# Supplementary Material (ESI) for Chemical Communications

Electronic supplementary information

## Experimental details

*Materials*

$D_2O$ (99.9%) was received from Cambridge Isotope Laboratories. $HAuCl_4 \cdot 3H_2O$ (99.99%), N-acetyl-L-cysteine (>99%) and sodium borohydride (98%) were purchased from Aldrich. Water was purified with a Milli-Q system ($\geq$18 MΩ cm). All other chemicals were analysis grade and used as received.

*Characterization of the particles by TEM, UV-vis and NMR*

$^1H$ and $^{13}C$ and DEPT NMR spectra were measured on a Bruker Avance 400 spectrometer at room temperature. Solutions were prepared in $D_2O$ at a concentration of 50 mg/ml. A relaxation delay of 5 s was used to allow adequate signal decay between pulses.

Transmission Electron Microscopy (TEM) images were recorded with a Philips C200 electron microscope operated at 200 kV. TEM samples were prepared by casting a drop of a 1 mg/ml solution in water onto a carbon-coated copper grid. UV-vis spectra of the particles in water were collected on a Cary 300 spectrometer.

*IR and VCD spectroscopy*

IR and vibrational circular dichroism (VCD) spectra were recorded on a Bruker PMA 50 accessory coupled to a Tensor 27 Fourier transform infrared spectrometer. A photoelastic modulator (Hinds PEM 90) set at l/4 retardation was used to modulate the handedness of the circular polarized light. Demodulation was performed by a lock-in amplifier (SR830 DSP). An optical low-pass filter (< 1800 cm$^{-1}$) put before the photoelastic modulator was used to enhance the signal/noise ratio. All solutions of N-acetyl-L-cysteine and N-acetyl-L-cysteine MPNs were prepared in $D_2O$. NaOD was added to deprotonate the carboxylic acid group. A VCD reference spectrum of $D_2O$ containing the same amount of NaOD was subtracted from the VCD spectrum of the dissolved molecules and MPNs, respectively. All spectra were recorded at room temperature with a resolution of 8 cm$^{-1}$ in a cell equipped with $CaF_2$ windows and a 50 μm Teflon spacer. Both sample and reference were measured for three hours in time slices of one hour, corresponding to about 24 000 scans in total for sample and reference, respectively. The spectra are presented without smoothing or further data processing. More information about the experimental procedure can be found elsewhere.[1, 2]

*Density functional theory calculations*

The adsorption of deprotonated N-acetyl-L-cysteine on a gold 19 cluster was investigated using the Amsterdam Density Functional (ADF) program.[3] The inner electrons were frozen for Au (up to 4f), S (2p), N (1s), O (1s) and C (1s). The core was modeled by a relativistically corrected pseudopotential using the ZORA (zero order regular approximation) method. A double–ζ basis set was used. The local part of the exchange and correlation functional was modeled using a Vosko, Wilk, Nuisar parametrization of the electron gas,[4] whereas the non-local part of the functional was modeled using the Becke correction for the exchange[5] and the Perdew correction for the correlation.[6] More computational details can be found elsewhere.[7]

The adsorption of deprotonated N-acetyl-L-cysteine on $Au_4$ clusters was studied using Gaussian03.[8] For the gold atoms an effective core potential was used. The calculations were performed using the b3pw91[9, 10] functional and a LanL2DZ basis set[11] for Au and 6-31G(d,p) basis set[12] for all other atoms. Vibrational frequencies were scaled by a factor of 0.98. IR absorption and VCD spectra were constructed from calculated dipole and rotational strengths assuming Lorentzian band shape with a half-width at half-maximum of 4 $cm^{-1}$.

