Rapid Synthesis of Gold Nanostructures with Cyclic and Linear Ketones

[†]Electronic Supplementary Information

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1 NMR Data

NMR data were collected for samples of cyclopentaone (Fig. 1), cycloheptanone (Fig. 2), acetone (Fig. 3), 1,3 cyclohexanedione (Fig. 5) and 3-hexanone (Fig. 4) in D_2O and compared with NMR spectra taken from the reaction of the respective substance with dilute HAuCl₄.

¹H, ¹³C and HSQC spectra were collected, however, due to the tiny quantities of chlorinated by-product formed (less than 3.9 μ mol in 10 ml) in the presence of large amounts of starting material and solvent, the signals are confined to the baseline of the spectra, and were only visible in ¹H spectra. There was also, however, a close overlap of the residual water peak and any potential proton peaks in that region, and this may have also obscured peaks. In order to combat this, solvent suppression was used where necessary, during NMR data collection.

Cyclopentanone and acetone experiments showed the appearance of two small peaks at around 4.4 and 4.5 ppm. Why the peaks are split is not immediately clear.

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The cyclopentanone experiment showed a triplet, consistent with the molecular structure of 2-chlorocyclopentanone (Fig. 1). Acetone showed singlets, again consistent with the NMR of chloropropan-2-one (Fig. 3).

Cycloheptanone and 3-hexanone present far more complex structures and hence spectra for analysis. No peaks were evident in the cycloheptanone spectra, however the very low solubility of cycloheptanone may have been a contributing factor in this (Fig. 2). Although some peaks are visible in the correct region of the 3-hexanone reaction-mixture spectrum, different peaks are visible in the specturm of pure 3-hexanone, which are not visible in the reactionmixture, throwing some doubt on whether a good scan was achieved, and thus the peaks may be artefacts (Fig. 4).

The diketones studied did not show any particularly obvious changes to their NMRs from starting material to product, that could not be explained by the acidification/dilution on addition of the acid (Fig. 5). This indicates that NMR is not an adequate technique to study these systems in detail.



Figure 1: NMR spectrum of cyclopentanone before mixing with $HAuCl_4$ and after formation of nanoparticles.



Figure 2: NMR spectra of cycloheptanone, before and after mixing with HAuCl₄, showing no obvious proton shifts.



Figure 3: NMR spectra of acetone, before and after mixing with HAuCl₄.



Figure 4: NMR spectra of 3-hexanone, before and after mixing with HAuCl₄. Some proton shifts may be visible, but * peaks are present in starting material and not reaction material, thowing doubt on the validity of the nmr.



Figure 5: NMR spectra of 1,3-cylcohexanedione after mixing with HAuCl₄. The integral at 5.4 ppm is much reduced from the expected value of just under 2, suggesting that the α -position has been deprotonated significantly, however this may just be an effect of dilution or pH change on addition of the acid.

2 UV-Visible Spectroscopy of Cyclopentanone



Figure 6: UV-visible spectra of cyclopentanone produced AuNPs at 24 hours and 4 months after reaction. The lines indicate the movement of the SPR band to lower wavelength, by ca. 10 nm. Also obvious is the loss in absorption intensity over time, particularly at longer wavelengths.

3 XPS analysis

XPS data were collected from freeze dried powders, as described in the main body of the paper.

The 4f peaks are given here, confirming the presence of gold in every sample, and the presence of unreacted Au³⁺ in those from linear ketones, suggesting an incomplete reaction at 24 hours (Fig. 7).

For samples produced with cyclohexanone, cycloheptanone and the cyclohexanediones there was good agreement between the $4f_{7/2}$ and $4f_{5/2}$ peaks with expected values (83.9 and 87.7 eV). Similarly the linear ketones, acetone and 3-hexanone had a good match to the expected Au⁰ and Au³⁺ peaks, however the acetone residue contained a far larger proportion of Au³⁺ than the 3-hexanone sample, in keeping with its lower pK_E.

However an oddity was the cyclopentanone produced AuNPs, showing $4f_{7/2}$ and $4f_{5/2}$ peaks similar to those samples containing Au³⁺. The peaks were also very broad. As the reaction time for this ketone was so long (13 hours) it is likely that there was still trace Au³⁺ present and this lead to the shit and the broadened peaks.



Figure 7: XPS data collected for the 4f Au peaks of AuNPs generated from reaction with a) cyclopentanone, b) cyclohexanone, c) cycloheptanone, d) acetone, e) 3-hexanone, f) 1,3-cyclohexanedione and g) 1,4-cyclohexanedione. Dashed lines show the postions of the ideal $4f_{7/2}$ and $4f_{5/2}$ peaks for Au⁰.

4 TEM analysis

HRTEM images were analysed by onscreen measurement and Fourier transform. A close up of the nanostars from reaction with 1,3-cyclohexanedione shows the sharp tips at the end of each arm (Fig. 8). These will localise the SPR, making nanostars an excellent prospect for SERS measurements. Close examination of plates produced by various ketones show a lattice spacing of 0.235 nm, corresponding to the (111)-plane. (Fig. 9).



Figure 8: HRTEM images of a) a nanostar and b) a close of up the circled area, showing a tip ca. 5 nm in diameter.



Figure 9: HRTEM images of a) a flat plate produced after 4 months b) Fourier transform showing the lattice spacing in inverse space, confirming the values ca. 0.235 nm.