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Monomeric and Polymeric Amines as Dual Reductants/Stabilisers for the Synthesis of Gold Nanocrystals: A Mechanistic Study

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Uniform, monodisperse gold nanocrystals have been prepared in a single-step synthesis by the addition of secondary and tertiary alkylamines, or a cationic polymer containing these moieties, to dilute solutions of gold tetrachloraurate. The acidic pH resulted in the formation of quaternary ammonium sites, scavenging loosely bound chloride ions from the tetrachloraurate species, lowering the overall potential and reducing Au^{III} to nanocrystalline Au^0. The secondary amino groups then served to stabilise the particles, preventing aggregation and collapse of the colloidal system. Addition of further capping groups was thus not required. The particles were characterised by UV/Visible spectroscopy, HR-TEM, X-ray diffraction, electrochemical potential and pH measurements (Eh-pH) and FTIR.

Introduction

Nanoscale metallic particles exhibit characteristics at variance with those of the bulk metal.[1] Increased surface area, susceptibility towards Brownian motion and restricted plasmon oscillation are observed. Interaction with electromagnetic radiation (Mie theory) and biological systems allows for potential applications in the next generation of data storage disks,[2] photovoltaic and photochemical devices, catalysis and antimicrobial surfaces.[3]

In general, nanocrystalline gold is prepared either by physical means, for example vapour deposition, or chemically through the reduction of tetrachlorauric acid. The latter is now accepted as being more flexible, due to the remarkable influence that the type and molar ratio of reductant to Au^{III}, in addition to reaction time and temperature, exert over the size and shape of the particles formed.[4] The reductant supplies the necessary electrons to affect the reduction from the ionic through to the metallic state. Use of trisodium citrate provides particle sizes of 1.6 to 140 nm with a relatively narrow size distribution, tuneable according to the molar excess of reductant present.[5] Sodium borohydride in conjunction with either an alkanethiol capping group[6] or a branched polyamine[7] to ensure the stability of the colloidal system, provides particles of 6 to 20 nm. Interestingly, glucose in the presence of sodium hydroxide has been shown to reduce Au^{III} to Au^0.[8] Alternatively, photochemical reduction may be employed[9] with the incoming photons generating the necessary electrons.

However, due to the precarious stability of the Au–Cl–H_2O system (Figure 1) weaker reductants may be employed to initiate the transition to the metallic state. While $AuCl_4^-$ is stable over a wide pH range (0–7.5), any slight reduction in electrochemical potential will result in destabilisation of the system with a subsequent transition to $AuCl_2^-$ at 920 mV. Further lowering of the overall potential will then cause a further redistribution of electrons, favouring Au^0 as the stable species. This change in potential may result from a change in concentration of one or more species present, the addition of a new compound, a deviation in temperature or pH.

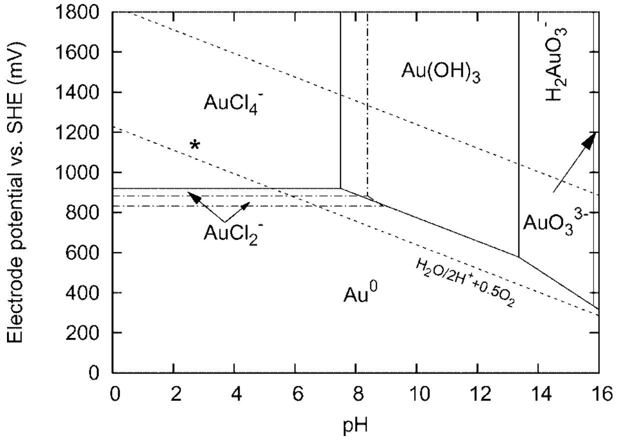

Figure 1. Pourbaix diagram for the Au–Cl–H_2O system at 298 K.[10] $a_{Au} = 10^{-3}$ and $a_{Cl} = 1$ (—), $a_{Cl} = 5$ (– · – ·), chloride treated as electro-inactive. Water metastability region (- - -) calculated assuming standard conditions. The resting potential for the $AuCl_4^-$ used in the present study is indicated at *.

