassware was washed with aqua regia followed by extensive rinsing with water prior to use.

The hydroxylamine reduced silver colloids (HRSC) were prepared according the standard procedure of Leopold and Lendl[1]. The silver particles prepared with this method have average diameter 80±16nm and the concentration of silver is 113 mg/L. The citrated reduced silver colloids (CRSC) were prepared according the standard procedure of Lee and Meisel[2]. The silver particles prepared with this method have average diameter 113±21nm and the concentration of silver is 107 mg/L. The 50 nm monodisperse Au colloid was obtained from British Biocell International Ltd (Cardiff U.K.). These particles are synthesised using a variation of the Frens citrate reduction[3] and the Au concentration is 56 mg/L. The total surface area for the gold colloid is 0.34 m^2 / L, for the HRSC is 0.804m^2/L for 80 nm particles and for CRSC for 113nm particles is 0.546 m^2/L

For SERS measurements, 50µl of colloidal solution were mixed with 50µl of analyte solution and 25µl of 0.1 mol dm^{-3} $MgSO_4$ solution. pH was adjusted using dilute aqueous NaOH. For the in-situ preparation of Ag^+ or Cu^{2+} complexes 50 µl of 0.01 mol dm^{-3} of $AgNO_3$ or $CuSO_4$ was added to the colloid prior the addition of NaOH. pH was checked using a standard pH meter (Mettler Toledo).

The SERS spectra were recorded on an Avalon Instrument RamanStation R1. This instrument uses a 785 nm diode laser and an echelle spectrograph. The laser power was 100mW and spectra were typically recorded with an exposure time of 2x10s in 96 well polyethylene microtitre plates.

DFT calculations were carried out using the Gaussian 03 package in the conventional way using the B3LYP functional and 6-31g(d) basis set for calculations on uncomplexed adenine. For calculations on Ag^+-adenine compounds the 6-31g(d) basis set was used for the N,C,O and H atoms and LanL2DZ for the Ag atom.

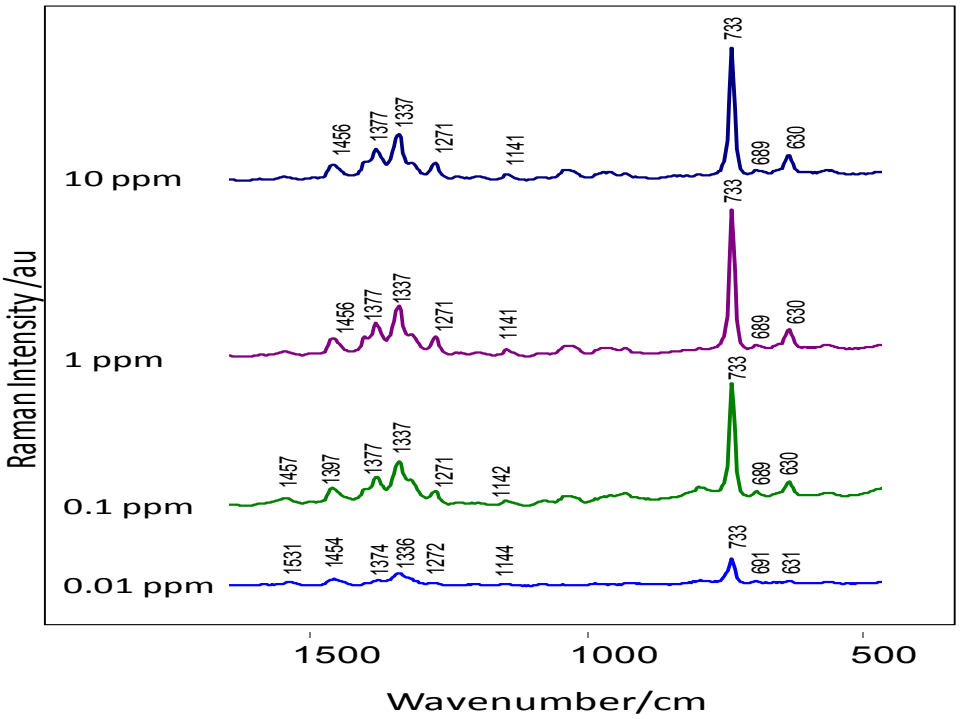

Fig. S1: 1 SERS spectra of adenine adsorbed on a CRSC at pH 11 and at the concentration values marked. The colloid was aggregated with MgSO4 (0.1 mol dm-3) and pH was adjusted with NaOH (aq).