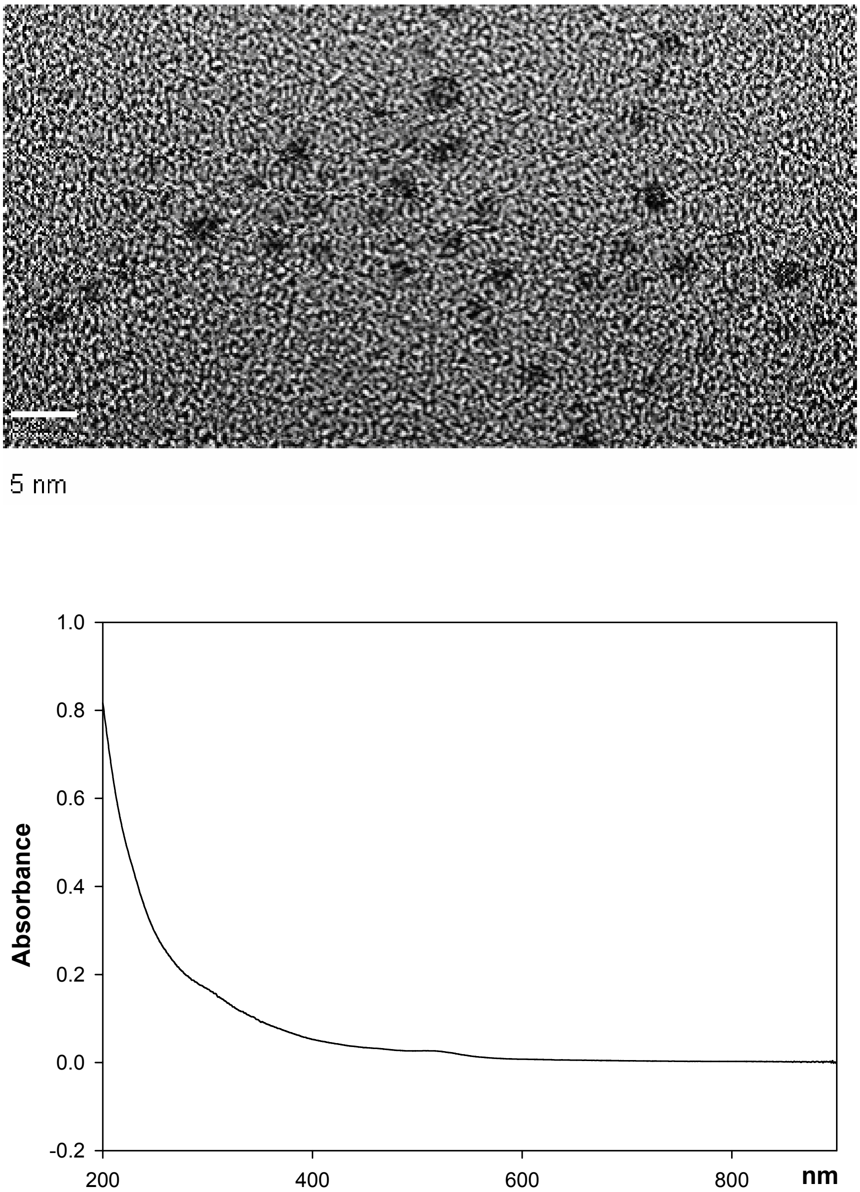


**Figure 1:** Top: Transmission electron microscopy (TEM) of N-acetyl-L-cysteine MPNs. Bottom: UV-visible spectrum of N-acetyl-L-cysteine MPNs in water (c = 0.0235 mg $ml^{-1}$).