While commonly used for the steric stabilisation of nanocrystals, polymeric amines have recently received attention for their potential role as dual reductants/stabilisers.[11,12] In a few studies the mechanistic route is reasonably clear, for

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example the degradation of *N*,*N*-dimethylacetoacetamide,[12] however in many it is not. This is particularly so when the amine is relatively stable towards oxidation compared to the metal complex that is to be reduced. Oxidation to an imine has been suggested,[13] however, no evidence of this route has yet been published. Furthermore, it is not difficult to disprove this hypothesis (see below).

Due to the difficulties in observing individual proton chemical shifts in highly branched polymers, an initial investigation was made into the ability of simple primary, secondary and tertiary amines to reduce $AuCl_4^-$, or at least destabilise the system such that metallic Au^0 would become the favoured species. In the present work, primary, secondary and tertiary amino groups are investigated as potential dual reductants/stabilisers for the synthesis of nanocrystalline gold. This allows some conclusions to be drawn regarding the use of cationic alkylamino polymers containing these groups.

Results and Discussion

Monomeric Amines: No reaction was observed between the primary amines, methylamine, ethylamine, and $AuCl_4^-$, either when heated to boiling or left under ambient conditions for several days. However, the secondary amine, diethylamine, reacted relatively slowly with the gold complex over 48 hours to form stable seed nanocrystals of 1.7 nm mean diameter, standard deviation 0.2 nm (Figure 2). The tertiary amine, trimethylamine, reacted relatively quickly to form nanocrystals within one hour; however, these began to aggregate immediately.

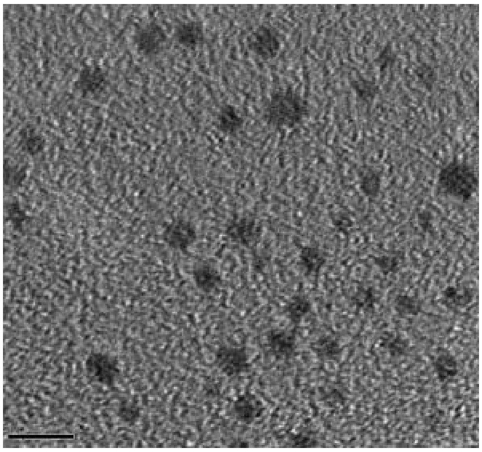

Figure 2. HR TEM of seed gold nanocrystals prepared with diethylamine. The scale bar represents 5 nm.

Examination of the proton nuclear magnetic resonance (NMR) spectrum of trimethylamine before and after nanocrystal formation showed a partial splitting of the single peak at $\delta = 3.35$ ppm into two tiers of peaks over the range 2.20 to 3.60 ppm. It is believed that this is due to partial coordination of the gold to the nitrogen, as no coupling constants were able to be distinguished. A similar effect was observed for diethylamine, with the exception that coupling constants of 7 Hz were observed, consistent with methylene protons (Figure 3). By contrast, the proton NMR spectrum of ethylamine was found to be unchanged after addition of $AuCl_4^-$ (save for the expected shift of the triplet and quartet peaks due to the change in pH).

