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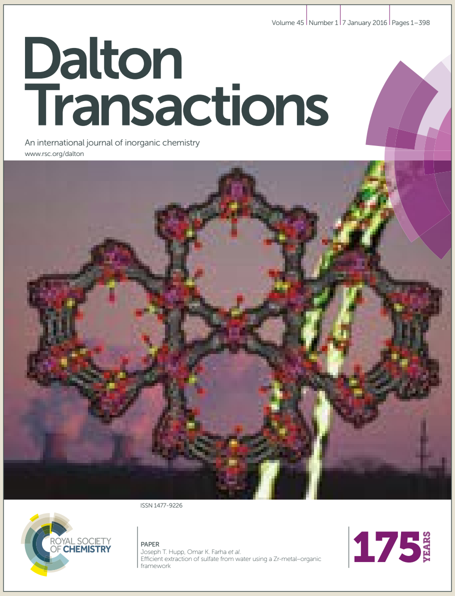

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# Stabilisation of Gold Nanoparticles by N-Heterocyclic Thiones

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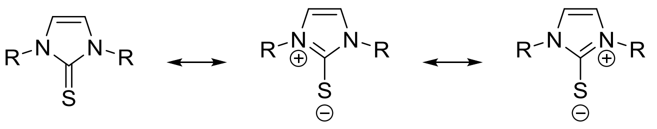
**Gold nanoparticles (Au-NPs) have been prepared using N-heterocyclic thiones (NHTs) as ligand stabilisers. These Au-NPs have been shown to be very stable, even in air, and have been characterized by a combination of several techniques (TEM, HR-TEM, STEM-HAADF, EDX, DLS, elemental analysis and $^1$H NMR). These nanoparticles are active in the catalytic reduction of nitroarenes to anilines.**

Gold nanoparticles (NPs) are nowadays being routinely utilised in a very diverse range of disciplines.[1] The way they are synthesised (reaction conditions, temperature, solvent, etc) have an important impact on their final structure and reactivity. To avoid agglomeration, the addition of stabilisers (usually in the form of ligands) is necessary and, at the same time, these ligands offer an opportunity to control the shape, surface state, reactivity and physical properties (electronics, sensing, etc).[2] In most cases, thiols, amines, phosphines and thioethers have been used as stabilisers. Thiolate-protected gold nanoparticles have had an enormous impact in the field of material science (development of self-assembled monolayers), biology (bioconjugate labelling, drug delivery, etc) as well as inorganic chemistry and catalysis.[3] More recently, N-heterocyclic carbene ligands have come into scene to form well defined nanoparticles of metals such as Au, Ru, Pt and Pd.[4] The major advantage of these ligands relies on the strength of their interaction with the metal centre, typically stronger than other ligands. Although *in situ* generation of less stable NHCs is possible, one of their drawbacks stems on the inherent stability of the type of ligands, making them less suitable when protic solvents are required in the formation of the nanoparticles. Therefore, the search for new neutral ligands able to stabilise gold NPs is highly desirable.

Having in mind that the covalent bond between gold and sulphur is rather strong,[5] we have envisioned the possibility of using N-heterocyclic thiones (NHTs) as ligand stabilisers (Scheme 1). The zwitterionic resonant structure[6] depicted in Scheme 1 would provide a stronger interaction with the gold surface than thioethers $R_2S$ (which do not form very stable gold nanoparticles) positioning these ligands halfway between the neutral N-heterocyclic carbenes and thioethers, but with distinct bonding situation than the anionic thiolates due to their intrinsic neutral (or zwiterionic) nature. Another benefit of these ligands is their stability in air and resistance to oxidation that, together with the easiness of tunability (both sterically and electronically) makes them very attractive.[7] In this communication, we report the synthesis of very stable gold nanoparticles stabilised by N-heterocyclic thiones, their characterization and their use in the reduction of nitroarenes.

The N-heterocyclic thiones were synthesised following a previously reported procedure through deprotonation of imidazolium salts in the presence of sulphur.[8] Once prepared, their reaction with gold complex (THT)AuCl (THT = tetrahydrothiophene) lead to the clean formation of the corresponding complexes (NHT)AuCl, **3** (Scheme 2). These compounds have been used as starting materials for the synthesis of the gold nanoparticles. In previous reports, it has been established that Au-NPs can be prepared by reduction of well-defined gold complexes by action of boranes such as 9-BBN, $NaBH_4$ or $LiHBEt_3$.[4b,9] Attempts to prepare the gold



**Scheme 1.** Resonant structures of N-heterocyclic thiones.

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† Footnotes relating to the title and/or authors should appear here.