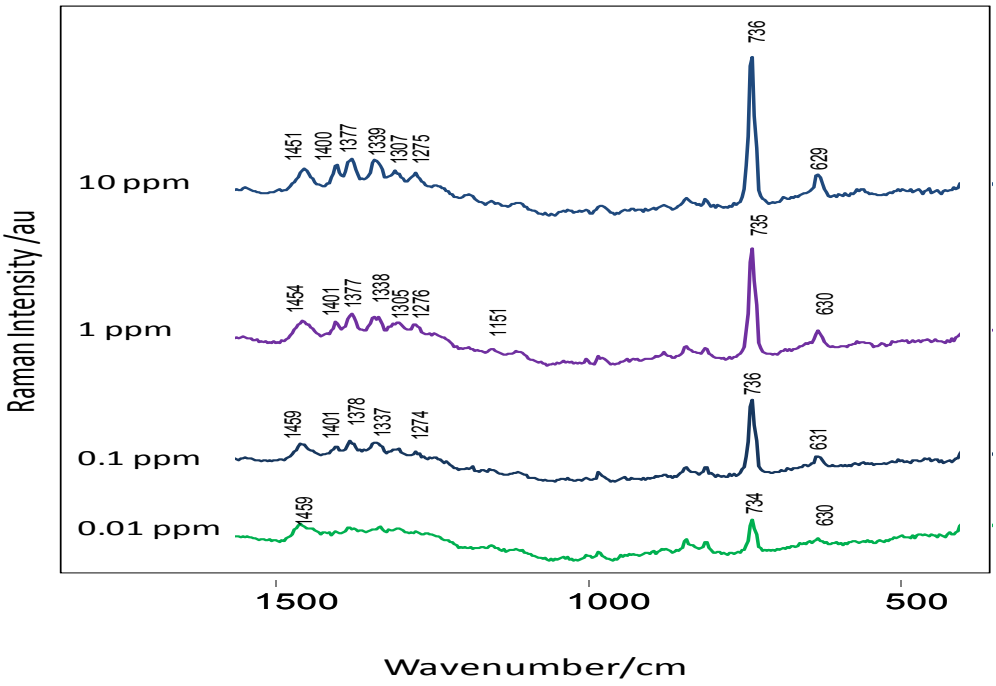

Fig. S2: 1 SERS spectra of adenine adsorbed on the Gold Colloid at pH 11 and at the concentration values marked. The colloid was aggregated with MgSO4 (0.1 mol dm-3) and pH was adjusted with NaOH (aq).

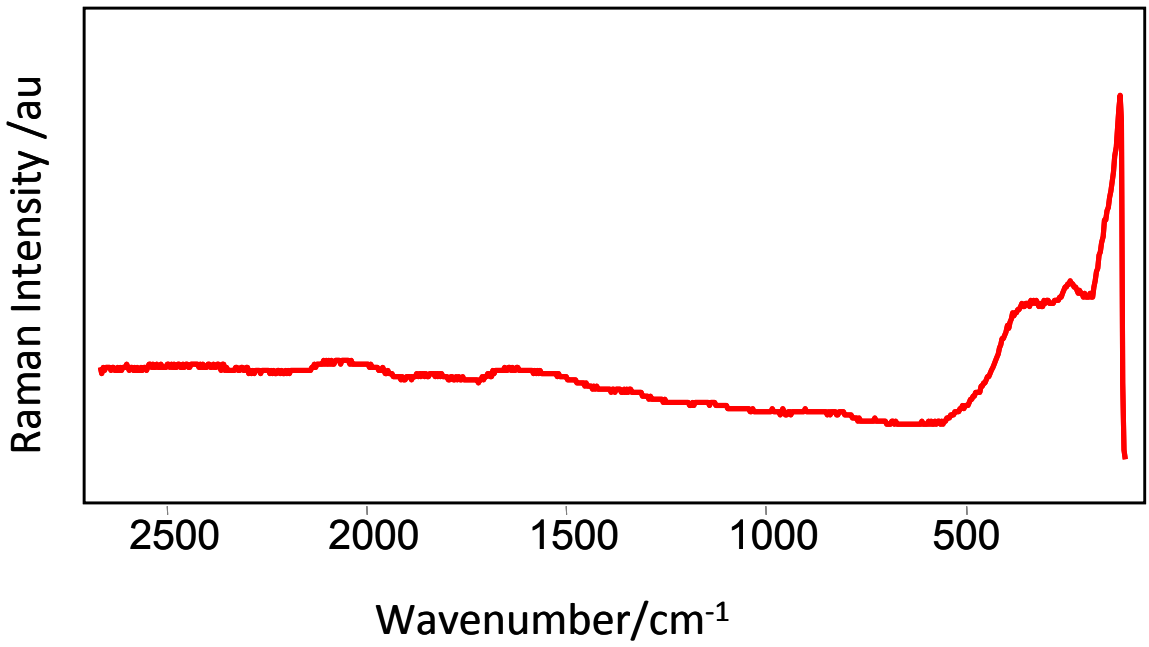

Fig. S3: Sample blank SERS spectra of HRSC aggregated with 0.1 mol dm^{-3} $MgSO_4$ at pH 11 and after addition of 0.01 mol $dm^{-3}AgNO_3$. Note that no new bands due to silver compounds are observed in the region 500- 2000 cm^{-1} .