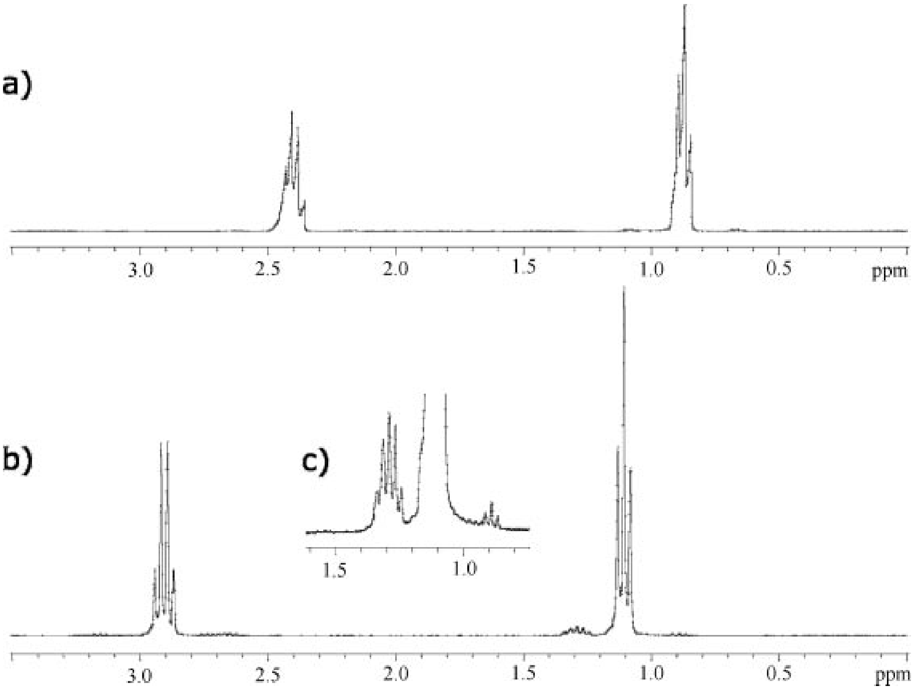

Figure 3. ^1H NMR spectra of a) diethylamine, b) nanocrystalline gold prepared with diethylamine, c) expansion of spectrum b) showing the 7 Hz coupling-constant multiplet downfield of the triplet.

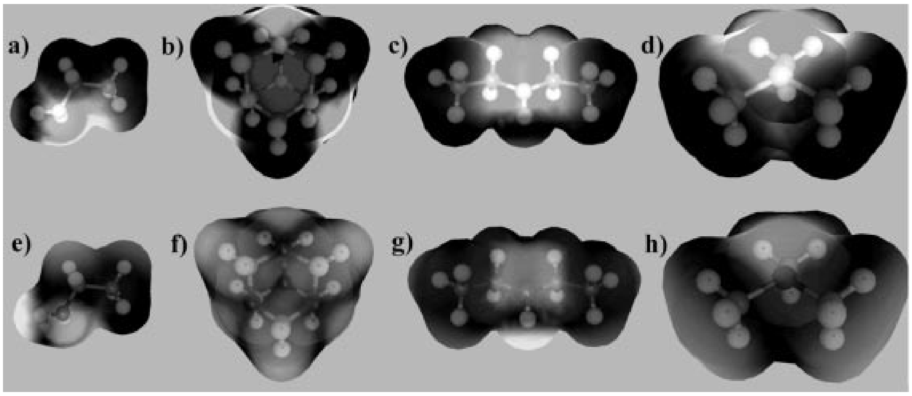

Figure 4. Molecular models of a) ethylamine (–0.18), b) hexamethylenetetramine (–0.20), c) diethylamine (–0.16) and d) trimethylamine (–0.13) showing the Van der Waals shell shaded white in areas of high electrostatic potential. Models on the second row represent e) ethylamine, f) hexamethylenetetramine, g) diethylamine and h) trimethylamine, respectively, redrawn to show areas of low electrostatic potential shaded white. Nitrogen charge in parentheses.

Length of the alkyl chain was also found to affect the ability of the amine to form nanocrystalline gold from the $AuCl_4^-$ solution. When the primary chain length was increased linearly to eight methylene (octylamine) units, colloid formation was observed. When the alkyl chain was cyclised (cyclohexylamine), however, no reaction was observed. Conversely, a longer alkyl chain in the secondary amines (dipropylamine, dibutylamine, dioctylamine) resulted in the formation of flakes of metallic gold. No reaction was observed with a shorter secondary amine chain length (dimethylamine). For the tertiary amines, the use of triethylamine rather than trimethylamine, while decreasing the volume of amine from 10 to 2 µL resulted in a colloid, which was stable for several days. The colloid was unstable with a greater volume of amine. No nanocrystal formation was observed with hexamethylenetetramine.

The differences in reactivity of the amino groups may be attributed to a combination of steric hinderence and extent of charge separation, in addition to their slightly different levels of basicity. Molecular modelling of the charge on the nitrogen and the steric hinderence (Figure 4) suggests that compounds better suited to interaction with gold nanocrystals are those with a charge on the nitrogen greater than than –0.16, in addition having the areas of minimum and maximum charge well separated. Access to the nitrogen atom is necessary if nanocrystal growth is to proceed. For example, addition of pyridine resulted in immediate formation of an unstable colloid, while the sterically hindered 1-methylpyridine provided a colourless solution – indicative of reduction to monoatomic gold. Gold colloid formation was not observed with the remaining amines.

Potential dissociation of the ammonium ion is also likely to affect formation of the nanocrystals. Diethylamine (as the ammonium ion) has the highest pK_a (10.94) while ethylamine and trimethylamine have pK_a values of 10.64 and 10.72, respectively.[15] While the increase in reactivity observed for longer chained secondary amines may be explained by their higher pK_a, only a minimal change in pK_a in the primary amines is observed as the chain length is increased. Greater intramolecular interaction, exemplified by the increase in boiling point from 16.6 to 176 °C as the chain length is increased from one to eight methylene units, is expected to take an additional role.