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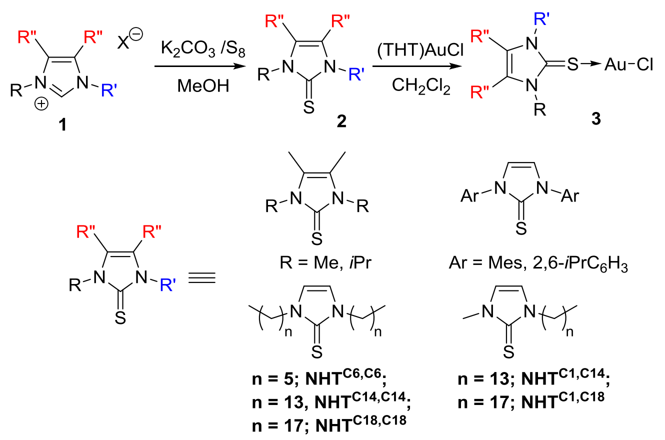

**Scheme 2.** Synthesis of gold complexes **3**.

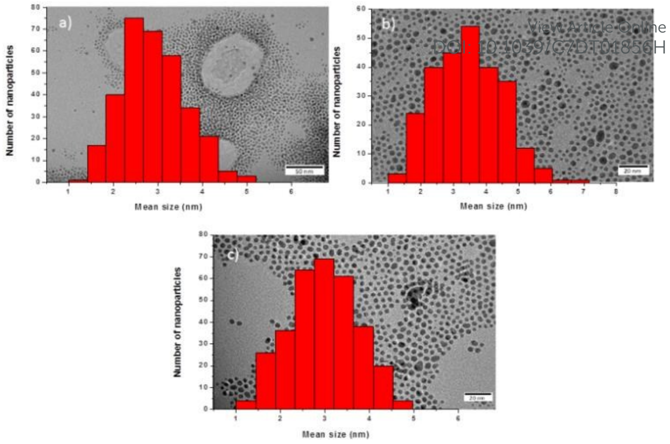

**Figure 1.** TEM images of gold nanoparticles and size distribution (inlet): a) AuNp-NHT $T^{C6,C6}$, b) AuNP-$NHT^{C14,C14}$, c) AuNP-$NHT^{C18,C18}$.

nanoparticles using alkyl- or aryl-substituted N-Heterocyclic thiones (R = Me, $^{i}$Pr; Ar = Mes, 2,6-$^{i}PrC_6H_3$, Scheme 2) using as reducing agent $KBEt_3H$, 9-BBN or $NaBH_4$ led to complete degradation of the starting material. However, TEM images of the as-synthesised particles indicated the presence of gold nanoparticles but, unfortunately, most of the metal present was in the form of agglomerates with independence of the reducing agent. Since this might be due to the lack of sufficient ligand stabiliser present in solution, reactions in the presence of variable amounts of the N-heterocyclic thiones (0.2 to 1 equiv with respect to the gold complex) were carried out. Nevertheless, the impact of the excess of the ligand had nearly no effect in preventing agglomeration. Although encouraging, these results indicated that further stabilisation is required to avoid formation of agglomerates. One way to prevent precipitation of bulk-gold involves the use of ligands with long-chain hydrocarbons to provide sufficient steric repulsions between particles.[3c] Therefore, we carried out the reduction of gold complexes **3**, bearing alkyl-chains of different lengths ($NHT^{C6,C6}$, $NHT^{C14,C14}$, $NHT^{C18,C18}$), with $KHBEt_3$ in THF at rt. A fast reaction takes place leading to ruby-red solutions characteristic of colloidal gold. No evidence for the precipitation of black gold was observed. TEM analysis of the as-prepared NPs indicated that well-disperse, spherical, crystalline nanoparticles have been formed, with no agglomerates present (Figure 1). The mean size of these Au-NPs range from 2.9(0.7) to 3.5(1.0) nm (Figure 1), with a rather narrow size dispersity. With the aim to determining the effect of a single long-chain arm on the NHT, gold nanoparticles bearing the unsymmetrical NHT ($NHT^{C1,C14}$, $NHT^{C1,C18}$) were synthesised following an identical protocol. As can be seen in Fig. S31 and S35 the TEM images also show the presence of Au-NPs with a mean size varying from 3.7(0.7) to 3.8(0.8) nm (see ESI).