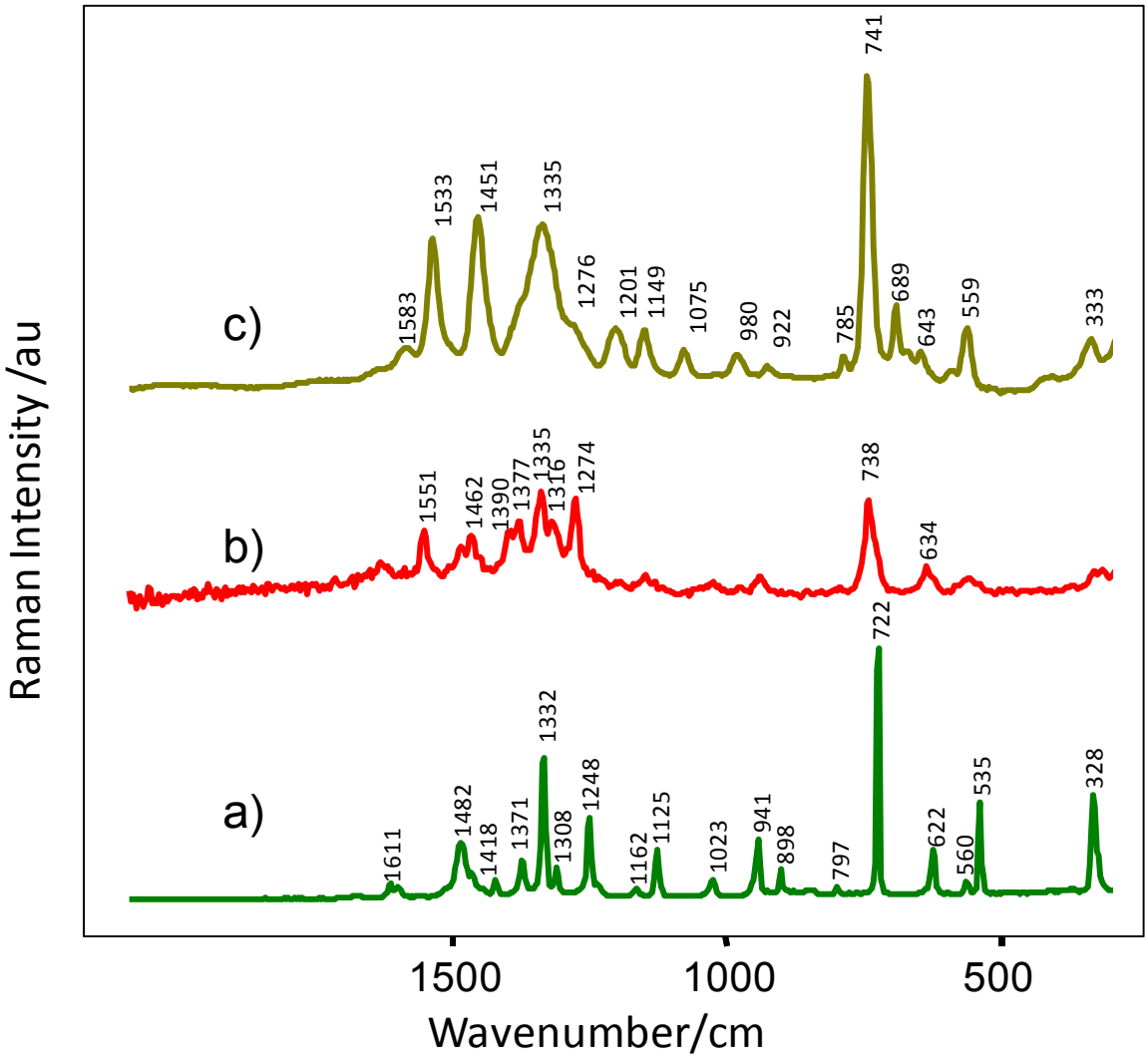

Fig. S4: Normal Raman spectra of **(a)** polycrystalline adenine (b) polycrystalline $Cu(C_5H_4N_5)_2$. Note the shift in the ring breathing mode from 722 to 738 cm^{-1} on complex formation. The crystalline complex was prepared according to Bruston *et al*[4].(c) SERS spectra on HRSC of 0.25 ppm adenine at pH 11.