The aromatic amines aniline, methoxyanilinesulfonate and benzylamine were also found to react readily with the $AuCl_4^-$ to form polyaniline (for the former) and nanocrystalline gold, in a similar fashion to that previously observed for 2-methoxyaniline[16] and pyrrole.[17] However, due to the ease of oxidation of these compounds relative to those discussed above, no further work was continued with these compounds.

While the above constitutes only an introductory investigation into the use of saturated monomeric amines as dual reductant/stabilising functional groups, it may tentatively be concluded that for short alkyl chains it is the tertiary amines that are the most effective at reducing Au^{III}, followed by longer chained secondary amines. However, secondary amines are more effective at providing the necessary coordination required for stabilisation of the nanocrystals as they are formed.

Polymeric Amines: No reaction was observed with polyacrylamide or polyvinylpyrrolidone containing primary and tertiary amino groups, respectively. The branched polyethylenimine (PEI) containing primary, secondary and tertiary amino groups reacted over a period of three hours to form the characteristic deep red colloid, stable over several months. Previous studies have confirmed its stabilising effect on nanocrystalline gold.[7] Due to the success observed with PEI, the remainder of the study focused on the use of this polyamine for nanocrystal synthesis.

Figure 5 shows the increase in the UV/Visible band at 525 nm associated with the transverse plasmon resonance[18] for these colloids (denoted type I, for the purposes of distinguishing the various colloids in the paper presented here). The mean particle size measured was 11 nm, with a standard deviation of 4 nm. Figure 6 and Figure 7 show the crystalline particles formed, together with a typical X-ray diffraction pattern. Type II colloids were prepared fortuitously when investigating the effect of temperature on formation of type I particles. On reaching 70 °C the solution rapidly underwent a colour change to deep red, which on examination under HR TEM showed that reduction had occurred and nanocrystals had formed. For comparison, similar colloids (denoted type III) were also synthesised according to the method of Sun[7] using $NaBH_4$ as reductant. Interestingly, the particles appeared more encumbered by the PEI used to stabilise the colloids when the reducing agent had been used, relative to the type I and II colloids.

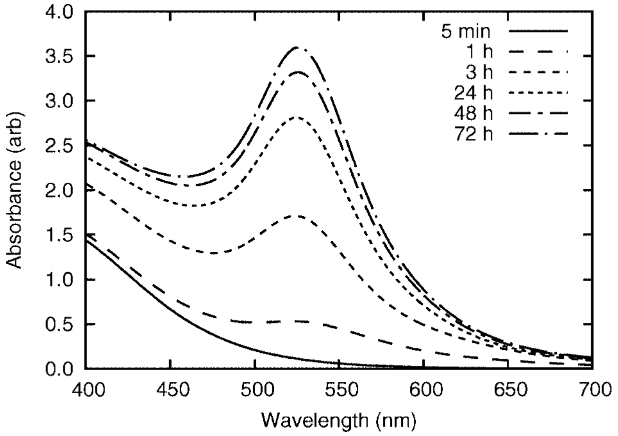

Figure 5. UV/Visible spectra of gold colloids (type I) prepared with PEI (N/Au ratio of 33:1) over the first three days, showing the development of the peak at 525 nm.

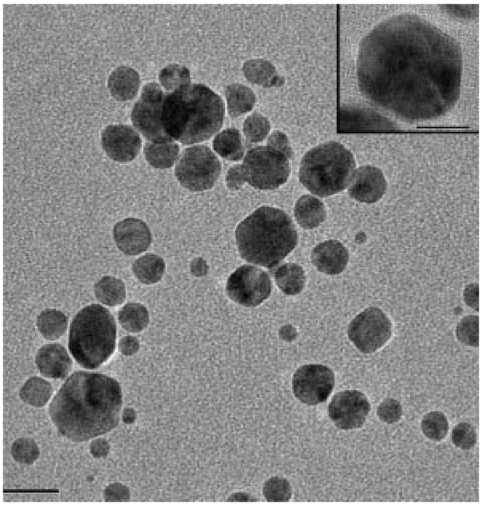

Figure 6. HR TEM of gold nanocrystals prepared with polyethylenimine (type I, N/Au 33:1). The scale bar represents 20 nm for the main picture, 10 nm for the inset.