All these NPs are soluble in aromatic solvents, yet insoluble in protic solvents such as ethanol. This allowed their purification by simple washing with ethanol providing a way to remove the N-heterocyclic thiones present in solution as well as inorganic salts. The composition of the purified nanoparticles obtained by Inductive Coupled Plasma (ICP) indicates a metal content of 55-90 %. Additionally, these nanoparticles are very stable both in solution and in the solid state, showing no degradation signs after exposing them to air for prolonged periods of time, according to TEM images of the gold nanoparticles stored in solution after ca. two months (see ESI). Therefore, the interaction of the NHTs with the metal atoms seems to be sufficiently strong to prevent decomposition, the stability being comparable to that of gold nanoparticles stabilized by neutral ligands such as N-heterocyclic carbene and considerably superior to those reported with thioethers.[10]

The UV-vis spectra are consistent with the mean size observed by TEM. A strong absorption band at 526 nm, characteristic of a plasmon band for nanoparticles bigger than 2 nm, have been recorded.[1h] On the other hand the good solubility of the nanoparticles allowed to obtaining the $^{1}$H NMR in which very broad signals spanning from 0 to 3 ppm are observed in all cases (see ESI), consistent with the existence of an interaction between the nanoparticles and the ligands, and excluding the presence of molecular gold complexes, for which well defined, narrow NMR signals are usually present. As previously observed for metal nanoparticles stabilised by N-heterocyclic carbene ligands,[4b,c,f] the olefinic protons at the back-bone of the imidazole fragment are not discernible in the $^{1}$H NMR. However, in contrast to N-heterocyclic carbene ligands, coordination of N-heterocyclic thiones to a metal centre likely induces a bending of the imidazole fragment towards the metal surface,[8] and therefore the relaxation effect due to the proximity of the olefinic CH protons is likely increased (Figure 2).

The hydrodynamic diameters of the NPs were determined by Dynamic Light Scattering (DLS). The values obtained (see ESI) indicate a good relationship between the length of the alkyl chain on the NHT and the diameter. For example, the diameter was found to be 4.4(0.5), 8.5(0.3) and 8.6(0.4) nm for the gold NPs $NHT^{C6,C6}$, $NHT^{C14,C14}$, $NHT^{C18,C18}$, respectively.[11] As mentioned before, the size distribution and morphology of the nanoparticles do not change when exposed to air in solution (see Figures S43 and S44). Similarly, DLS measurements of solutions of the nanoparticles exposed to air for two weeks clearly indicate that no agglomeration takes place, preserving

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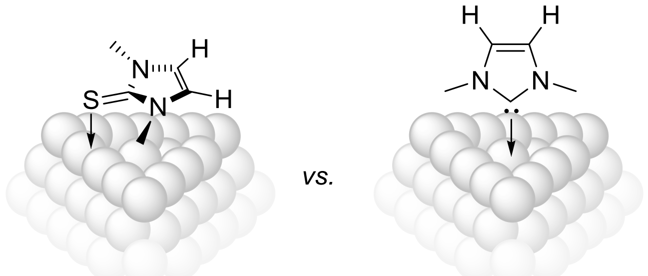

**Figure 2.** Possible orientation of the NHT on the gold surface.

the hydrodynamic radii (see Figures S49 and S50), while [1]H NMR spectra of their solutions remain unaltered.

The gold NPs composition at the nanoscale was confirmed by coupling high angle annular dark field imaging (HAADF) with energy-dispersive X-ray spectrometry (EDX) mapping using scanning transmission electron microscopy (STEM) (Figure 3, bottom). As can be seen in Figure 3, the EDX spectrum recorded across one NP presents three peaks related to gold at around 2.1, 9.7 and 11.5 keV, in addition to the carbon and copper peaks due to the grid support (see Figure 3 bottom left). A very good match is also observed between the HAADF image and the 2D elemental map of gold which allow confirming the synthesis of pure gold NPs. High-Resolution TEM (HRTEM) analysis unequivocally indicated the crystalline character of the gold nanoparticles, in which the interplanar distances are characteristic of Au ccp structure (Figure 3, top). The Fast Fourier transformed (FFT) shows the main reflections corresponding to the [110] zone axis.