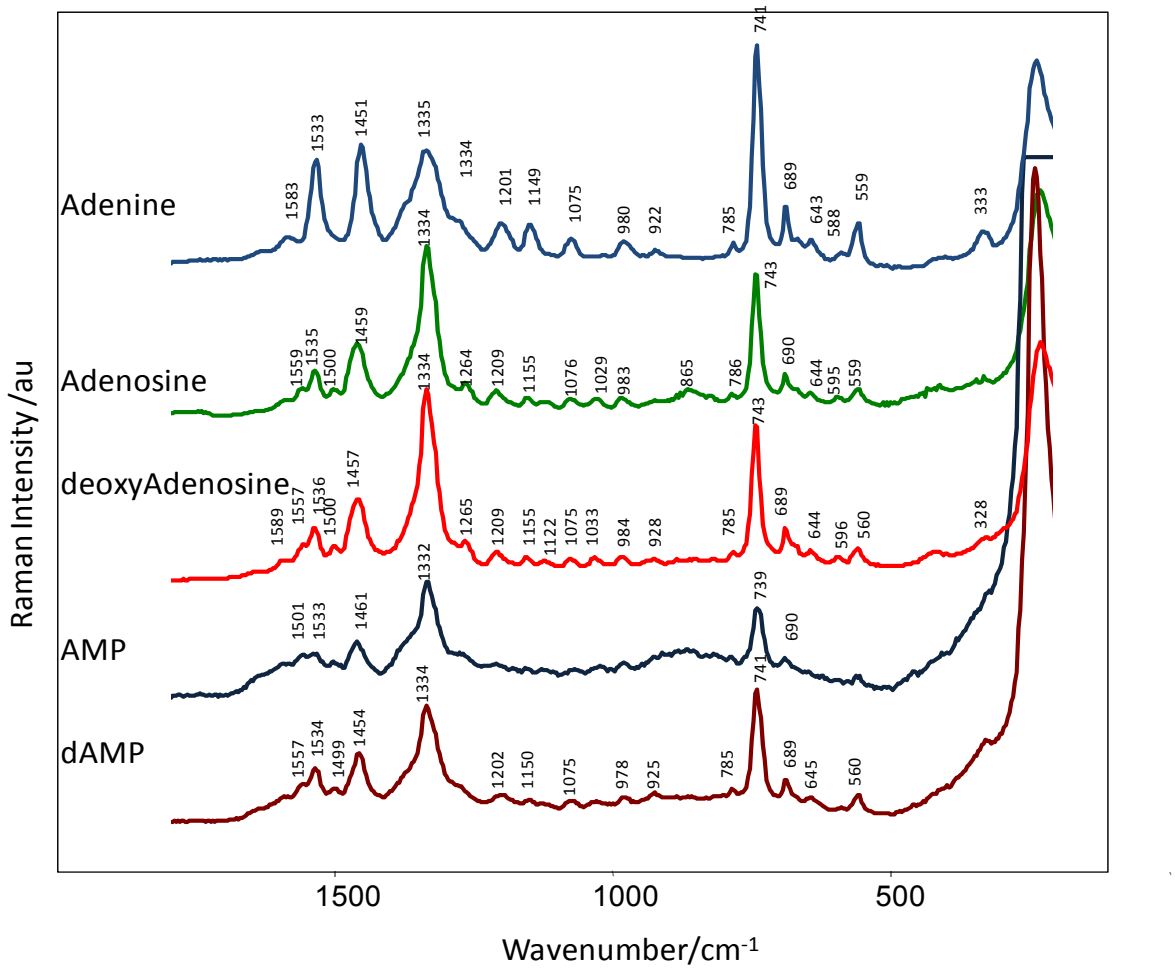

Fig. S5 SERS spectra of Ag^{+} complexes of 0.25 ppm ($1.8x10^{-}$ mol dm^{-3}) adenine, 0.27ppm (10^{-6} mol dm^{-3}) adenosine, 0.25ppm (10^{-6} mol dm^{-3}) deoxyadenosine, 1.7ppm (5×10^{-6} mol dm^{-3}) 5'-AMP and 1.8 ppm (5×10^{-6} mol dm^{-3}) 5'-dAMP on HRSC at pH 11. Other conditions as in Fig. 1

(1) Leopold, N.; Lendl, B. *Journal of Physical Chemistry B* **2003**, *107*, 5723-5727.
(2) Lee, P. C.; Meisel, D. *Journal of Physical Chemistry* **1982**, *86*, 3391-3395.
(3) Frens, G. *Nature-Physical Science* **1973**, *241*, 20-22.
(4) Bruston, F.; Vergne, J.; Grajcar, L.; Drahi, B.; Calvayrac, R.; Baron, M. H.; Maurel, M. C. *Biochemical and Biophysical Research Communications* **1999**, *263*, 672-677.