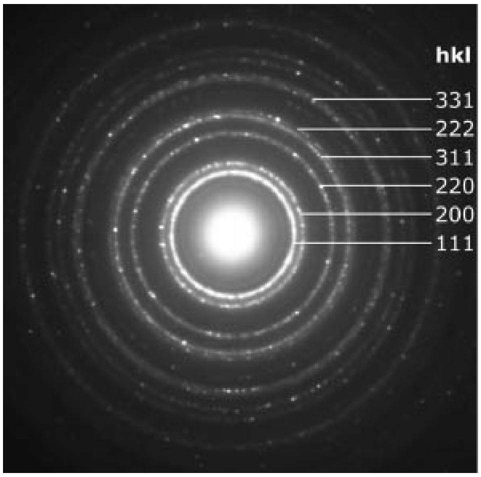

Figure 7. Typical diffraction pattern of multi-crystalline nanoparticulate gold prepared with PEI (type I, 33:1 N/Au, camera height = 80 cm).

Use of a lower concentration of PEI, measured as the average number of amino groups present, resulted in the formation of some metallic gold (though none at the nanometer scale) which settled rapidly to the bottom of the vial Figure 7. With a 1:1 N/Au ratio, the colloid aggregated within several hours – a minimum ratio of 33:1 was required to ensure stability of the system. As the ratio of N to Au was increased from 33:1 to 330:1, a gradual colour change from red to blue was observed in the colloidal system. This is seen in the UV/Visible spectra (Figure 8) as a broadening towards higher wavelengths of the principle absorbance peak. The change in absorbance was due in part to a slightly higher mean particle size; however, a greater tendency towards aggregation into larger "clumps" of 50 to 100 nm, was the over-riding factor. Increasing the N/Au ratio further had no noticeable effect. However, if the ratio of N/Au was kept at 33:1 and the colloid aged for up to four months, then a decrease in size distribution (standard deviation 1 nm) and concurrent increase in mean particle size (13 nm) due to Ostwald ripening, is observed. A corresponding shift in absorbance to longer wavelengths was also noted.

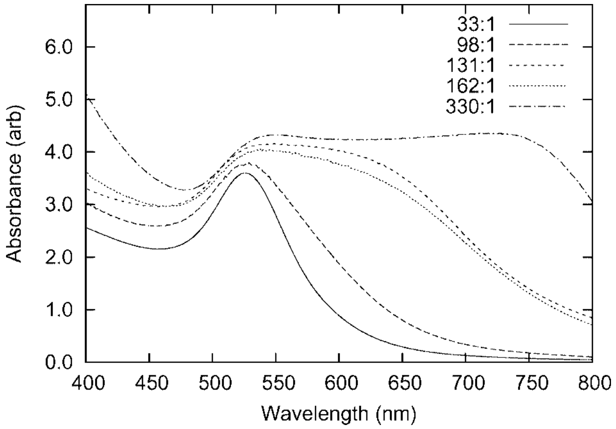

Figure 8. UV/Visible spectra of type I colloids at increasing molar ratios of amino nitrogen to gold, after four days.

The mechanism by which the reduction occurs is likely to be complex and remains unresolved at present. It has been postulated that the amino groups on the polymer are oxidised to imino moieties,[13] and indeed this is the obvious source of electrons by which the reduction of Au^{III} could take place. No evidence for the required carbon–nitrogen double bond has been published, however. NMR analysis of the PEI–colloid system before and after synthesis of the colloid should show the appearance of a proton bound to a carbon with a carbon–nitrogen double bond. However, proton and HSQC NMR spectra lack such a peak in the polymer both before and after reduction of the Au^{III}, confirming the absence of the imine group.