We have evaluated the catalytic activity of the gold nanoparticles in the reduction of nitroarenes to anilines. We first investigated the benchmark reaction of reduction of nitrobenzene using $NaBH_4$ in $THF/H_2O$ mixtures as solvent media using a catalyst loading of 1%. After screening of different reaction conditions, we found out that the best results were obtained using a $THF/H_2O$ mixture (2:5 ratio) and as low as 5 equiv of $NaBH_4$ as reducing agent (note that this is an improvement with respect to previous results that required usually an excess of 50-100 equiv of $NaBH_4$).[12] All gold nanoparticles showed good catalytic activity under mild reaction conditions, but those bearing the longest alkyl chains (AuNP-NHT$^{C18,C18}$ and AuNP-NHT$^{C1,C18}$) in one or two sides on the NHT were slightly less efficient in terms of conversion of the starting material.[13] On the other hand, nanocatalysts AuNP-NHT$^{C14,C14}$ and AuNP-NHT$^{C6,C6}$ exhibited nearly identical behaviour, although the selectivity of the former towards the aniline was somewhat inferior (Table 1). A similar effect was observed when the unsymmetrical NHT nanoparticle AuNP-NHT$^{C1,C14}$ was used (Table 1, entry 4). With respect to a decrease in activity upon increasing the length of the alkyl arms on going to AuNP-NHT$^{C14,C14}$ to AuNP-NHT$^{C18,C18}$, there are several precedents that indicate that a lengthening in the chain is detrimental in catalytic activity due to a less access of substrates to the metal core.[14] Under this optimized reaction conditions, we explored the scope of the process using AuNP-NHT$^{C14,C14}$ (Table 2). The process is tolerant to the presence of both electron-donating and electron-withdrawing groups. Significantly, the presence of halogen groups at the aromatic ring (Table 2, entries 4 and 5) does not lead to the formation of the corresponding dehalogenated anilines. However, partial dehalogenation (10%) leading to *m*-bromoaniline was observed when 2,5-dibromonitrobenzene was used (Table 2, entry 6). The reaction can be even carried out in the presence of –CN and –COOEt, and –CH=CHCOOEt groups (Table 2, entries 3, 8 and 9). Nevertheless, keto groups undergo a reduction process leading to an alcohol (Table 2, entry 10).

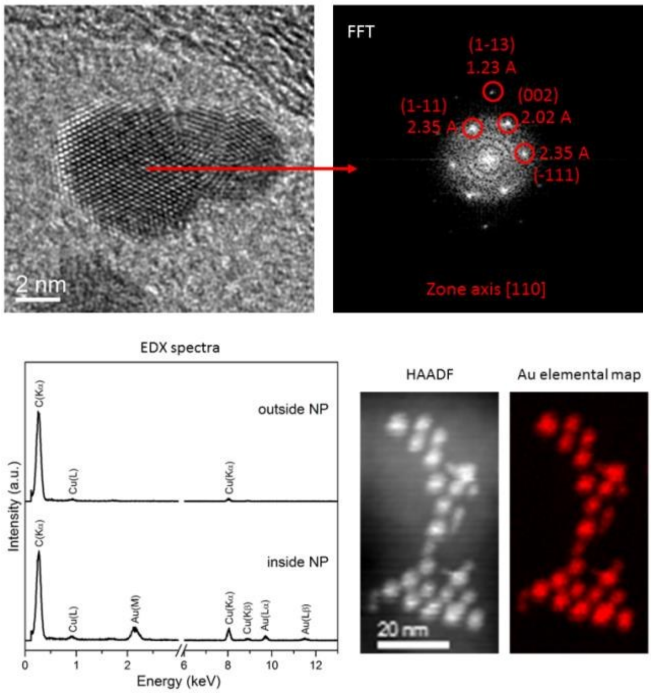

**Figure 3.** Top: HRTEM imaging and FFT analysis for gold nanoparticles AuNp-NHT$^{C14,C14}$. Bottom left: EDX spectra recorded inside and outside the NPs. Bottom right: STEM-HAADF image and STEM-EDX Au elemental map obtained by reconstructing the STEM-EDX spectrum image with a window of 0.3 eV around the Au(M) peak.