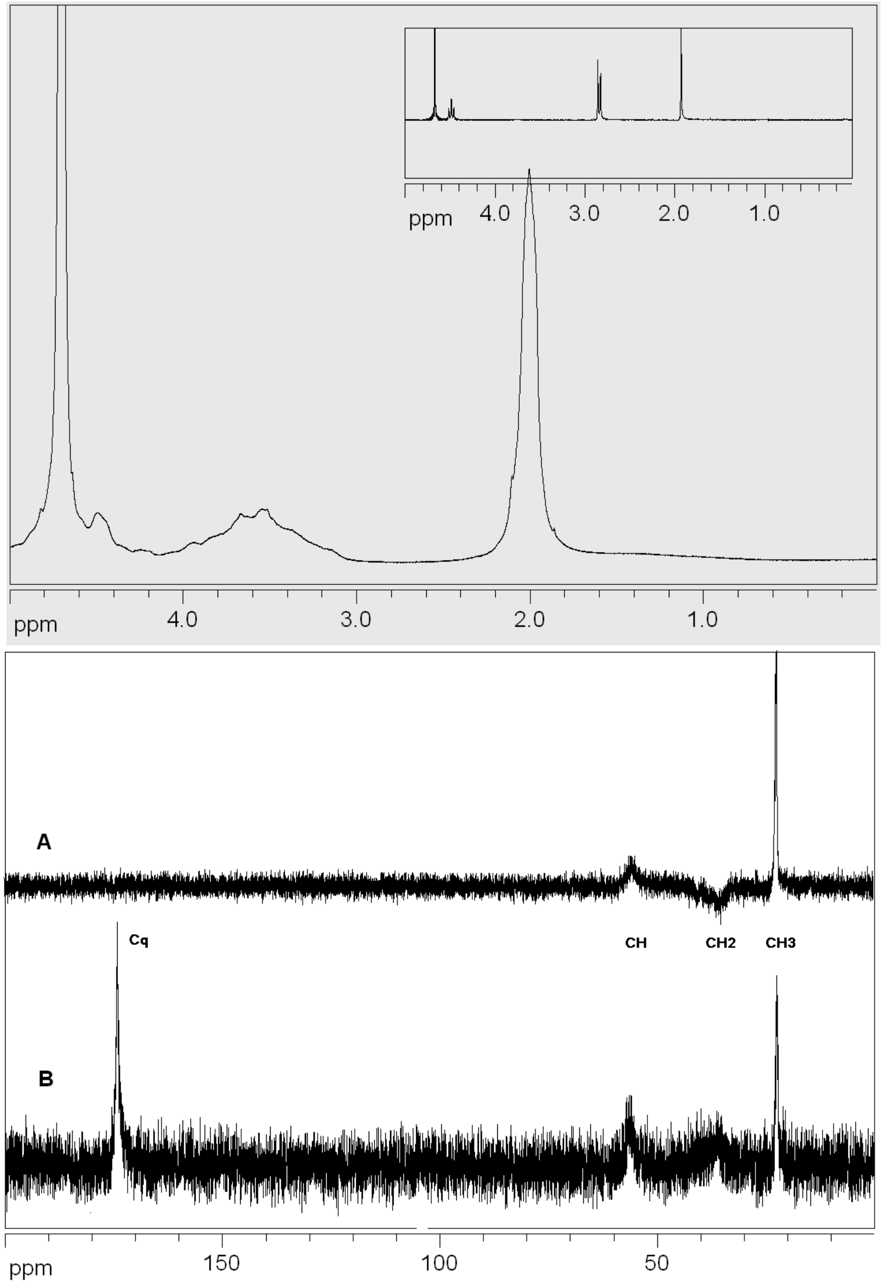
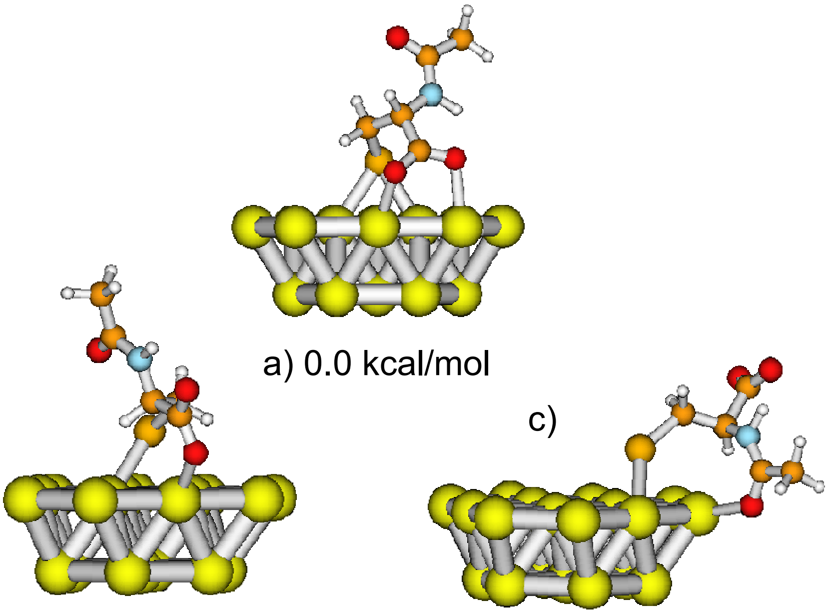