It has also been suggested that the loss of the peak at 1570 cm^{-1} in the IR spectrum after ten days[13] attributed to the N–H bending vibration, is evidence for the oxidation of the amino groups. Considering that nanocrystal formation is observed in less than three hours and is essentially complete within 24 hours, this is unlikely. Furthermore, the expected concurrent appearance of the carbon–nitrogen double-bond at 1700 cm^{-1} is not observed. Oxidation of the amino groups to nitrate was eliminated as a possibility by the negative "Brown Ring" test.[14]

However, some suggestions towards a mechanism must be made. Formation of type I and II particles is believed to proceed initially through transfer of protons from the acidic gold solution to the nitrogen groups of the polymer to form quaternary ammonium sites, the resulting cationic species attracting the chloride ions initially complexed to the gold. In order to test the hypothesis that this "doping" of the amino groups on the polymer was required for the reduction, parallel experiments were conducted where the polymer was first treated with excess chloride before addition of the gold. Upon subsequent addition of $AuCl_4^-$ no reaction was observed. This suggests that availability of the nitrogen lone electron pairs, as cationic quaternary ammonium sites under acid pH, is requisite to formation of the nanocrystals. Revisiting the secondary and tertiary amines, a similar effect was found, with no reduction of the tetrachloraurate.

The main difficulty is locating the source of the electrons required for reduction of Au^{III} to Au^0. Analysis of the oxidation–reduction potential (ORP) of the H_2O–PEI–$AuCl_4^-$ system with various concentrations of PEI, corresponding to multiples of the number of moles of chloride ion present, shows that at a molar ratio of nitrogen to gold ions of approximately 1:1, a lowering of the potential is observed (Figure 9). A slight reduction in pH is observed concurrently, followed by an increase to a pH of 7.3. Due to the potential of the system initially being in that where water is only metastable (Figure 1) some water may have been oxidised concurrently with the initial stages of nanocrystal formation. Nanoparticulate gold is known to catalyse the reduction of oxygen to peroxide[19] thus it is possible that the equivalent oxidation may also be thus affected. The resulting protons would lead to the observed lower pH, simultaneously providing the electrons required for the reduction of the gold. Once all required electrons have been provided and the reaction with the gold species is complete, the presence of additional, excess amino groups only serves to increase the overall system pH.

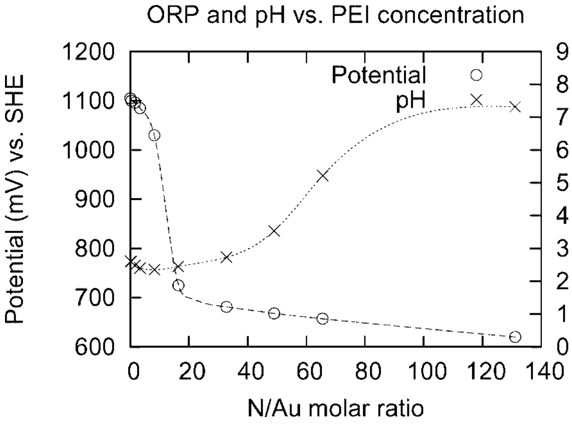

Figure 9. Oxidation–reduction potential vs. the standard hydrogen electrode (SHE) and pH as a function of the molar ratio of polymeric amino nitrogen to gold.

Conclusions

Crystalline gold nanocrystals of 6 to 100 nm diameter have been prepared using both monomeric and polymeric amines in a dual reductant/stabilising role, the latter containing both primary, secondary and tertiary amino groups. The secondary groups were found to be the most amenable to the synthesis and stabilisation of the nanocrystals, while the tertiary amines were able to reduce the Au^{III} but unable to stabilise the colloid. The mechanism by which reduction takes place is expected to be complex, but is believed to involve the formation of quaternary ammonium sites on the monomer or polymer, together with possible oxidation of water to provide the necessary electrons. A significant advantage of the processes used to form the nanocrystals is the simplicity of the synthesis (one pot, one step). This allows ready scale-up of the synthesis. Additionally, the three compounds used are relatively benign at the concentrations used, leaving no undesirable by-products for disposal or further treatment.