## Conclusions

In summary, we have developed a method for preparing very stable gold nanoparticles using readily available N-heterocyclic-2-thiones. The nature of the substituents flanking the nitrogen atoms determines the formation of the gold NPs, with both small alkyl groups and aromatic substituents favouring agglomeration processes, and long alkyl chains favouring their stabilisation. Since the structure of NHTs can be easily modified, unsymmetrical systems bearing one long and one short chains can be also synthesised leading to the corresponding Au-NPs. These nanoparticles are stable both in solution and in the solid state, even in air. We have evaluated the ability of these nanosystems to act as catalyst in the reduction of nitroarenes. Although most of them show good activity in this process, Au-NPs bearing two C14 alkyl chains are slightly superior to those with longer aliphatic fragments (C18), or unsymmetrical ligands. Considering the rich

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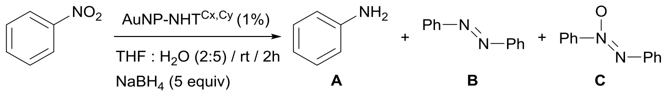
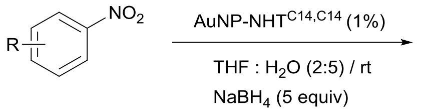
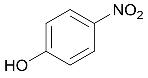
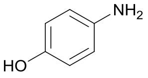
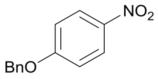
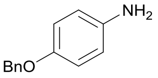
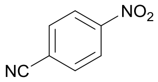
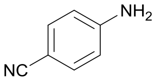
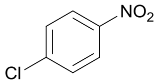
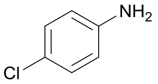
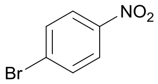
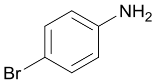
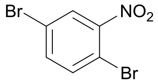
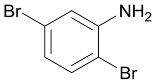
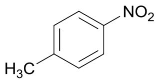
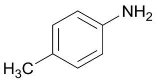
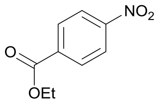
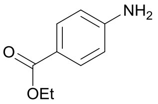
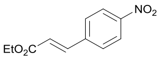
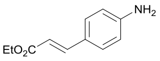
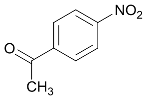
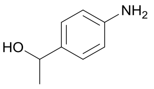
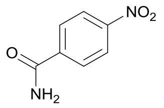
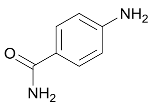
**Table 1** Nitroarene reduction by AuNPs-NHT.



| Entry | Catalyst | Conversion [%] | Yield [%] |
|---|---|---|---|
| 1 | AuNP-NHT$^{C6,C6}$ | > 99 | 83 (**A**), 7 (**B**), 10 (**C**) |
| 2 | AuNP-NHT$^{C14,C14}$ | > 99 | 98 (**A**), 2 (**B**), 0 (**C**) |
| 3 | AuNP-NHT$^{C18,C18}$ | 82 | 62 (**A**), 8 (**B**), 12 (**C**) |
| 4 | AuNP-NHT$^{C1,C14}$ | 94 | 71 (**A**), 7 (**B**), 16 (**C**) |
| 5 | AuNP-NHT$^{C1,C18}$ | 72 | 55 (**A**), 7 (**B**), 10 (**C**) |

**Table 2** Reaction scope of the reduction of nitroarenes.[a]



| Entry | Substrate | Product | Conversion [%] (t [h]) | Yield [%][b] |
|---|---|---|---|---|
| **1** |  |  | >99 (0.25) | 99 |
| **2** |  |  | >99 (2.0) | 99 |
| **3** |  |  | >99 (4.0) | 96<br>(4,0) |
| **4** |  |  | >99 (6.0) | 99 |
| **5** |  |  | >99 (0.5) | 93<br>(4,3) |
| **6** |  |  | >99 (2.0) | 90[c] |
| **7** |  |  | >99 (9.0) | 87<br>(8,5) |
| **8** |  |  | >99 (3.0) | 84<br>(16,0)[d] |
| **9** |  |  | >99 (0.5) | 93[e] |
| **10** |  |  | >99 (5.0) | 96<br>(4,0)[f] |
| **11** |  |  | >99 (1.0) | 97<br>(3,0)[d,f] |

[a] Reaction conditions: nitroarene (0.45 mmol), NaBH$_4$ (2.25 mmol), AuNP-NHT$^{C14,C14}$ (1.0% mmol) THF/H2O 2:5 (7 mL), rt. [b] The amount of azo (**B**) and azoxy (**C**) (see Table 1) compounds are given in parenthesis. [c] 10% of *m*-bromoaniline was detected. [d] 4.48 mmol of NaBH$_4$ were used. [e] 7% of ethyl 3-(*p*-aminofenil)propanoate. [f] Determined by $^1$H NMR.

structural variability available for N-heterocyclic thiones, this type of ligands might be complementary to the ubiquitous anionic thiolates but, obviously, their structure and neutral character would provide different electronic properties.

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## Notes and references

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