**Figure 2:** Top: 400 MHz $^{1}$H spectrum of N-acetyl-L-cysteine MPNs in $D_2O$ at 298 K. The inset shows the free ligand for comparison. The resonance at 4.8 ppm is due to water. Bottom: 100 MHz NMR of N-acetyl-L-cysteine MPNs in $D_2O$. (A) Distortion less enhancement by polarization transfer 135° (DEPT), (B) $^{13}$C NMR.



a) 0.0 kcal/mol

b) 6.8 kcal/mol

c) 8.2 kcal/mol

**Figure 3:** Calculated conformers of deprotonated N-acetyl-L-cysteine on a $Au_{19}$ cluster. The structures were optimized using ADF.[3] The numbers indicate the relative stability with respect to the most stable conformation a. For the calculations the structure of the $Au_{19}$ cluster was fixed. For computational details see the experimental part.

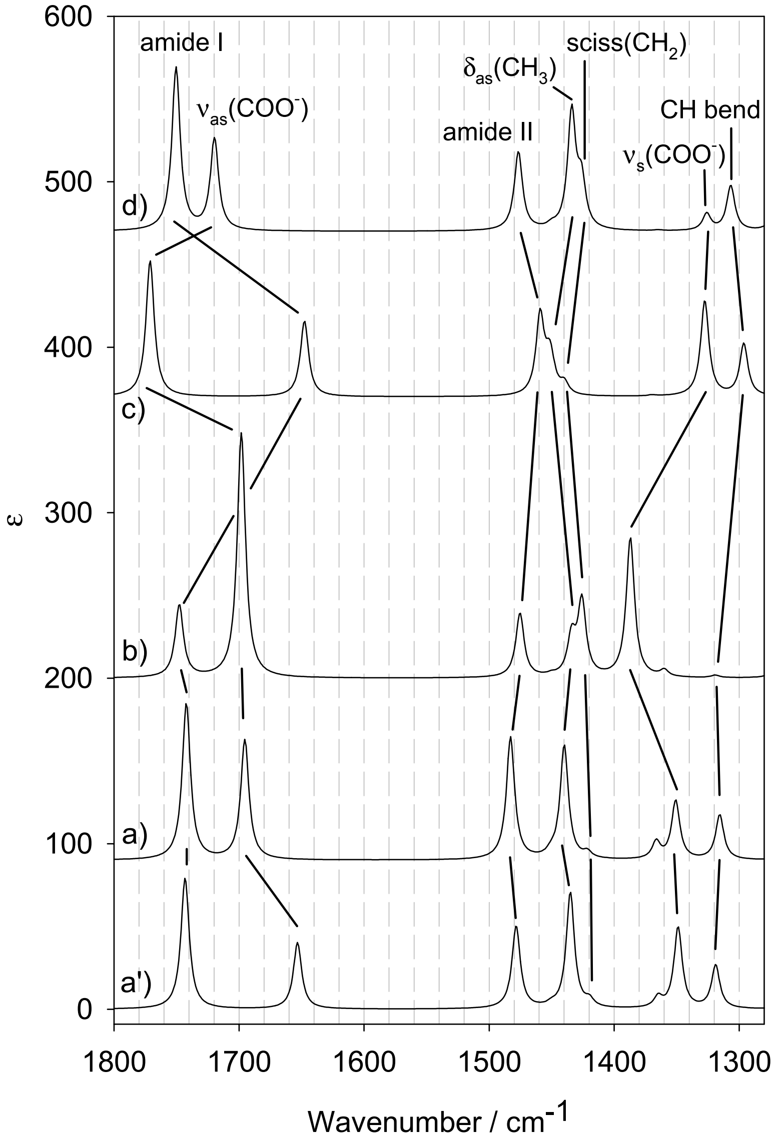


**Figure 4:** Calculated infrared spectra for the structures shown in Fig. 2 of the manuscript. Solid lines connect vibrational bands with similar character.

References (including full references 16 and 17 from the manuscript)

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