Experimental Section

Synthesis of Colloids

Monomeric Amines: $HAuCl_4$ (40 µL, 1.24 wt.-%) was added to Millipore water (5 mL, 15 MΩ·cm^{-1}) with rapid stirring. After one min, the amine [methylamine (40 wt.-%, aqueous), ethylamine (70 wt.-%, aqueous), octylamine, cyclohexylamine, benzylamine, ethylenediamine, phenylethylamine, 1,1,3,3-tetramethylguanidine, dimethylamine (26 wt.-%, aqueous), diethylamine, dipropylamine, dibutylamine, dioctylamine, aniline, methoxyanilinesulfonate, pyrrole, pyridine, 1-methylpyridine, trimethylamine (25 wt.-%, aqueous), triethylamine, hexamethylenetetramine](1 to 10 µL) was added and stirring continued for a further minute before leaving to stand for 2 to 72 hours. A duplicate sample of the diethylamine-Au colloid was evaporated to dryness before dispersion in D_2O in preparation for ^1H NMR analysis (300 MHz, D_2O, 25 °C): $\delta = 1.11$ (t, $J_{H,H} = 7$ Hz), 1.29 (m, $J_{H,H} = 7$ Hz), 2.90 (m, $J_{H,H} = 7$ Hz), in addition to a further sample of the trimethylamine-Au colloid (300 MHz, D_2O, 25 °C): $\delta = 2.42$ (s), 2.49 (s), 2.55 (s), 2.60 (s), 2.67 (s), 2.73 (s), 2.80 (s), 2.83 (s), 2.87 (s), 2.91 (s), 2.97 (s), 3.05 (s), 3.22 (s), 3.24 (s), 3.53 (s) ppm.

Polymeric Amines: Stock solutions of surfactant were prepared using dry polyethylenimine (PEI) (A: 18 wt.-%, B: 0.18 wt.-%, average Mw 25000, Aldrich), polyvinylpyrrolidone (C: 1 wt.-%), polyacrylamide (D: 1 wt.-%) and Millipore water (15 MΩ·cm^{-1}).

Type I nanocrystals were prepared by the addition of $HAuCl_4$ (40 µL, 1.24 wt.-%) to Millipore water (5 mL) with rapid stirring, followed by the required amount of solution A to D. The reaction mixture was left to stand for a minimum of 24 hours in a sealed vial, whereupon a characteristic colour change to deep red was observed. NMR samples were prepared by evaporating to dryness a duplicate volume (5 mL) of the PEI–Au colloid, prior to redispersion in D_2O. ^1H NMR (300 MHz, D_2O, 25 °C): δ = 4.74 (s), 4.67 (s), 4.61 (s), 4.41 (s), 3.33 (m), 3.21 (s), 3.17 (m), 3.02 (m), 2.83 (m), 2.28 (s), 2.13 (s), 2.06 (s), 2.00 (s), 1.85 (s), 1.80 (s) ppm. ^{13}C NMR (from HSQC at 300 MHz, D_2O, 25 °C): δ = 35.5 (s), 36.7 (s), 43.9 (s), 44.0 (s), 45.1 (s), 49.7 (s), 72.9 (s), 138.1 (s), 153.5 (s) ppm. Type II nanocrystals were formed in the same manner as type I, with the PEI/$HAuCl_4$ solution being heated momentarily to 70 °C. The vial was cooled to ambient temperature prior to further analysis. Type III nanocrystals were prepared according to the method of Sun (2003).[7] $HAuCl_4$ (80 µL, 1.24 wt.-%) was added to a 15 mL glass vial containing water (10 mL) and a magnetic stirring bar. After stirring rapidly for one min, PEI (20 µL, 18 wt.-%) was added to the mixture, whereupon a colour change to faint red was noted. After a further minute of stirring, $NaBH_4$ (2.0 M in dimethyl ether/ethylene glycol, Aldrich) was added dropwise until a colour change to deep red was observed.

Analysis

High-resolution transmission electron micrographs (HR TEM) and diffraction patterns were recorded with a Jeol 2010 instrument at 200 keV acceleration voltage with the samples mounted on carbon-coated copper grids (200 mesh). Ultra-violet/visible (UV/Visible) spectra were measured using matched quartz curvettes and a Varian Cary 100 system. A Bruker Tensor 27 system attached to a Pike Technologies single-reflectance horizontal-attenuated total reflectance (ATR) attachment was used to obtain Fourier Transform infra-red (FTIR) spectra. pH and oxidation–reduction potentials (ORP) were measured using Mettler Toledo and Hanna probes, respectively, with a Hanna 8521 instrument. ^1H and gradient heteronuclear single quantum correlation (HSQC) nuclear magnetic resonance (NMR) spectra were recorded on a Varian Inova spectrometer at 300 MHz.

Molecular Modelling

Modelling of the charge density on the compounds was undertaken using the Polak Ribiere conjugate gradient algorithm, on HyperChem. 7.5 (Gainesville, Florida). Rendering of the molecular models was achieved using Ghemical 1.91[20] and the Massively Parallel Quantum Chemistry system (MPQC).[21]

Acknowledgments

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